STUDIES IN PHOTOCHEMISTRY

a thesis submitted by

ALAN COX

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ABSTRACT

The biogenesis of some groups of natural products is reviewed with particular reference to the Barton and Cohen concept of phenol oxidation. Photochemistry is also reviewed generally.

An investigation has been carried out of methods for generating phenoxide radicals photochemically, with a view both to discovering photosensitive protecting groups for phenols, and also to performing coupling experiments with these radicals, thus simulating, at least in principle, the biogenesis of those groups of natural products which are thought to arise by a phenol oxidative mechanism.

In addition, a study of the photochemistry of the aromatic sulphenyl carboxylates has been made.

ACKNOWLEDGEMENTS

I should like to express my deep gratitude to Professor D.H.R. Barton for the privilege of working under his supervision and for his stimulating discussion and help at all times.

I should also like to thank Dr. G.W. Kirby for his friendly guidance throughout the course of this work and Messrs D.R. Aldrich and I.M. Scobbie for their valuable technical assistance.

To the U.S. Rubber Company I wish to express my thanks for the award of a bursary.

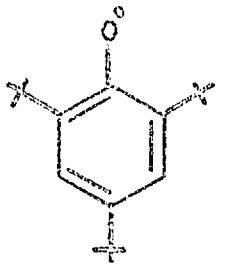
Finally, I should like to thank my wife for typing the manuscript.

CONTENTS

BIOGENESIS AND PHENOL OXIDATION

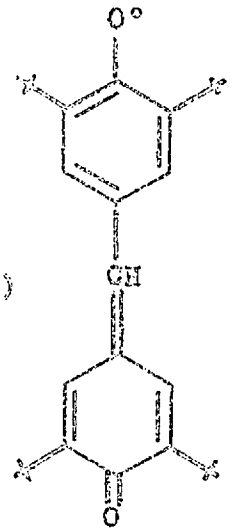
The purpose of this review is to correlate the structures of various natural products with one unifying reaction mechanism by which they have been produced; this mechanism is the coupling of phenol radicals[1]. The variety of products obtainable when phenols are oxidised by one electron transfer oxidising agents such as ferric chloride, potassium ferricyanide, silver oxide, lead dioxide, lead tetracetate and manganese dioxide is clearly indicated by examples from the classical work of Dianin, of Pummerer, of Erdtman and by more recent work[2,3,4,5].

While phenol radicals in general are very unstable species, the presence of large substituents, for example t-butyl groups or phenyl residues, at the ortho and para positions stablises the primary oxidation products i.e. the free phenoxy radicals. Some of these free radicals form dark coloured crystals, for example, (1)[6,7,8] and (2)[9,10,11], others, however, undergo association in the crystals to form colourless dimeric quinol ethers which in solution dissociate to varying degrees into radicals, for example (3)[12,13,14] and (4)[15,16,17].



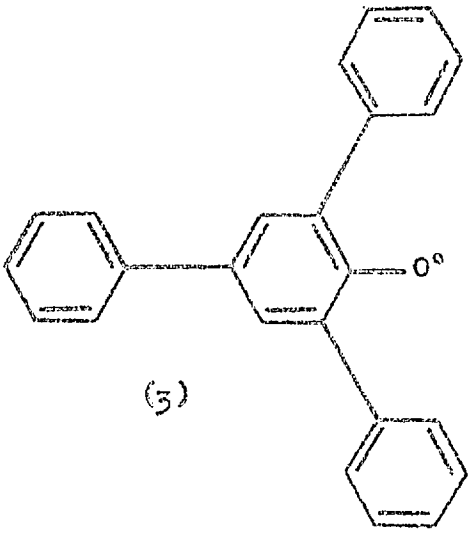
(1)

Soln: deep blue
Cryst: deep blue



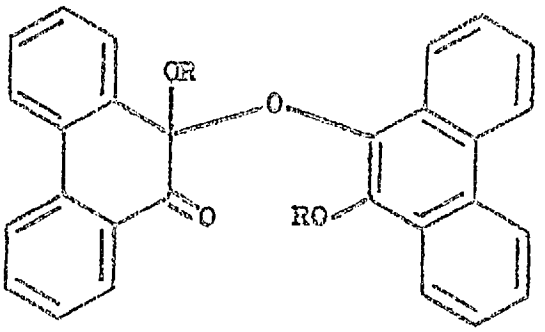
(2)

Soln: λ_{max} 423 mμ
Cryst: deep blue

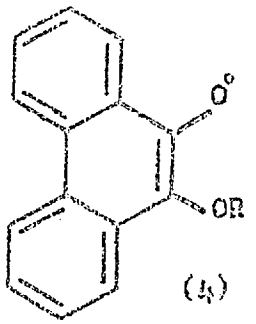


(3)

Soln: red
Cryst: colourless dimer



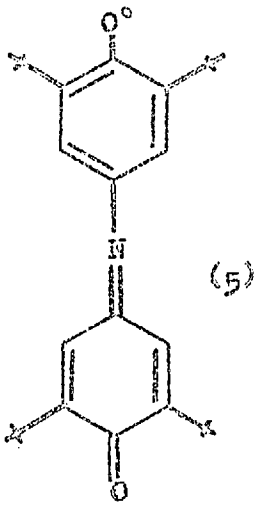
Colourless R = Me, Et.



(4)

Yellow/green

Nitrogenous radicals such as (5) [18] and diradicals such as (6) [19] can be prepared,



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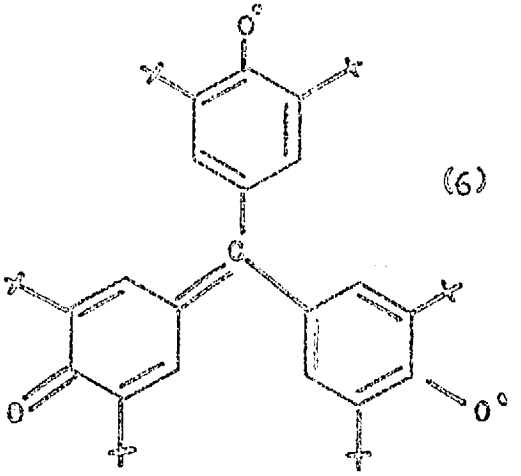
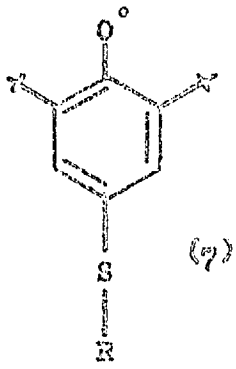


(6)

and the existence in solution of the unstable red radicals containing sulphur and phosphorus, (7) [20] and (8) [20] respectively, has been demonstrated.



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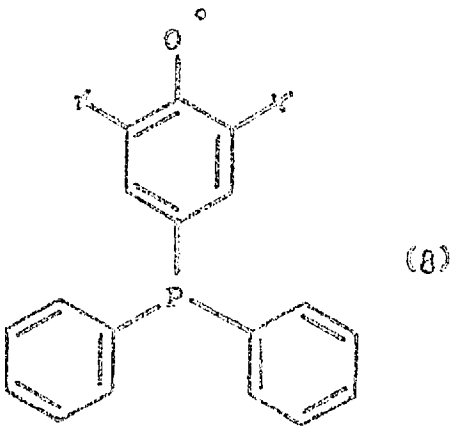


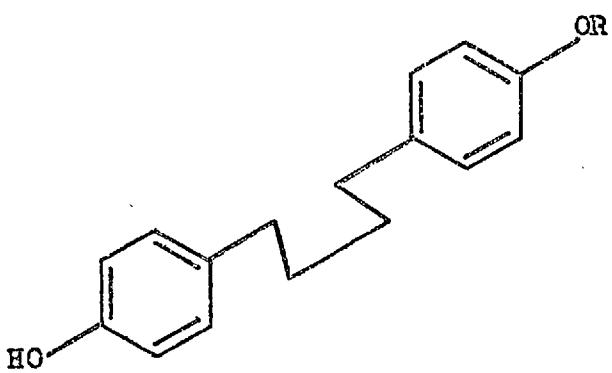
(8)

Once phenol radicals have been generated they will in general undergo further reactions very rapidly leading ultimately to stable molecular species, it being assumed that the radicals are not of the "stable" type discussed above. This object may be accomplished by several processes. Reduction gives back the parent phenol [6,18,16,22,23,24,25], coupling with reactive molecules, for example, oxygen and bromine, affords non-radical products [6,7,8,22], self coupling furnishes dimers. The latter can be formed by C-C (ortho-ortho, ortho-para or para-para) or C-O coupling. The first named process is the most important, pertinent examples being discussed in the sequel.

However, before doing this, it will be convenient at this stage to distinguish in principle between the coupling process, tacitly assumed above, and the possibility of a substitution process. Both mechanisms predict o-p type substitution[1,2,26], in the final product but have different implications for biogenesis. Generally, C-C or C-O bond formation can occur in one of two ways. Two radicals can dimerise (A) to give the cyclohexadienone (9) which in the case of the 2,6-t-butyl compound, can be isolated and which rearranges in methanol to the dimeric phenol (10)[11,27].

Alternatively, when oxidation is slow, dimerisation is less likely to occur because of the low radical concentration. Under these conditions in particular, it is possible that phenoxide ions or phenol molecules which are present in high concentrations, undergo electrophilic substitution by the radical (B), the radical (11) being dehydrogenated further to give the dienone or diphenol. However, we have shown that if p-cresol, a phenol whose oxidation has been thoroughly studied [28,29] be oxidised in the presence of a ten-fold excess of veratrole, no -OMe residues can be detected in the phenolic products [30]. Similarly, oxidation of the monohydric phenol (12: R = Bz) gives no monomeric coupling product whereas the corresponding dihydric phenol (12: R = H) is smoothly cyclised [31]. In so far as -OMe and -OBz can be equated with -OH for the process of radical coupling, a substitution mechanism seems improbable. However, radical substitution into a phenolate anion [32] cannot as yet be excluded.

(12)

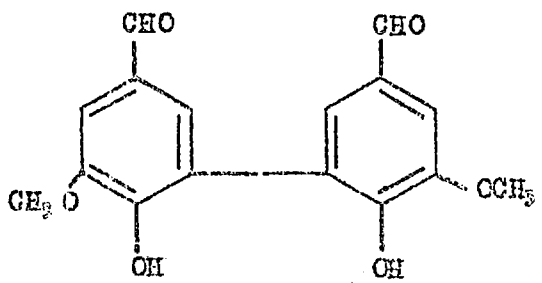


Phenol coupling can, of course, be carried out in neutral or acidic pH and under these conditions the anion substitution process can hardly be important. For the remainder of this discussion, radical coupling will be accepted without further qualification.

Carbon - carbon coupling.

(i) ortho - ortho

Examples of this type of coupled product are afforded by dehydrodivanillin (13) [33,34], dehydrodi-o-cresol (14) [35] and dehydrodi-β-naphthol (15) [36].



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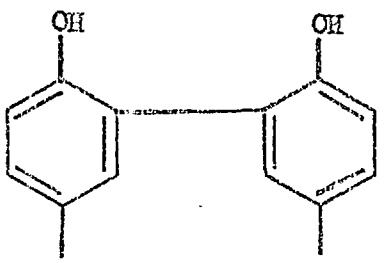

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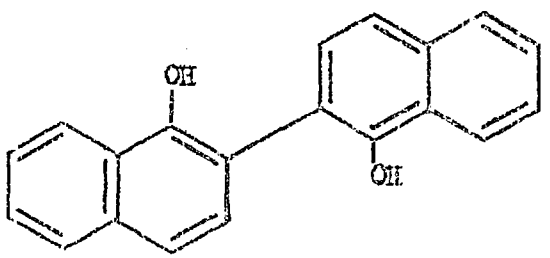
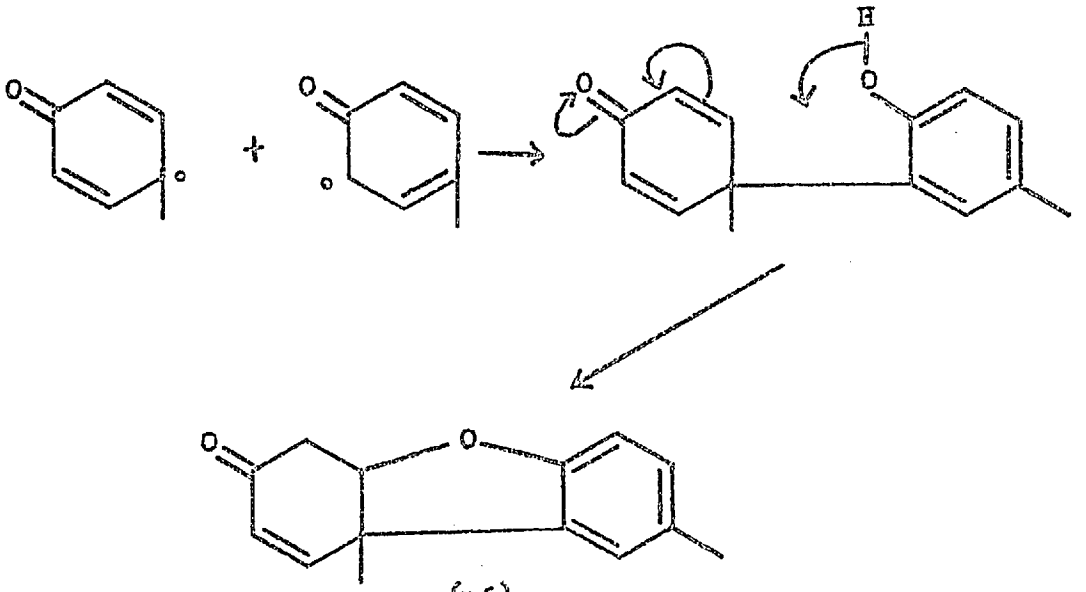


(15)

(ii) ortho - para

Examples of this type of coupling are not very numerous and possibly the best authenticated case is afforded by the oxidation of p-cresol [37, 38, 39] which gives a relatively high yield of the crystalline ketone (16) [28], the so-called "Pummerer's" ketone, formed as outlined below.

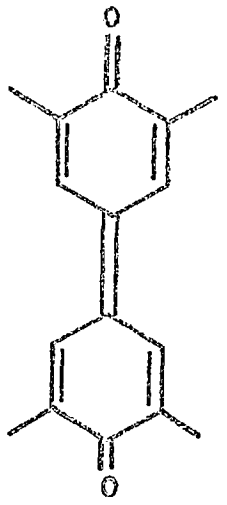


(16)

(iii) para - para

Examples of this type of coupling are 4,4'-dihydroxybiphenyl (17) [35], the diphenoquinone (18) [35, 39, 40] and the quinone (19) [41, 42].

(17)



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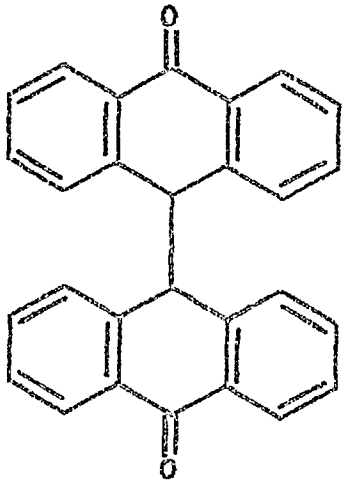
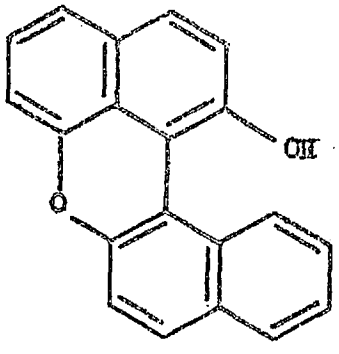


(19)

Carbon - oxygen coupling

Oxidation of dehydrodi-β-naphthol by potassium ferricyanide [42] gives (20) and (21)



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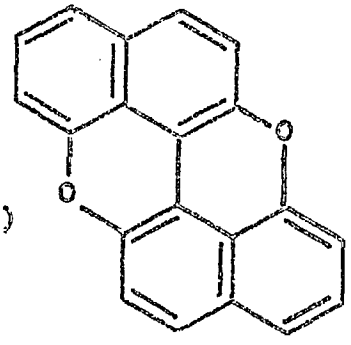
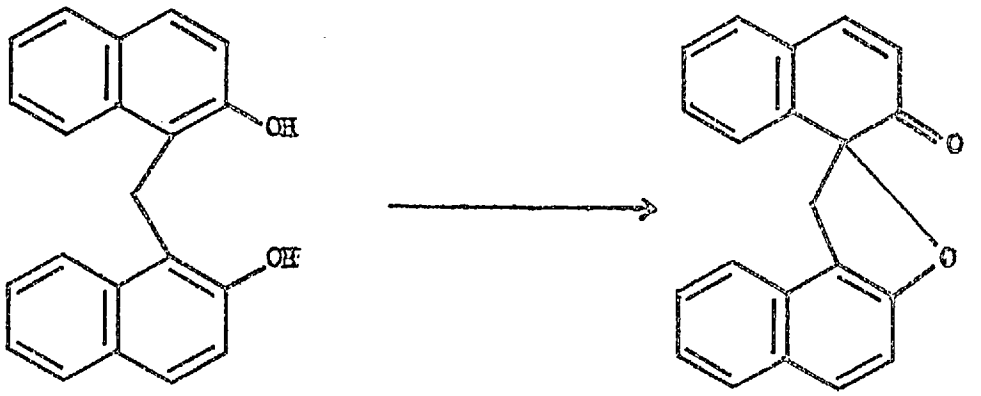


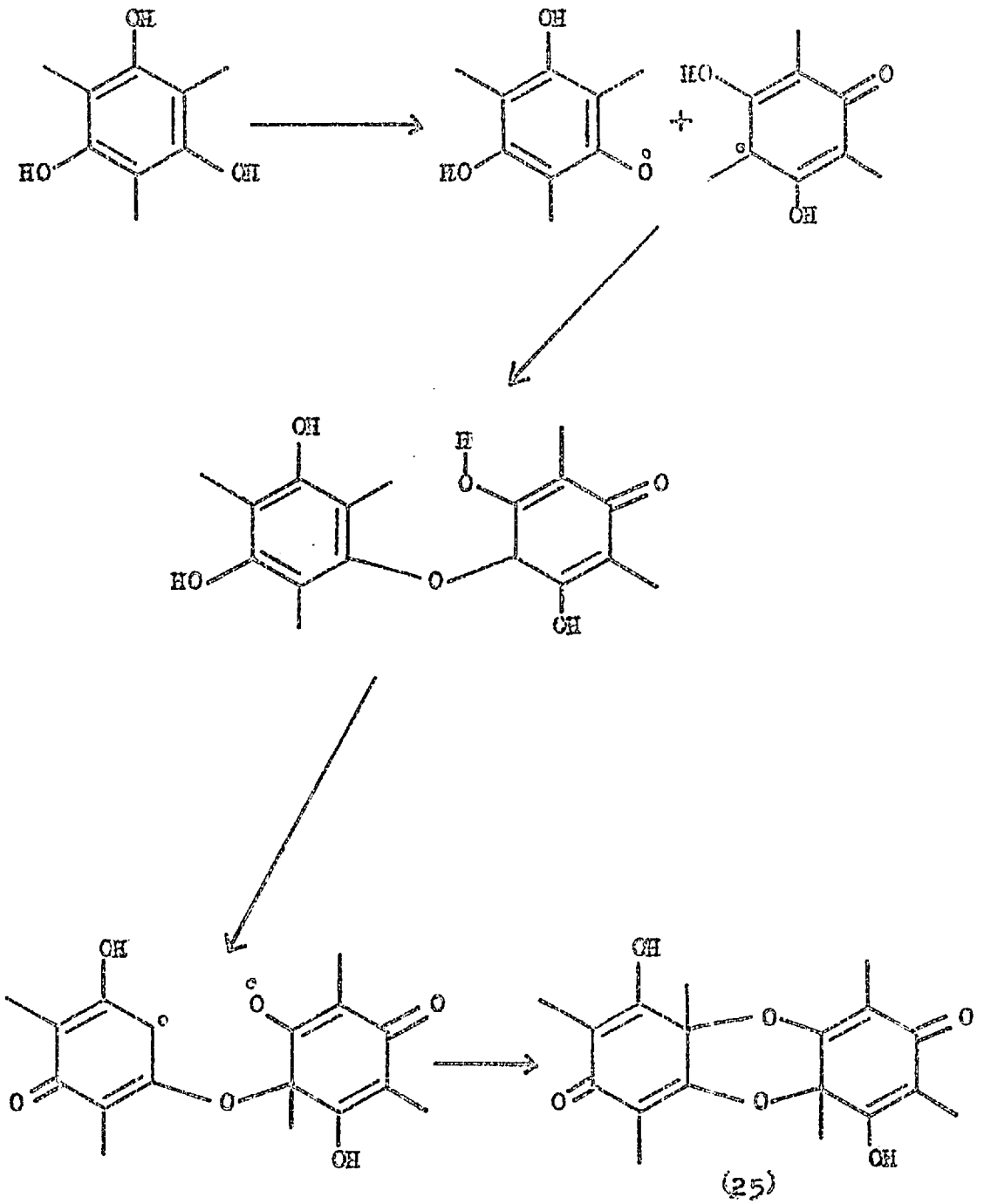
(21)

Similarly, oxidation [48] of the methylene-bis-β-naphthol (22) affords the spiran (23).



(22) (23)

Finally, oxidation [44] of trimethylphloroglucinol (24) yields "cedrone" (25). The mechanism of formation of "cedrone" requires either two successive diradical couplings or one tetraradical coupling. The first scheme (illustrated) is acceptable provided that enolised 1,3-diketones can be oxidised like phenols. The radical resulting from such an oxidation is, of course, resonance stabilised like the phenoxy radical.

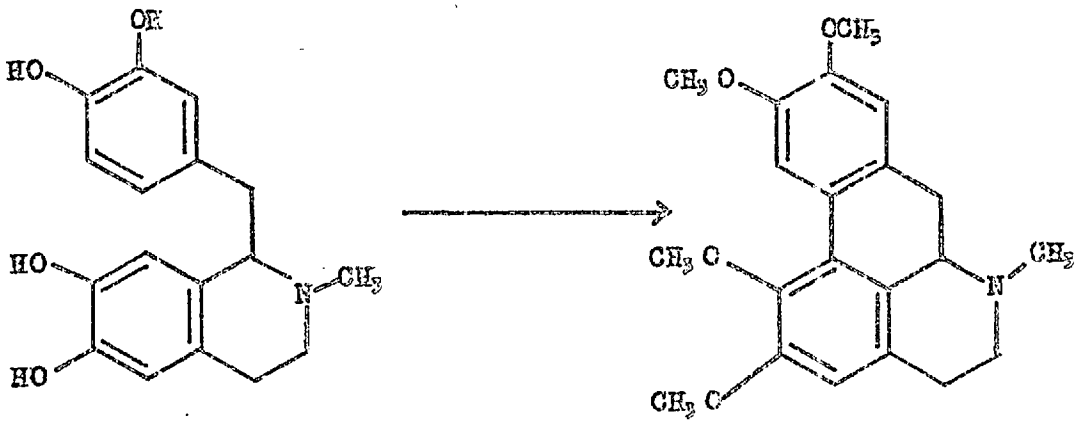


(25)

It was stated at the outset that the object of this review was to attempt to correlate the structures of certain natural products under a unifying reaction mechanism. Having dealt with the mechanism, attention will now be turned, therefore, to the structures and, with this mechanism in mind, the biogenesis of some groups of natural products discussed. Only a few of many examples will be given to illustrate the general scope of this process.

1. Alkaloids

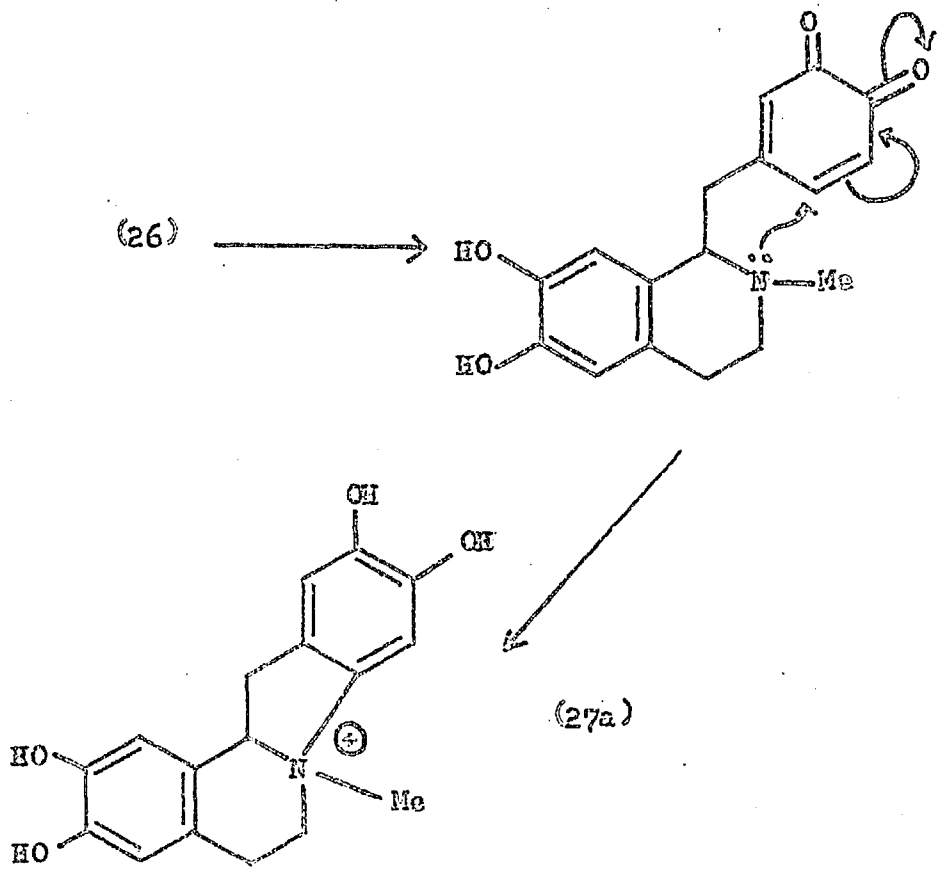
As early as 1911, Gadamer [45] attempted to explain the biosynthesis of glaucine (27) by assuming that laudanosoline (26) was dehydrogenated in the plant cells.



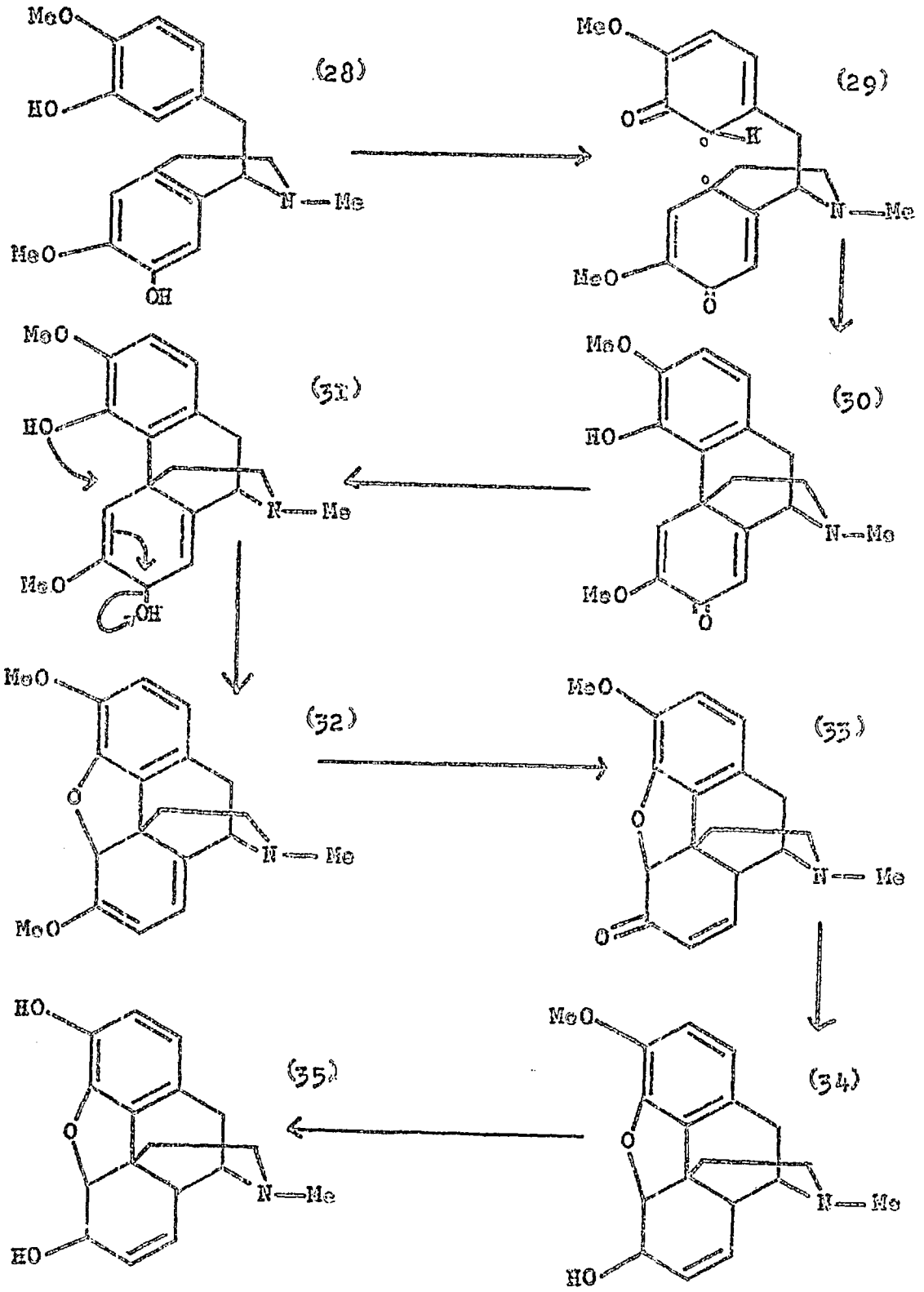
(26) (27)

Later, Robinson [46, 47, 48] attempted to simulate Nature's pathway to the morphine alkaloids by mild oxidation of laudanoscline (26). The product of reaction was, however, dehydrolaudanosoline

(27a) presumably, formed by the mechanism indicated, and not a compound possessing the morphine skeleton.

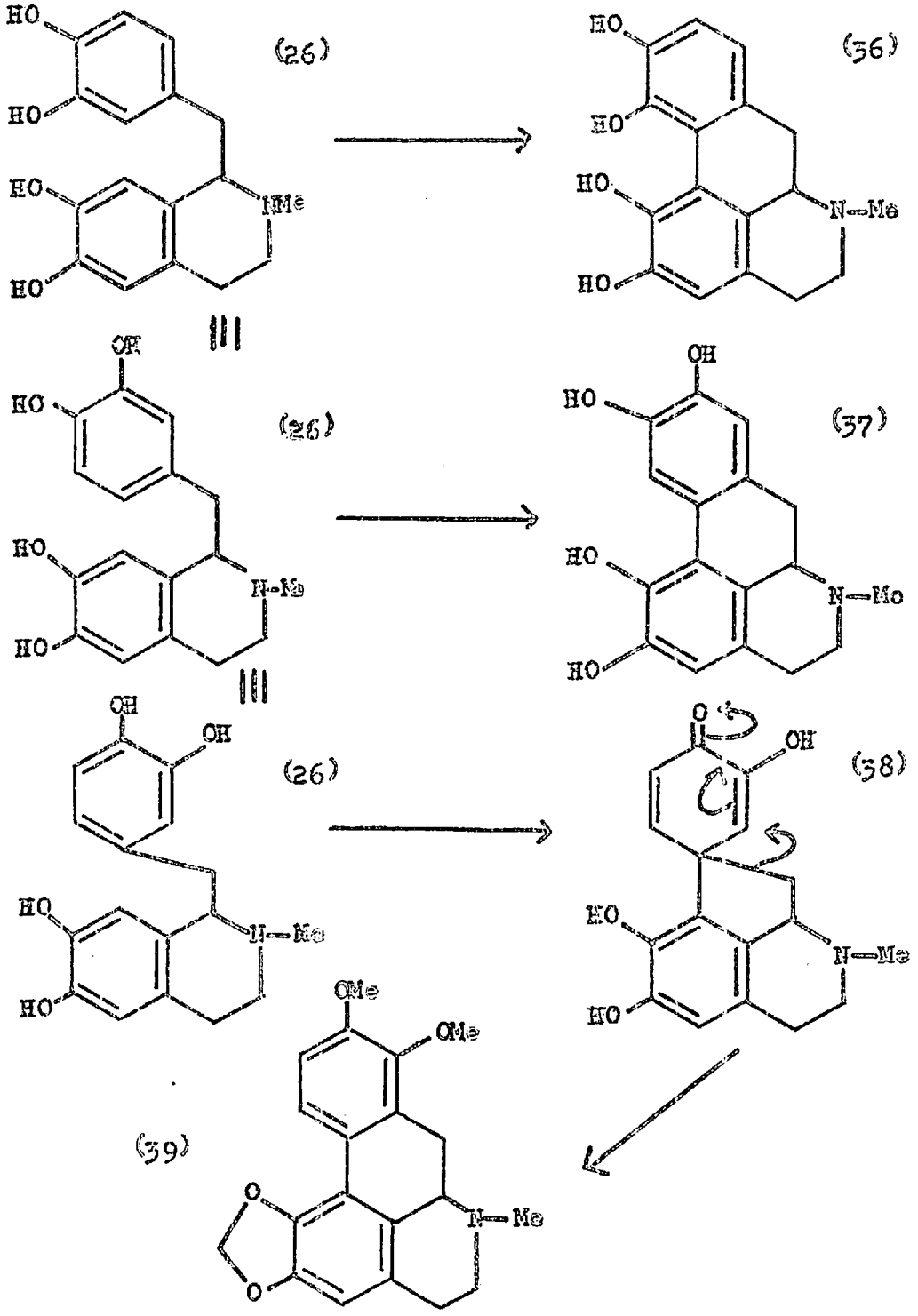


In the years following these proposals, many mechanisms for the oxidative cyclisation leading to the morphine skeleton have been put forward[3, 46, 49, 50] but only one scheme, namely that of Barton[1] has stood the test of experiment. This scheme is outlined in its most recent [51] form.


MeO
HO
(28)
N—Me
MeO
OH
MeO
(29)
O
H
N—Me
MeO
O
(31)
HO
N—Me
MeO
OH
MeO
(30)
HO
N—Me
MeO
O
(32)
O
N—Me
MeO
MeO
(33)
O
N—Me
O
(35)
HO
O
N—Me
HO
MeO
(34)
O
N—Me
HO

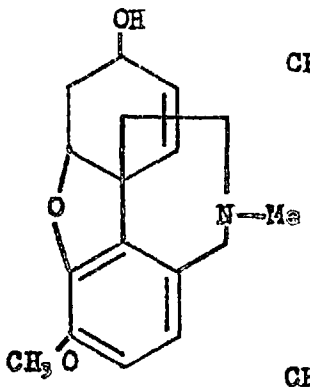
The benzylisoquinoline on oxidation by a one electron transfer process gives the diradical (29). Coupling of this diradical gives dienone (30) which exists, peculiarly enough, in the "open" form. Reduction with sodium borohydride affords two stereoisomeric alcohols (31). Both of these alcohols under extremely mild acid conditions (aqueous solution at pH 3 to pH 4), are converted spontaneously at room temperature and in fair yield into thebaine (32). Simple changes then give codeinone (33), codeine (34) and morphine (35). All the steps in this scheme have now been firmly established [31, 32, 33, 34, 35] with the one exception that the intermediacy of codeinone has to be demonstrated.

The majority of the aporphine alkaloids [36] can be derived from the same type of precursor by interchange of the coupling positions. Thus an ortho - ortho coupling of the laudanosoline (26) skeleton would give rise to alkaloids of the corytuberine family (36), whilst ortho - para coupling would lead to the glaucine type skeleton (37). Alkaloids such as crebanine (39) whose biogenesis is not immediately obvious can also be incorporated in the general scheme by a series of reactions involving a dienone - phenol rearrangement of an intermediate such as (38).


HO
HO
HO
HO
NMe
(26)
(36)
N—Me
OH
(37)
(38)
OMe
(39)
O
N—Me

The amaryllidaceae alkaloids constitute a large group of naturally occurring compounds which have been the subject of intense investigation over the last few years [57]. They are of widely diverse functionality and structural type but can be divided into three main classes based on (a) a dibenzofuran system, for example, galanthamine (39), (b) a pyrrolophenanthridine skeleton, for example, galanthine (40), and (c) an ethanophenanthridine skeleton, for example, haemanthamine (41).

In principle, the other classes of these alkaloids can be derived from these by cleavage, rearrangement and recyclisation. Oxidative cleavage of type (40) at the indicated position could lead to alkaloids based on a benzpyranoindole skeleton, for example, homolycorine (42) and oxidative cleavage of the haemanthamine type, followed by internal oxidation-reduction and recyclisation can give the tazettine (43) type [58].



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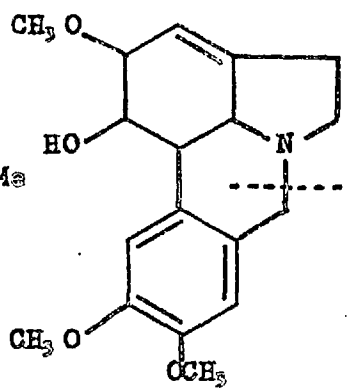

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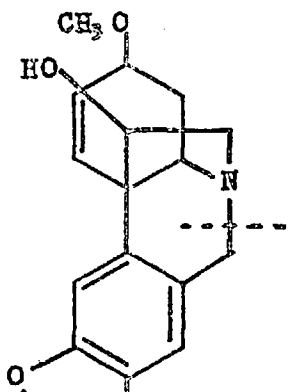

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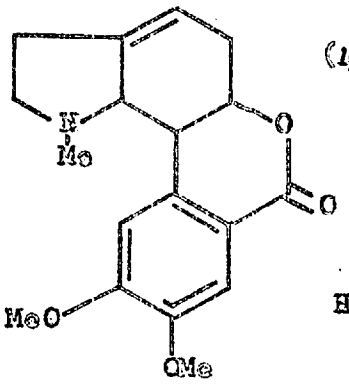

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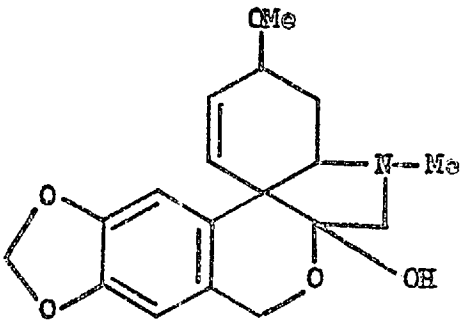

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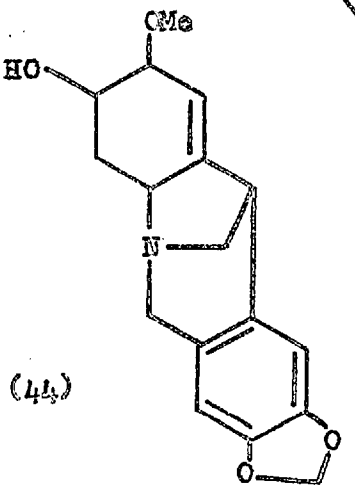
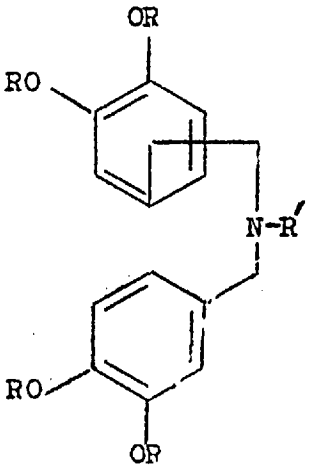


(44)

Another rearrangement with migration of the methylene-dioxyphenyl ring can give rise to alkaloids based on the methanomorphenanthridine skeleton, for example, montanine (44) [59]. It can be seen that all these alkaloids are closely related in that they contain a common hydroaromatic C_6-C_2 and an aromatic C_6-C_1 unit. Again, it has been suggested [b, 59] that all these alkaloids arise by an oxidative coupling of a precursor of general type (45), where R = H or suitable blocking groups which could be alkyl or part of an enzyme surface. Variations of para-para and ortho-para coupling reactions give rise to three main types of alkaloid.



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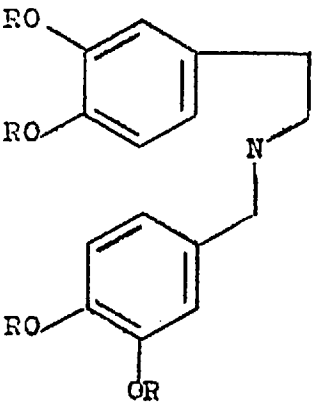
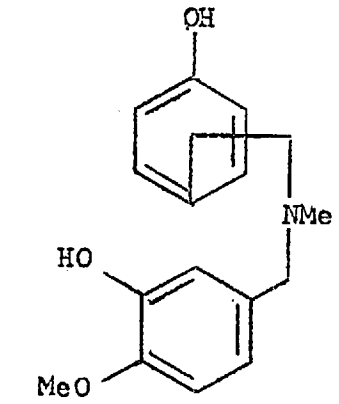


(46)

Para - para coupling in the precursor (45) gives rise to the haemanthamine skeleton and ortho - para coupling of the same precursor (45 = 46) the lycorine skeleton. It should be stressed, however, that one of the oxygen atoms in the phenylethylamine fragment might be introduced after coupling.

Further, oxidation of (47), a deoxy form of the precursor (45), to the diradical (48) followed by radical pairing would give the dienone (49). Aromatisation of the lower ring, followed by addition of the hydroxyl group across the unsaturated system (50) leads to the oxide bridge in narwedine (51). Galanthamine (52) is obtained by reduction.



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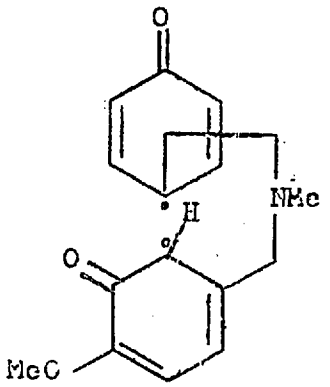
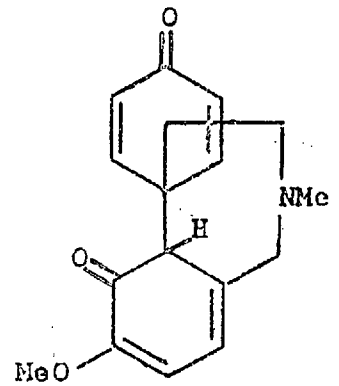
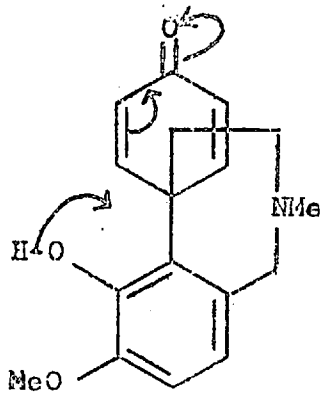


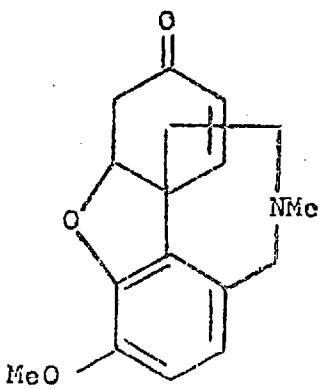
(48)



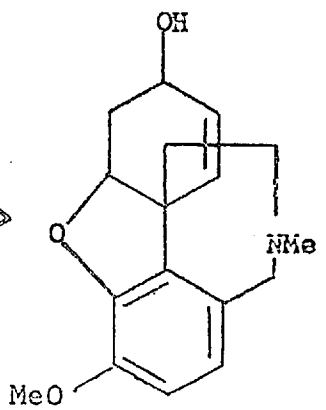
(49)



(50)



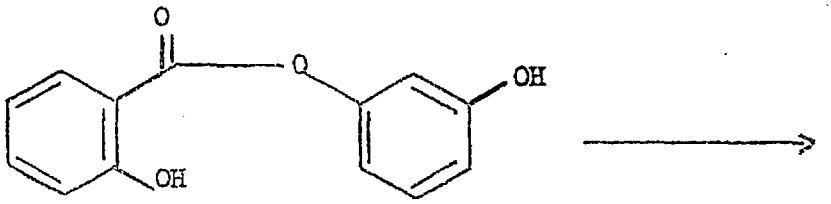
(51)



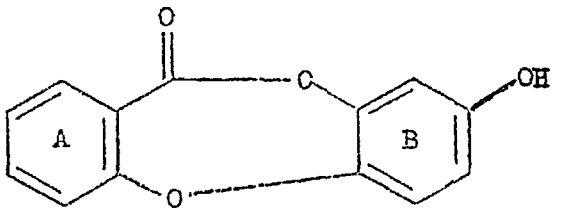
(52)

2. Fungal Metabolites

Examination of the structures of a series of depsidones (parent skeleton 54) reveals that hydroxyl or methoxyl groups are never present ortho or para to the other linkage in ring A, but there is always one of these groups in this relationship in ring B. The most probable mode of biogenesis of the depsidones is, therefore, phenol coupling of the depsidones (parent skeleton 53).

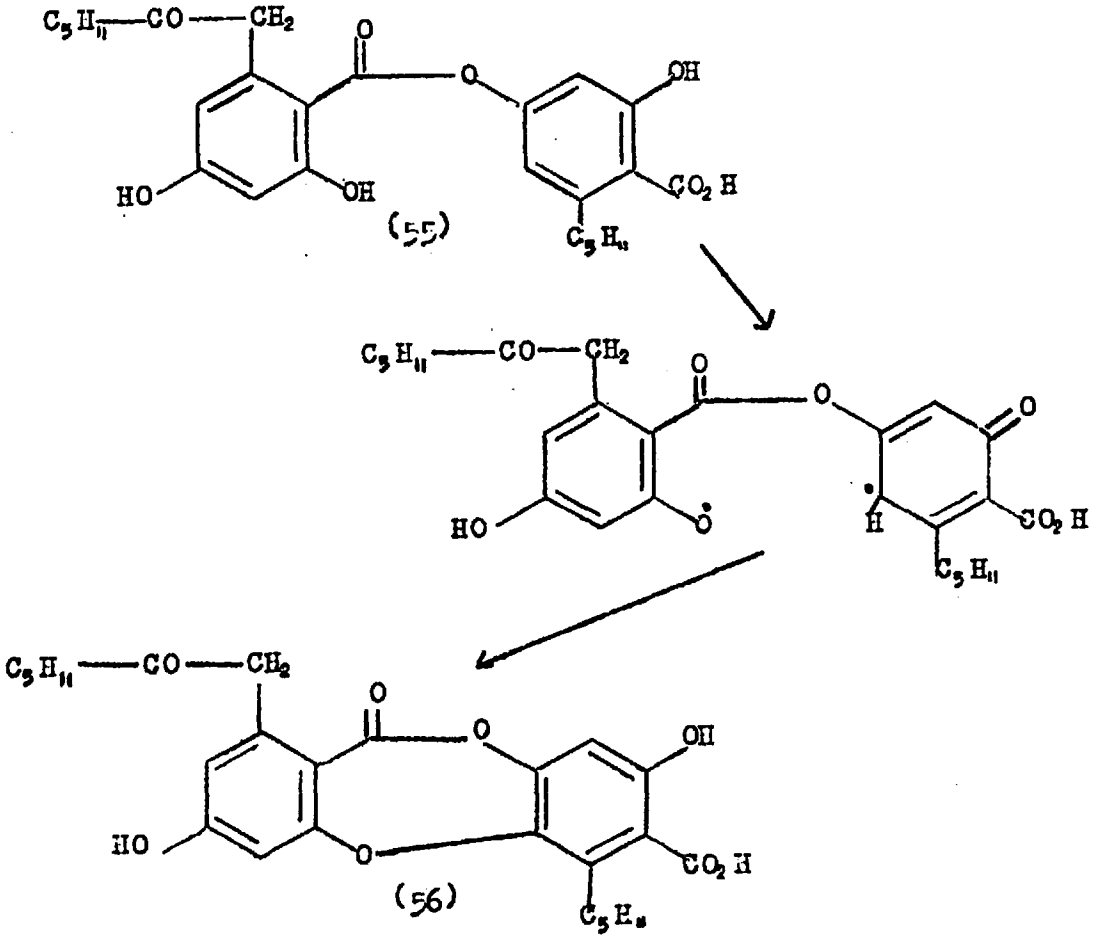


(53)

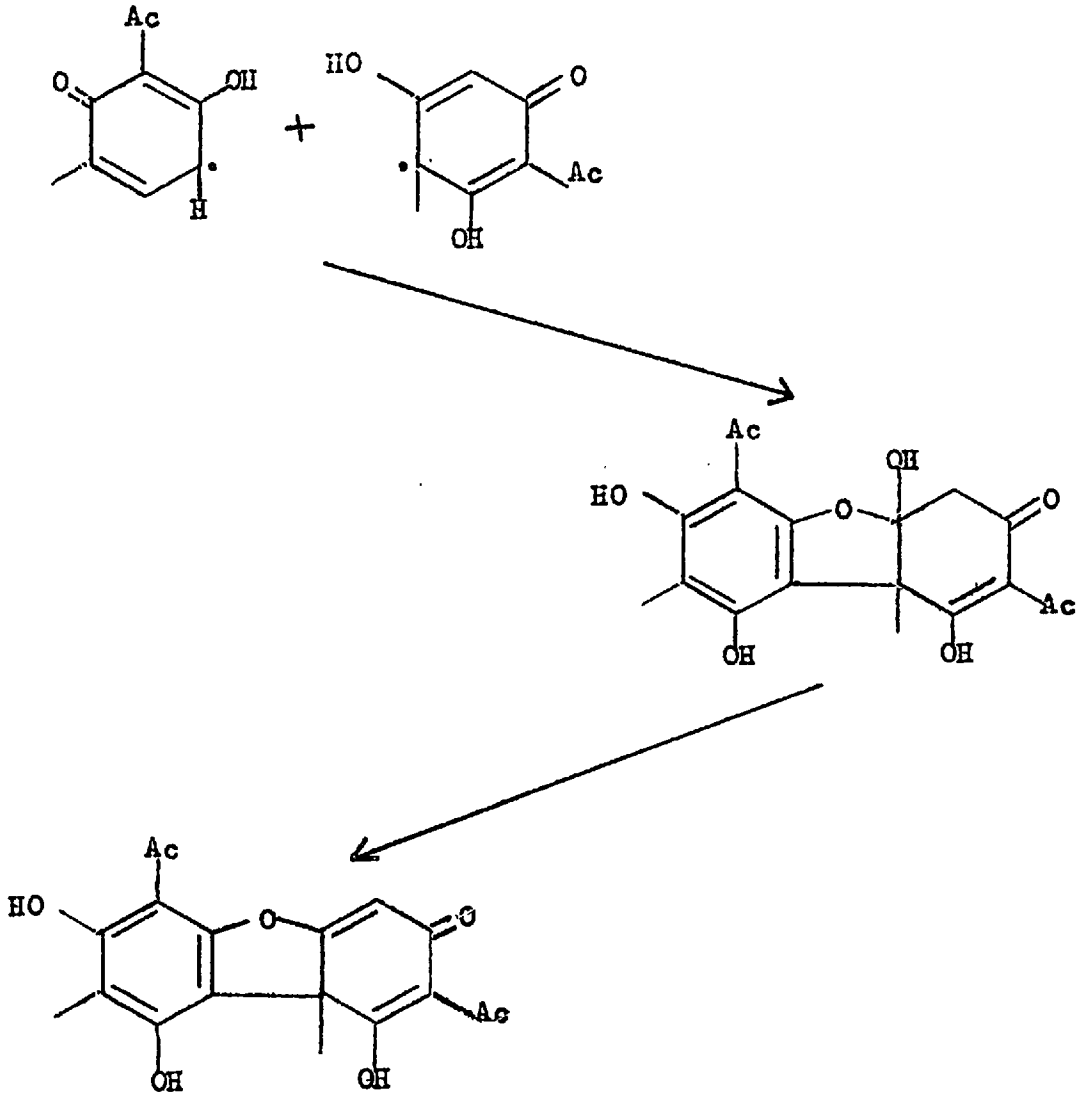


(54)

This suggestion can be illustrated by considering the case of olivetoric acid (55) and physodic acid (56). Both of these metabolites occur in the same genus of lichens. The relationship between them is such that phenol coupling as indicated should convert (55) into (56) and thus represent the final step in the biosynthesis of (56).

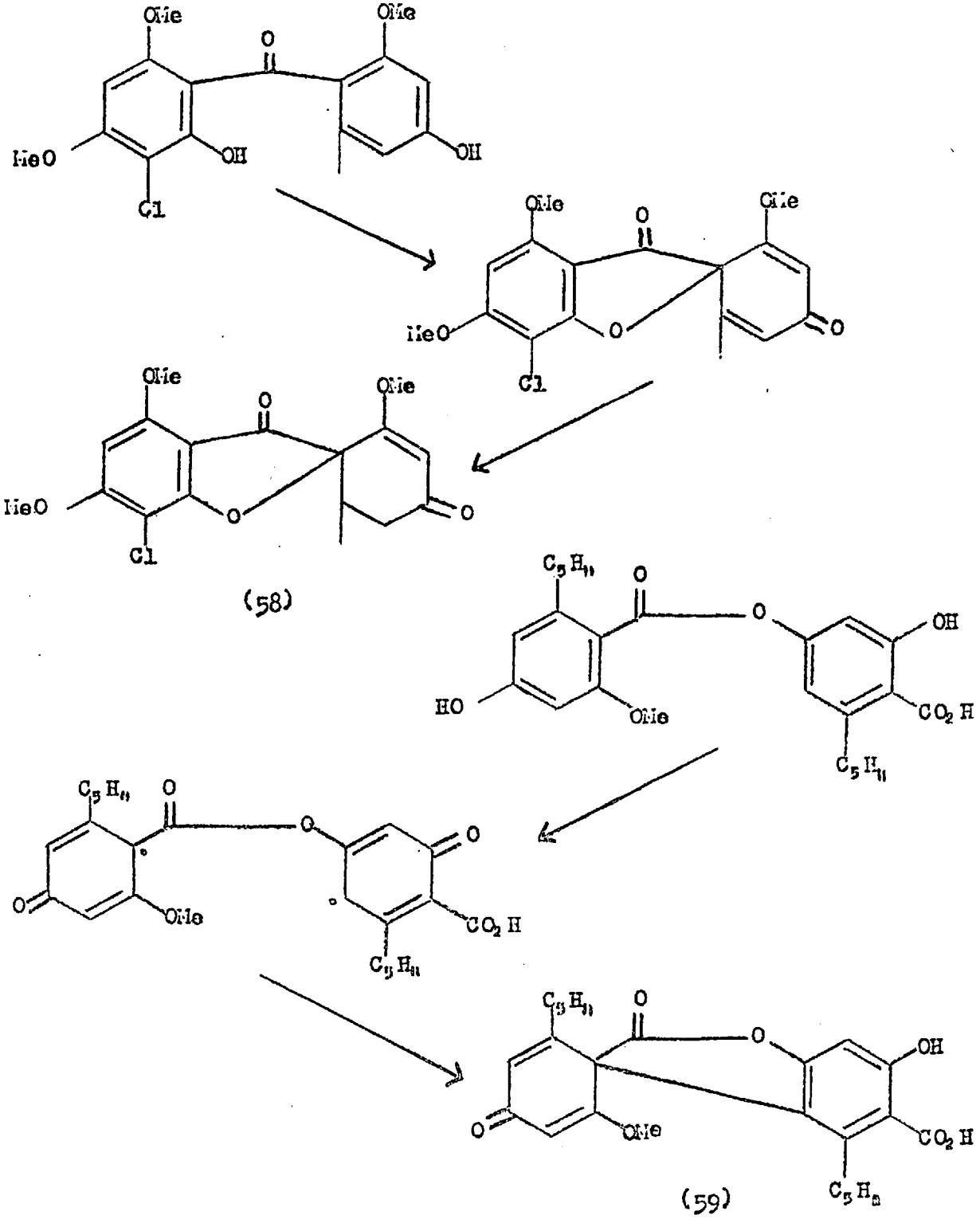


Another class of lichen substances is that based on the dibenzofuran skeleton, the most well known member being usnic acid (57). In 1956 a spectacularly simple synthesis of this substance was published [28] by Barton, Deflorin, and Edwards using a route that is undoubtedly the one employed in Nature.



(57)

Similarly, the mould metabolites griseofulvin (58) and picrolichenic acid (59) are also derivable by this type of phenol oxidation.

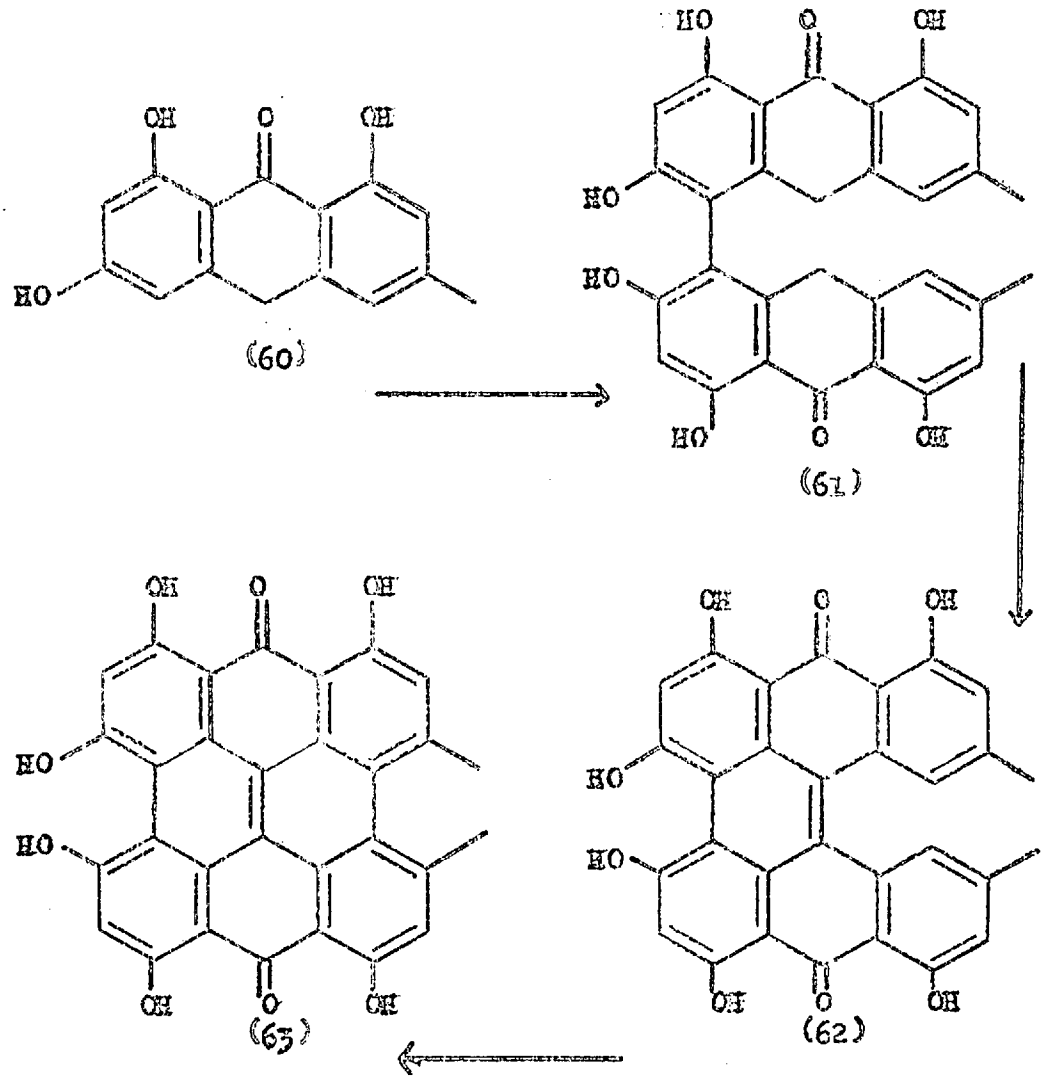

OMe
O
OMe
MeO
OH
OH
Cl
OMe
O
OMe
MeO
O
O
Cl
OMe
O
OMe
MeO
O
O
Cl
(58)
C_5H_{11}
O
O
OH
HO
OMe
CO_2H
C_5H_{11}
C_5H_{11}
O
O
O
O
OMe
CO_2H
C_5H_{11}
C_5H_{11}
O
O
OH
O
OMe
CO_2H
C_5H_{11}
(59)

Recently, Scott and his coworkers have published [60,61] biogenetically patterned syntheses of both of these substances.

3. Plant Products other than Alkaloids

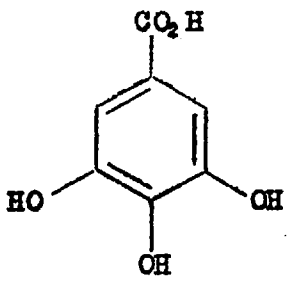
Very many examples could be cited under this heading but for the sake of brevity, however, only a few will be mentioned.

Protohypericin (62) has been synthesised [62] from

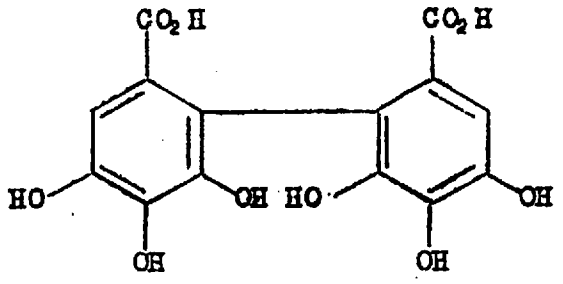


emodin anthrone (60), and protohypericin on irradiation yields hypericin (63); both of these substances occur in association in Nature. The fungal metabolite penicilliopsin [63] has the constitution (61) and thus represents the first step in the oxidation sequence.

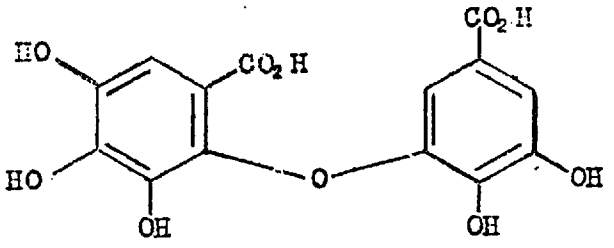
Another group of natural products of interest are the tannins [64]. They possess structures based on glucose esterfied with gallic acid (64) or with acids clearly derived from gallic acid by phenol coupling. The simplest of the latter are (65), (66) and (67).



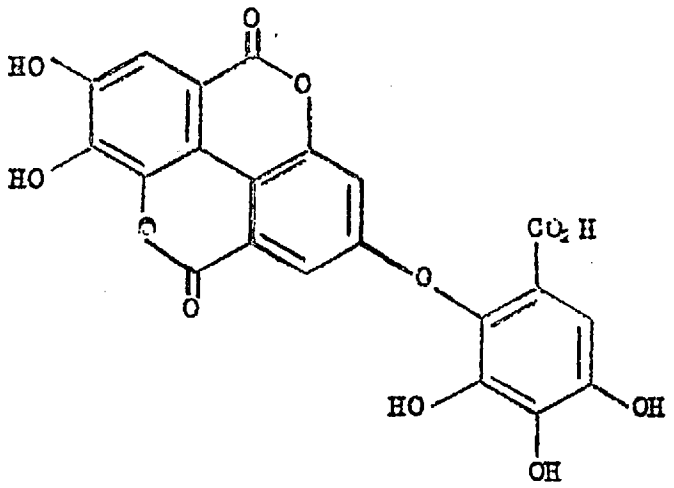
(64)



(65)



(66)



(67)

PHOTOCHEMISTRY

1. Introduction

By 1900 it had become realised that organic molecules could be induced to react under the influence of radiant energy. However, examples of such reactions were few and those that were known were not very well authenticated. The reasons for this are numerous. Firstly the availability of light sources was strictly limited and their design somewhat primitive. Secondly, most of the reactions which had been investigated gave rise to a complex mixture of products, often difficult to separate. And finally, many of the reactions induced photochemically could be carried out more simply and more cleanly by other means.

Organic photochemistry had thus the tendency to be regarded as the alchemical interest of a few sophisticates and to have no real synthetic usefulness. Recently, however, there has been a surge of interest in the field and the literature has become flooded with new and interesting reactions. This revival has been largely associated with the work of Barton, Büchi, Schenk and Schönberg and if one were called upon to justify the study of photochemistry other than in an "ars gratia artis" sense, the citation of the Barton reaction [65,66] as the sole example would surely suffice.

2. Mechanistic Approach

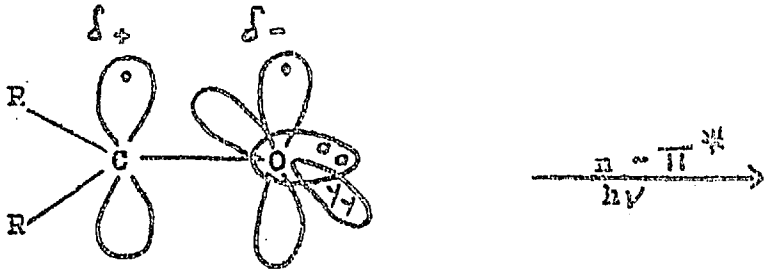
Before any photochemical reaction can take place, energy has clearly to be absorbed by the substrate. Immediately, reactions fall into three groups, those which obey Einstein's Law, those which have a quantum efficency greater than unity and those which have a quantum efficiency less than unity. Reactions of the first type are such that one molecule reacts per quantum of energy absorbed. Reactions of the second type are self-perpetuating, that is to say they are chain reactions; while in examples of the third type, energy is lost by processes, for example, collision, other than by chemical reaction.

The early organic photochemists contented themselves with a non-mechanistic approach to their work and have discussed photochemical reactions purely in terms of starting materials, conditions and products. However, due to the pioneering work of Zimmerman in particular a mechanistic approach seems to be emerging. First, reasonable descriptions of the excited states i.e. the species which are actually undergoing the reaction, are presented, and secondly, the principle that molecular transformations proceed by "continuous electron redistribution processes" is employed. What is meant by this last statement is that reacting species follow the energy valleys and avoid the energy maxima. This approach will now be described briefly

in terms of the two electronic excitation processes most frequently encountered in organic photochemistry.

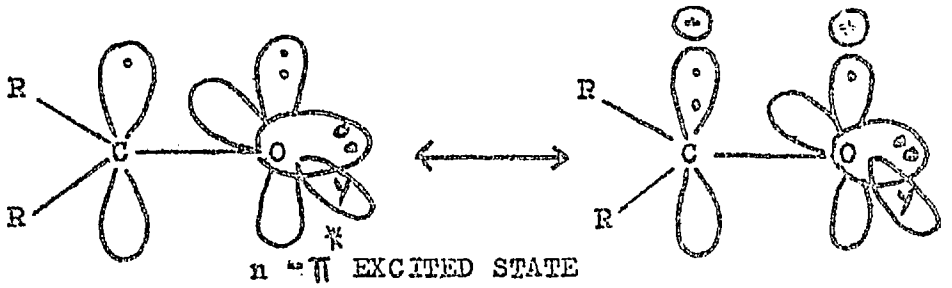
(i) $n - \pi^*$ excitation

The extinction band in the 280 - 360 $m\mu$ region of the U.V. spectra of aldehydes and ketones has been attributed to the promotion of a non-bonding electron (i.e. "n") to an anti-bonding π^* orbital [67]. This is called an $n - \pi^*$ process and is conveniently depicted as:-



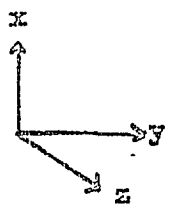
GROUND STATE

(1)



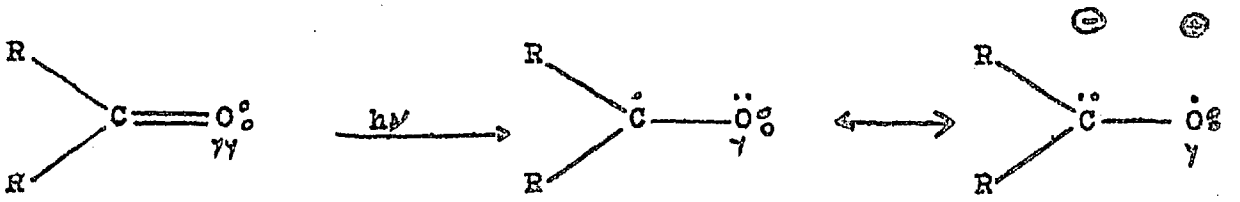
$n - \pi^*$ EXCITED STATE

(2a) (2b)



The representation implies that one of the non-bonding electrons in a p_y orbital on oxygen is promoted to a p_x orbital, this being the one (by convention) that is associated with the electron on carbon in the π electron framework. Species (2a) is thus obtained. Clearly, this is only one of a pair of canonical forms, the other being (2b).

A more convenient notation for the same process which allows depiction of a three dimensional species in two dimensions is shown below.



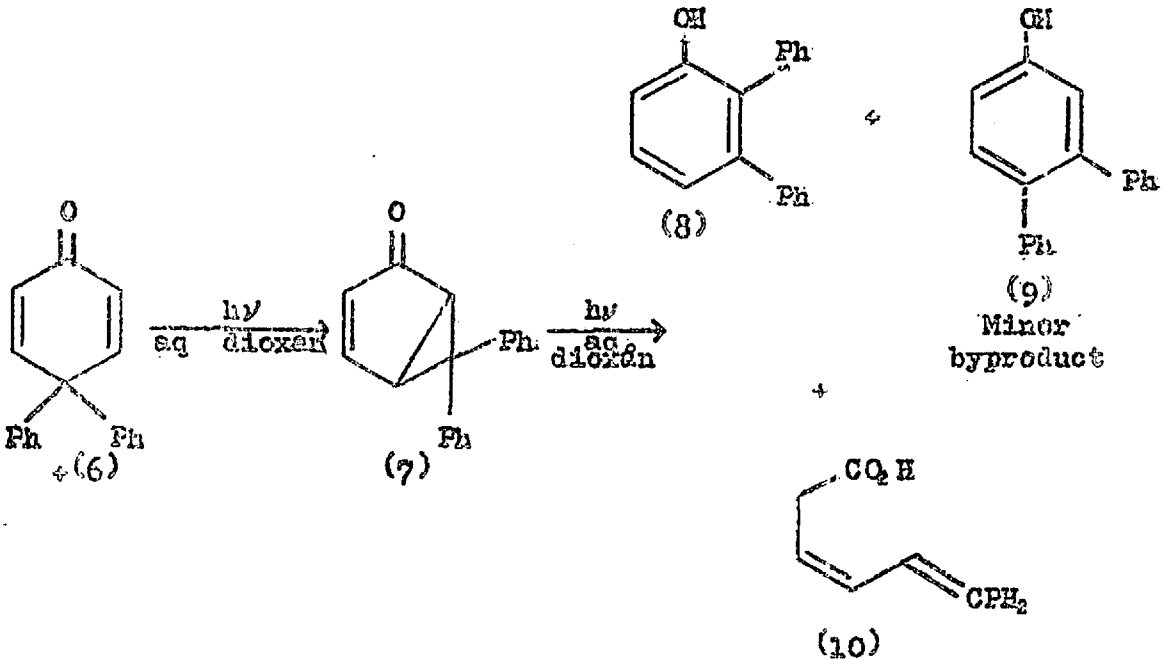
GROUND STATE $n - \pi^*$ EXCITED STATE

(4) (5a) (5b)

Structures (2b) and (5b) imply a reversal of the normal polarisation of the carbonyl group. That this is actually the case has been recognised for some time and has both experimental and theoretical support [68,69,70,71].

The application of these ideas to a specific example,

namely the photochemical rearrangement of 4,4-diphenylcyclohexadienone (6) will now be considered. It has been shown [72,73] that irradiation of this compound in aqueous dioxan affords the bicyclic ketone (7) which on further irradiation gives 2,3-diphenylphenol (8), 3,4-diphenylphenol (9) (a minor byproduct) and the carboxylic acid (10).

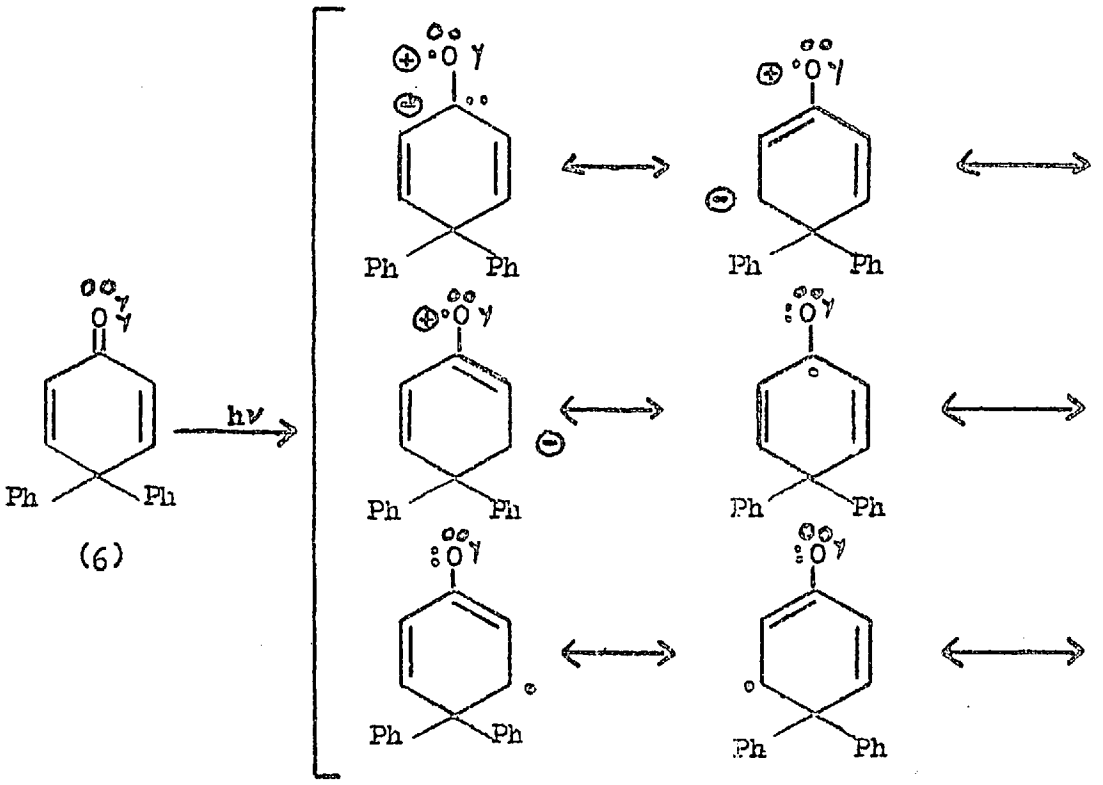


Reminiscent of the santonin photolysis, it was further shown [74] that on irradiation in 50% aqueous acetic acid the amounts of 2,3-diphenylphenol and 3,4-diphenylphenol became approximately the same.

The approach to a rational mechanistic interpretation of this rearrangement is as follows:-

(a) $n \rightarrow \pi^*$ excitation

This excitation proceeds as below:-

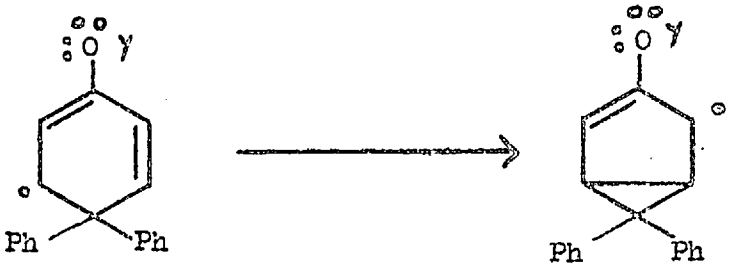


(6)

(11)

(b) A continuous electron redistribution process of the $n \rightarrow \pi^*$ state i.e. "bond alteration".

The most reasonable bond alteration process is as follows:-

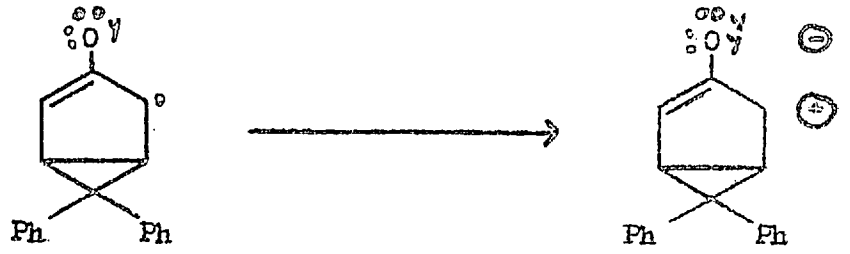


(11) (12)

Two factors favour the formation of (12) in preference to other structures. The first is that there are four resonance forms contributing to it (other possible structures have less than this), and secondly it involves a minimum of electron localisation. It should be pointed out, however, that bond alteration processes of the type depicted above are in direct competition with radiationless transitions leading back to the ground state of 4,4-diphenylcyclohexadienone, and ground state formation with radiation. If the transition is from the $n - \pi^*$ singlet, this radiation is fluorescence and if from the $n - \pi^*$ triplet it is phosphorescence.

(c) π^* - n electron demotion.

The demotion process is as follows:-

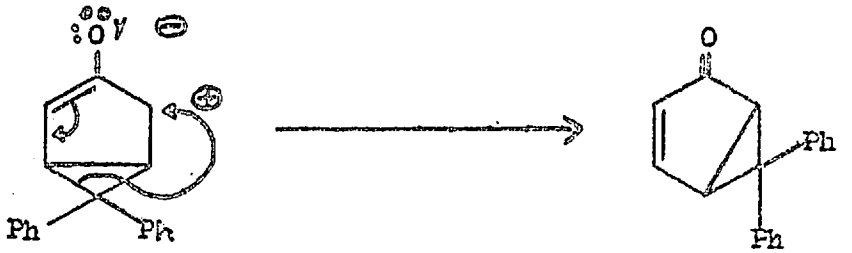


(12) (13)

In this connection it is important to note that (12) and (13) are different species and not simply different resonance forms, and secondly, that the π electron system includes the oxygen atom. Thus demotion does not involve a large movement of the electron in space.

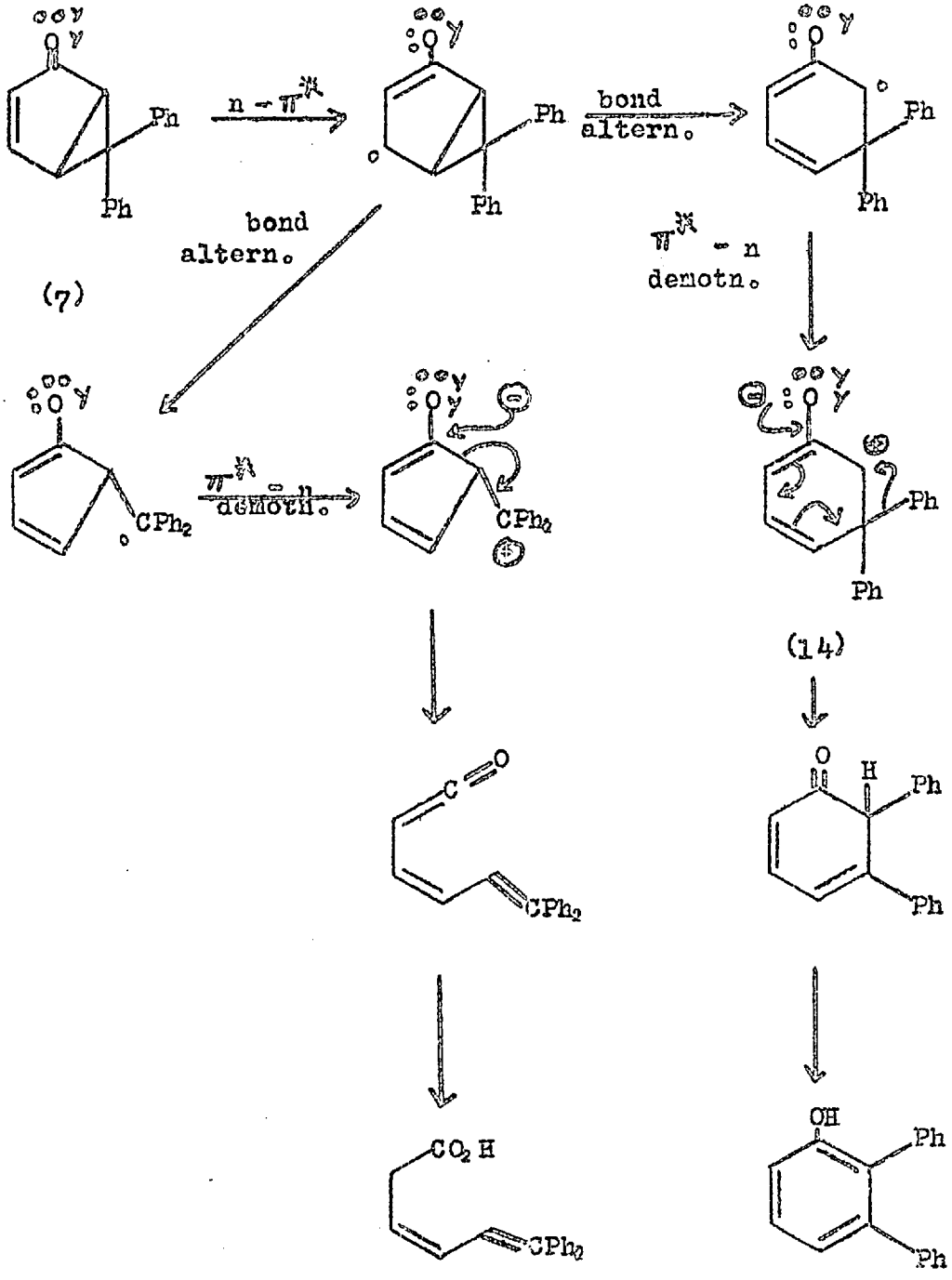
(d) Continuous electron redistribution processes of the species formed.

The mesionic species (13) now collapses smoothly to give the bicyclic ketone (7). This takes place by conventional electron redistribution processes.

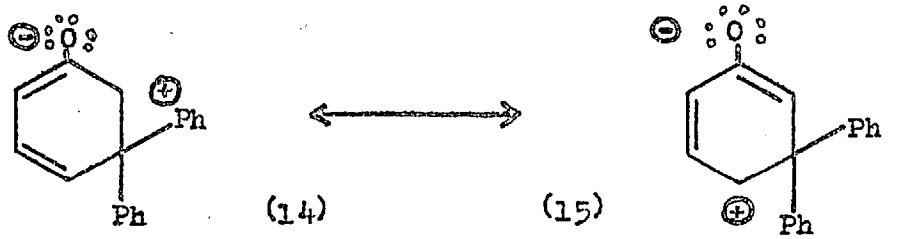


(13) (7)

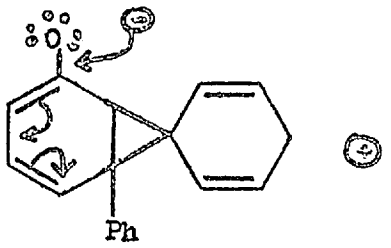
Application of the same type of processes allows for the formation of the other products viz:-

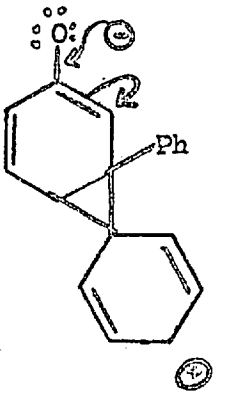


One must now enquire why 2,3-diphenylphenol is the predominant product in aqueous dioxan whereas in aqueous acetic acid approximately equal quantities of 2,3-diphenylphenol and 3,4-diphenylphenol are produced. Considering intermediate (14), it is clear that a second resonance form (15) is possible, and that it is this form which leads ultimately to 3,4-diphenylphenol.



(14) (15)

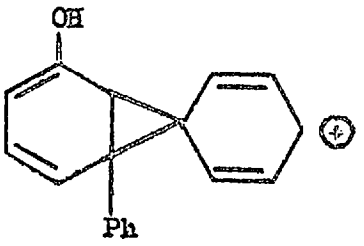




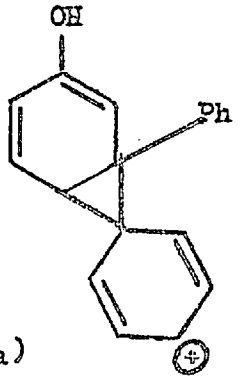
(16) (17)

Inspection of the phenonium ion intermediates in the migration of the phenyl group to C_2 (16) and in the migration to C_3 (17) shows that there is greater electron delocalisation in the former than in the latter, hence 2,3-diphenylphenol arises as the major product.

In aqueous acetic acid, however, electron delocalisation from the oxygen atom is largely suppressed and consequently neither form (16a) nor (17a) is appreciably more favoured than the other. As a result, the yields of 2,3-diphenylphenol and 3,4-diphenylphenol are roughly the same.



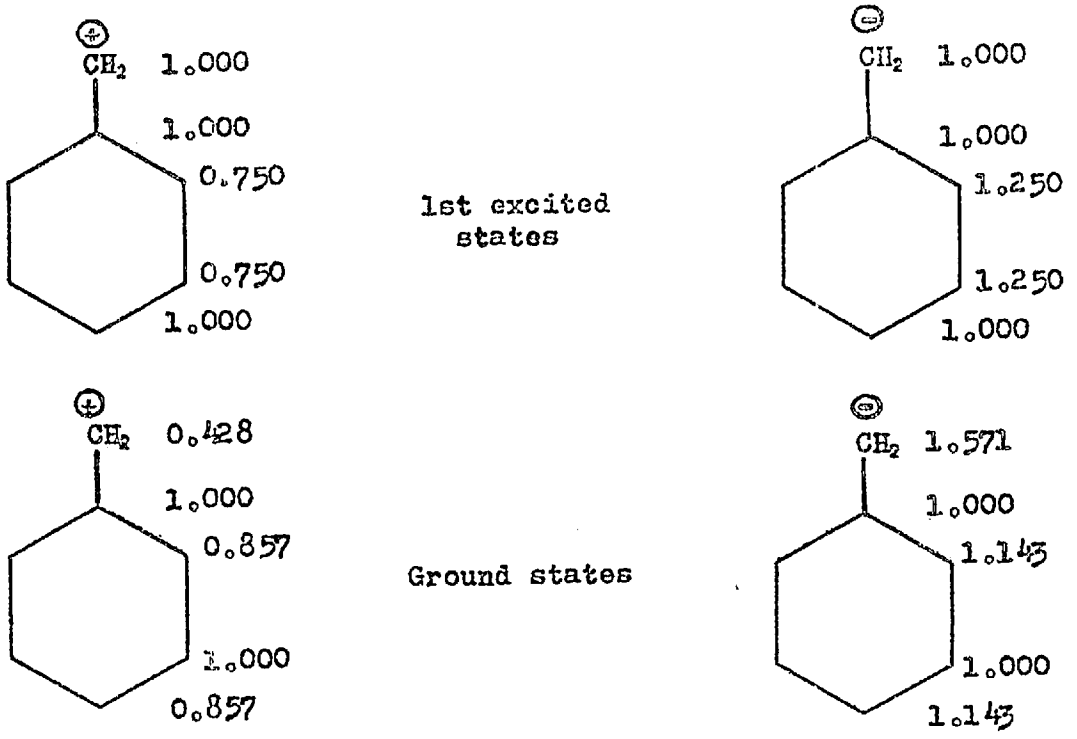
(16a)



(17a)

(ii) $\pi - \pi^*$ transformations

Calculations have shown [75] that the electron densities for the ground and first excited states of a pair of substituted benzenes, one containing an electron withdrawing group, $-CH_2^{\oplus}$, and the other an electron donating group, $-CH_2^{\ominus}$, are as follows:-

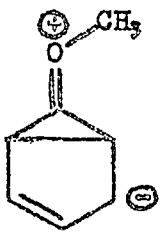


The numbers refer to π electron densities.

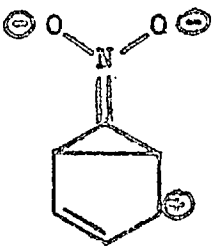
(Similar charge distributions can be compiled for other electron withdrawing and electron donating groups.)

In contrast to the ground states which show the typical ortho, para electron withdrawal by $-CH_2^{\oplus}$ and ortho, para electron donation by $-CH_2^{\ominus}$, the first excited states show an ortho, meta transmission.

For general use it is found to be more convenient to adopt an approximate form of the MO results as embodied in the valence bond structures (18) and (19).



(18)

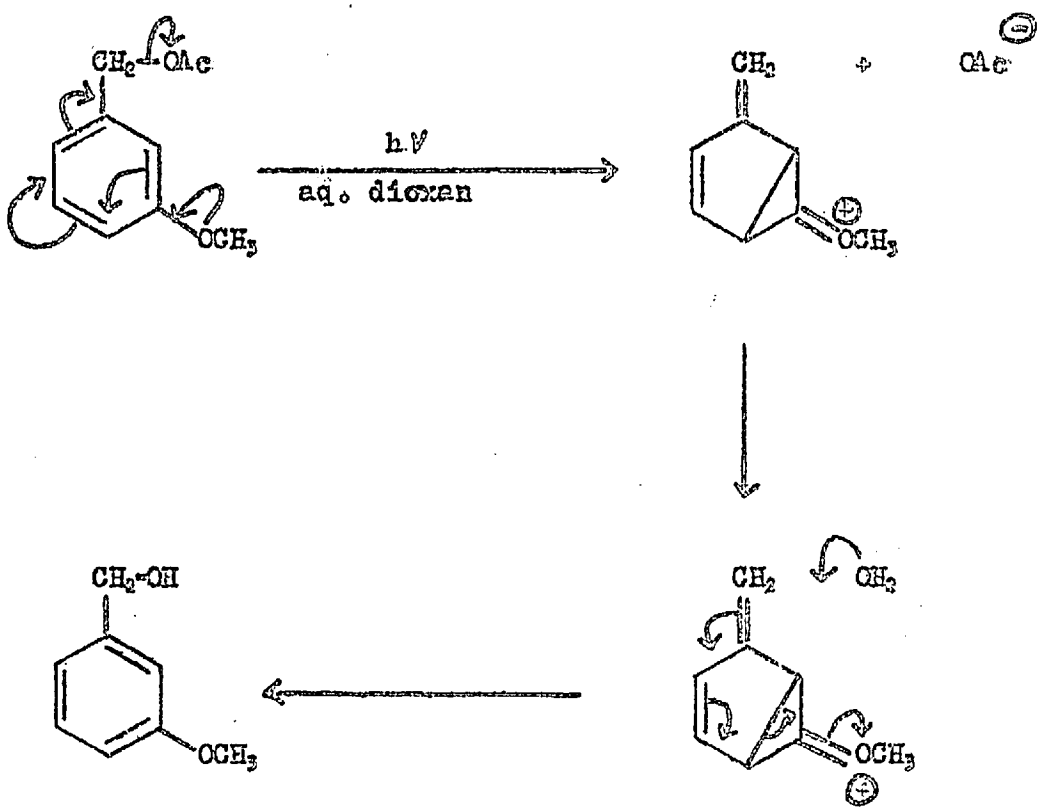


(19)

Experimental support for the results of the MO calculations has been forthcoming and is tabulated below.

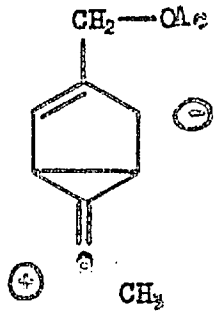
COMPOUND PHOTOLYSED	QUANTUM YIELD	PRODUCT DISTRIBUTION
4-Methoxybenzyl acetate in aq. dioxan	0·016	Mainly free radical products, $Ar.CH_2.CH_2.Ar$, $Ar.CH_2$-dioxan, dioxanyldioxan
3-Methoxybenzyl acetate in aq. dioxan	0·13	Somewhat greater quantities of 3-methoxybenzyl alcohol than free radical products
3-Methoxybenzyl acetate in aq. ethanol	0·10	3-Methoxybenzyl alcohol and 3-methoxybenzyl ethyl ether plus free radical products
3,5-Dimethoxybenzyl acetate	0·10	Cleanly 3,5-dimethoxybenzyl alcohol as only isolable product

The mechanism of the solvolytic reaction is formulated as follows:-



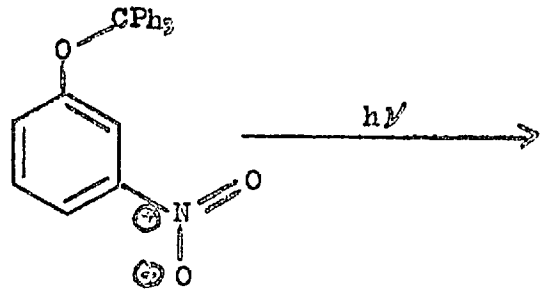
However, for the p-methoxy derivative there is no such high electron density on the benzyl carbon as is shown in structure (20).

(20)

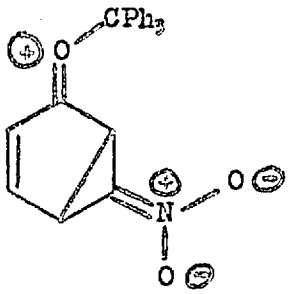


Experimental support for the calculations has also been given [76,77] for the case of the electron withdrawing groups. For example, it has been found that in the dark p-nitrophenyl trityl ether solvolyses smoothly in 90% aqueous dioxan while the meta isomer is recovered unchanged. Conversely, on irradiation under the same conditions m-nitrophenyl trityl ether is smoothly solvolysed while the solvolysis of the p-isomer is scarcely altered.

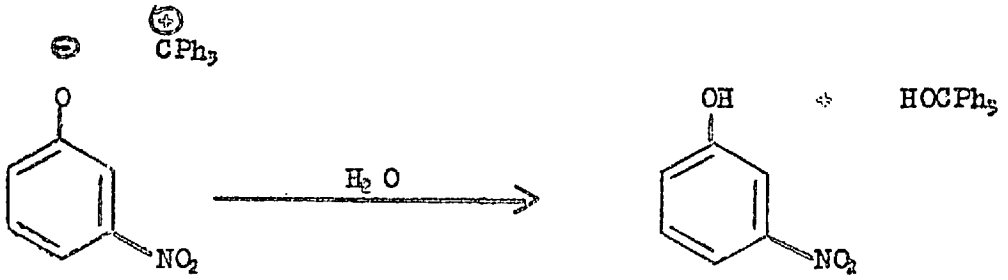
These solvolytic reactions may be formulated as follows:-

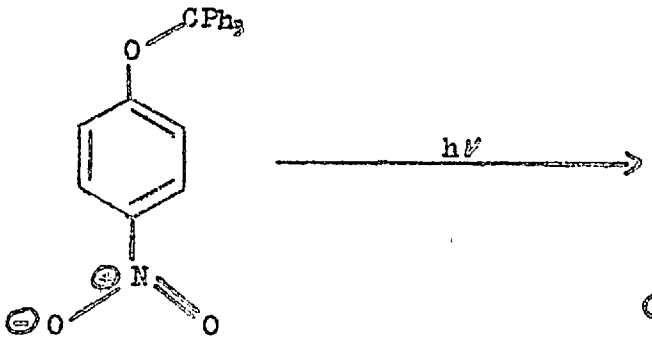


Electron distribution unfavourable for heterolytic fission.

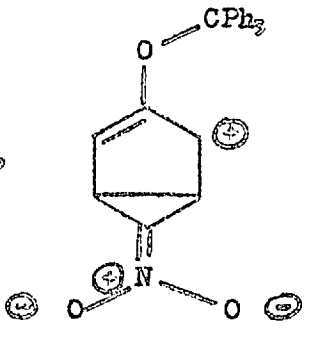


Electron distribn. favourable for heterolytic fission.





Electron distribn. favourable for heterolytic fission.



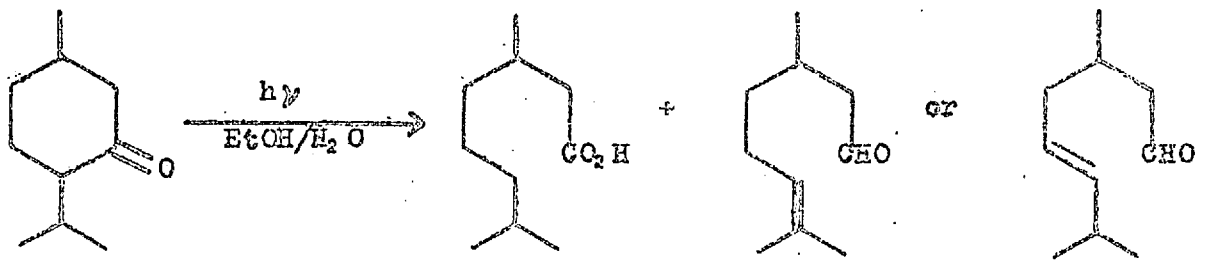
Electron distribn. unfavourable for heterolytic fission.

3. General Survey

Attention will now be turned to giving a general survey of organic photochemical reactions. The scope will, of necessity, be limited and the treatment inexhaustive.

(i) Saturated Ketones

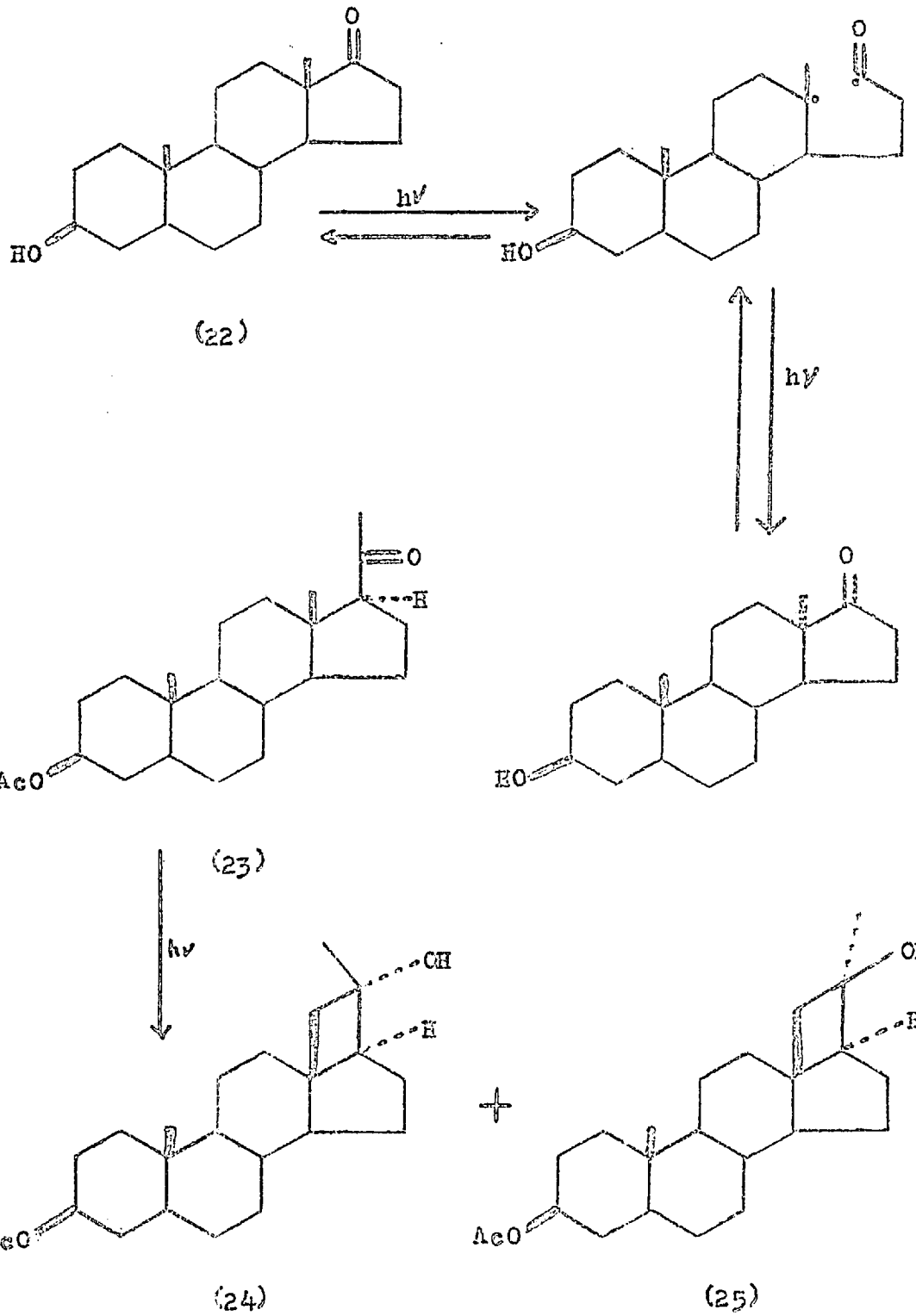
On irradiation, saturated ketones can be induced to undergo α-cleavage [7,8] as exemplified below by the photolysis of menthone (21).



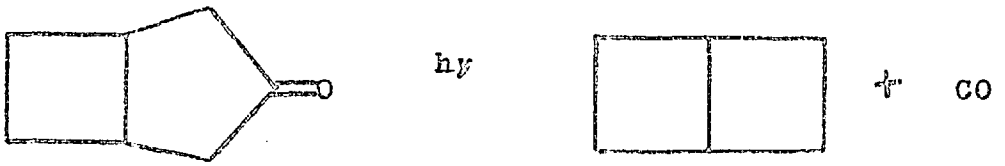
(21)

Sometimes, however, recyclisation of the intermediate radical takes place often in a different stereochemical sense as in the epimerisation [9] of androsterone (22).

These ketones will also undergo γ-hydrogen transfer. This can be particularly useful in the steroid series where it can constitute a method of direct attack on the C_{18}-methyl group. For example, irradiation of 3β-acetoxy-20-oxo-5α-pregnane (23) gives the alcohol (24) (60%) and the alcohol (25) (20%).


O
HO
hν
O
HO
(22)
hν
O
H
AcO
O
HO
(23)
hν
OH
H
AcO
+
OH
H
AcO
(24)
(25)

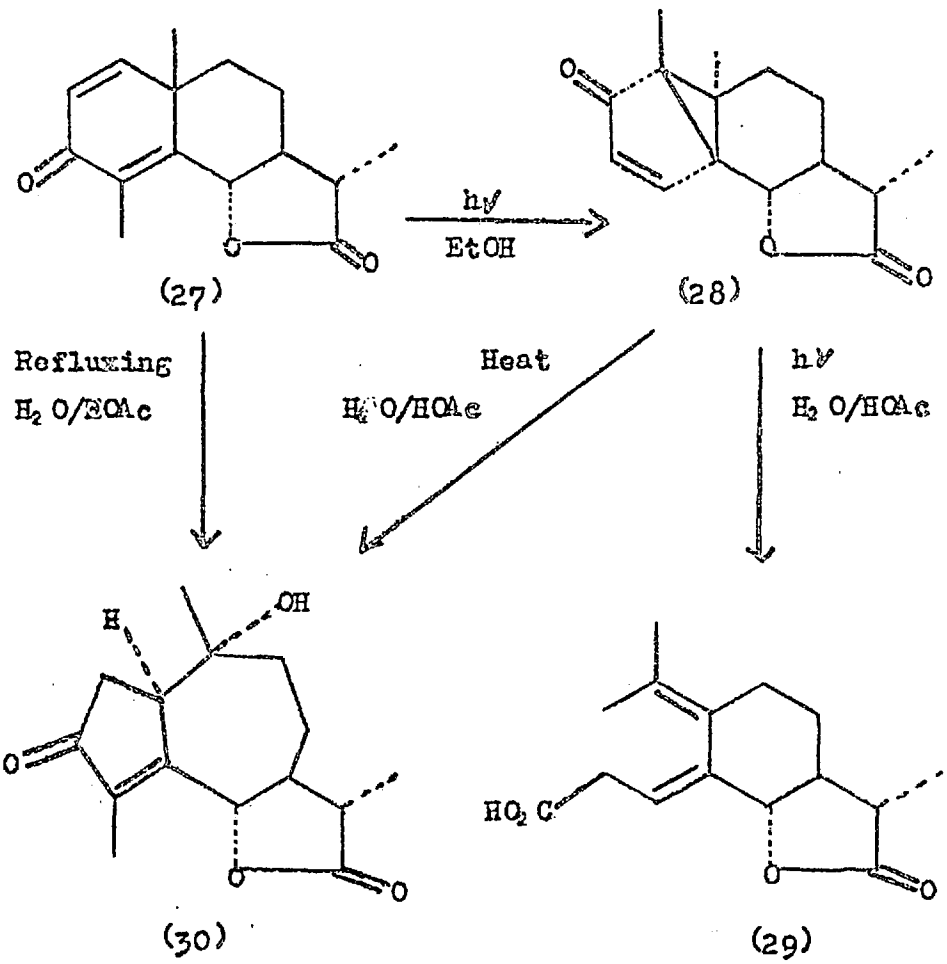
Extrusion of carbon monoxide can also take place, often leading to unusually strained systems as in the case of the formation of bicyclo[2.2.0]hexane (26).



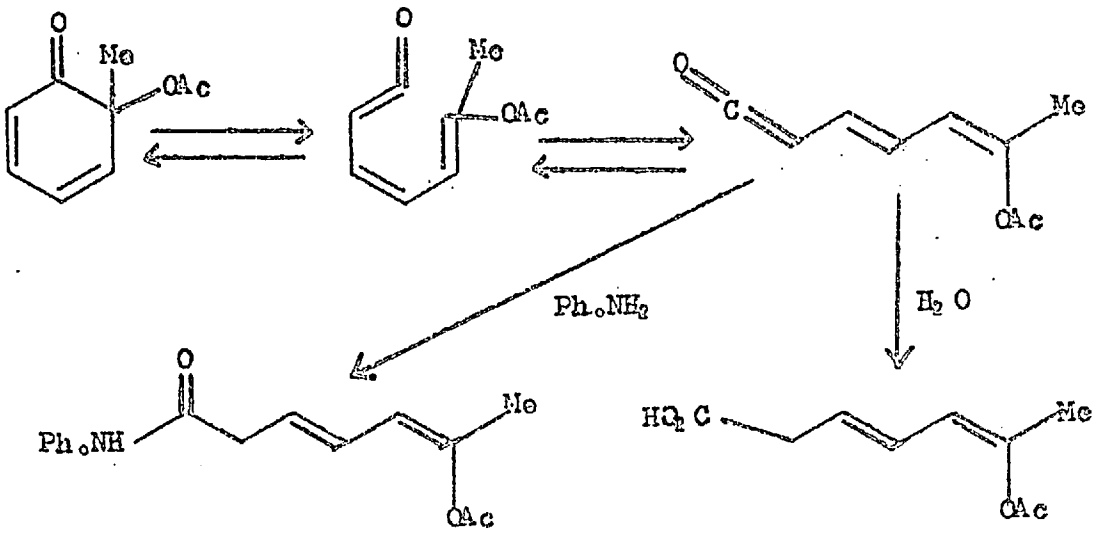
(26)

(ii) αβ-Unsaturated Carbonyl Compounds

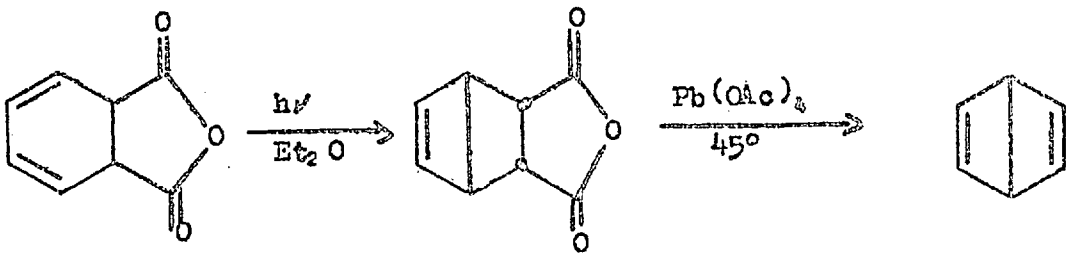
One of the most interesting examples is the photochemistry of santonin (27). Depending upon the conditions, lumisantonin (28), photosantonic acid (29) and the hydroazulene, isophotosantonic lactone, (30) are all produced [82, 83, 84, 85, 86, 87].


hν
EtOH
(27)
(28)
Refluxing
H2O/EtOAc
Heat
H2O/HOAc
hν
H2O/HOAc
OH
H
HO2C
(30)
(29)

2,4-Cyclohexadienes also undergo photochemical reactions [88].



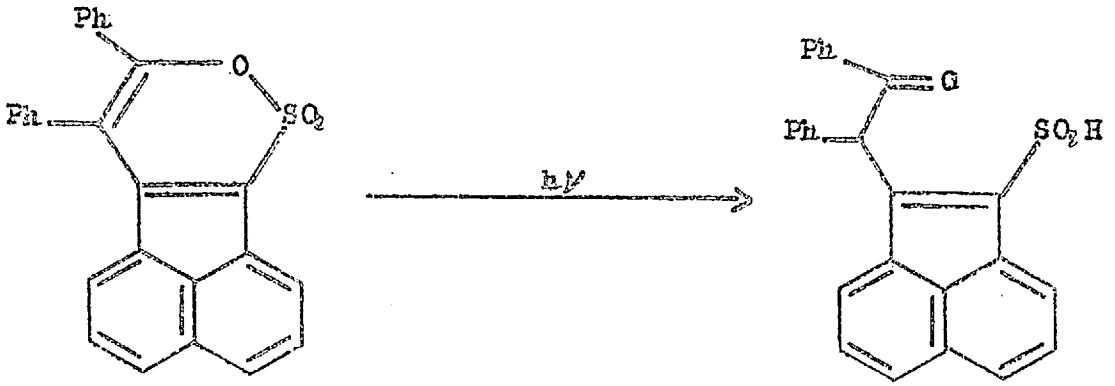
A most interesting example of a photochemical rearrangement of a 2,4-cyclohexadiene is the transformation seen below. Anhydride (31) on treatment with lead tetraacetate then gives [89] "Dewar" benzene.



(31)

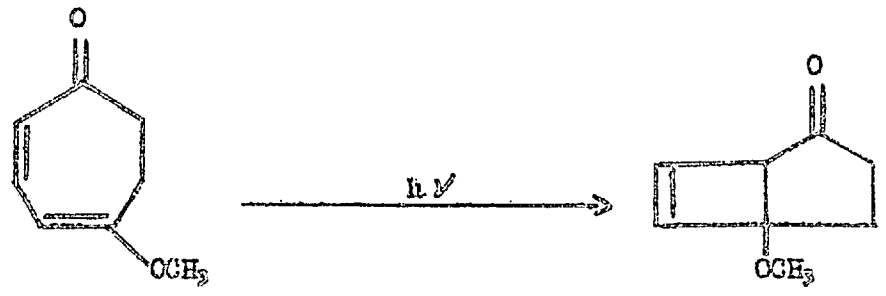
Heterocyclic analogues such as the sultones (32,34) give [90] sulphonic acids (33,35).

(32) (33)



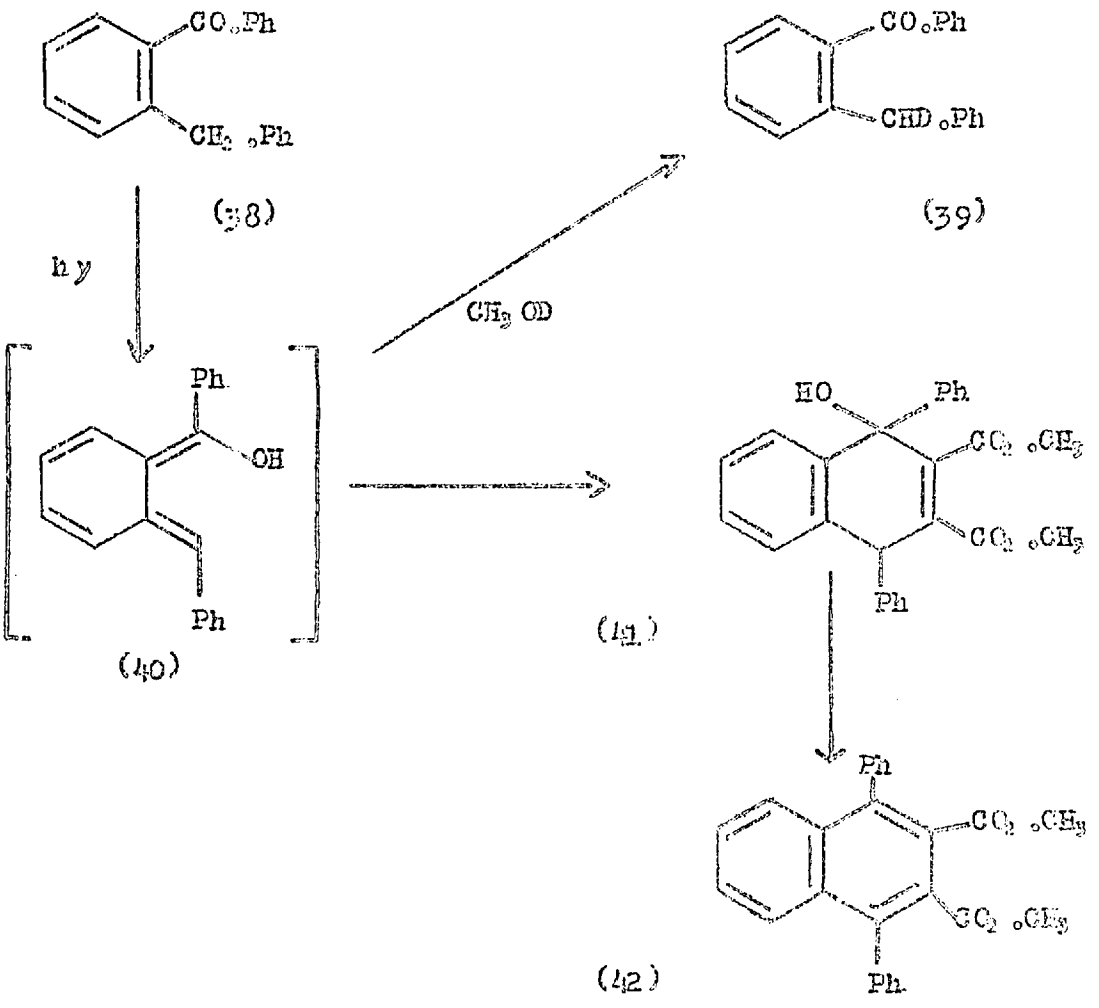
(34) (35)

Cycloheptadienones are also photosensitive. Irradiation of 5-methoxy-2,4-cycloheptadienone (36) gives [91] the bicyclic ketone (37).

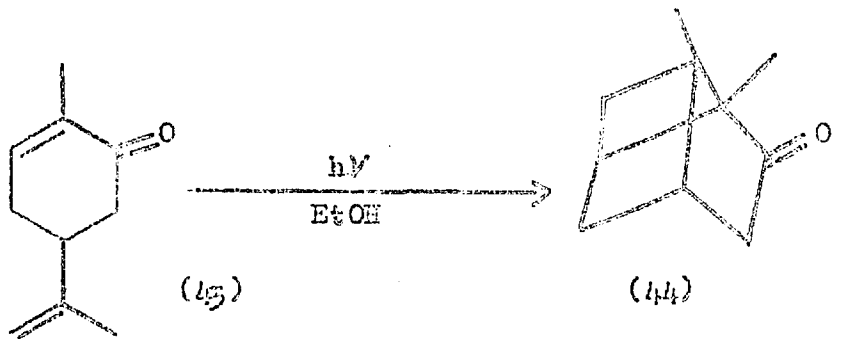


(36) (37)

Conveniently considered here is the photochemical enolisation of o-benzylbenzoylbenzene (38). Irradiation of this compound in methanol-O-D gives rise to incorporation of 1·04 to 1·09 deuterium atoms per molecule (39). The intermediate enol (40) can be trapped [92] by irradiation in the presence of acetylenedicarboxylic dimethyl ester giving first (41), and subsequently, on dehydration, the naphthalene (42).



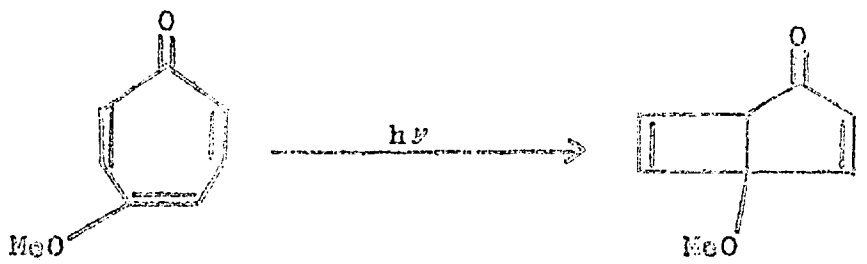
Intramolecular photoaddition can also be induced, the first authentic example reported being the conversion of carvone (43) to carvone camphor [95] (44).



(43) (44)

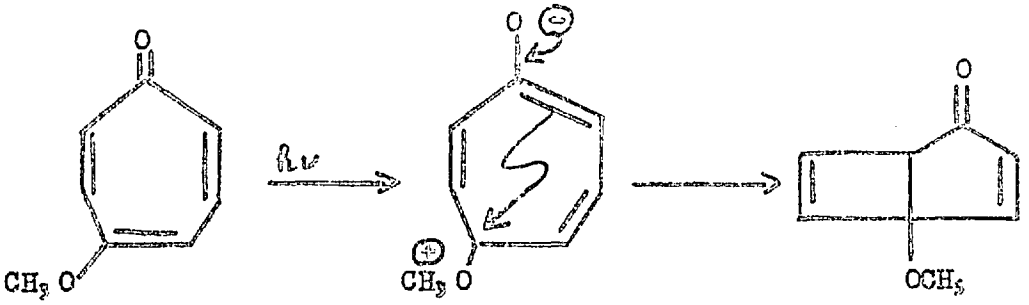
(iii) Troponoid Systems

Simple tropolones such as γ-tropolone methyl ether (45) photoisomerise [24] readily to give the bicyclic ketone (46).



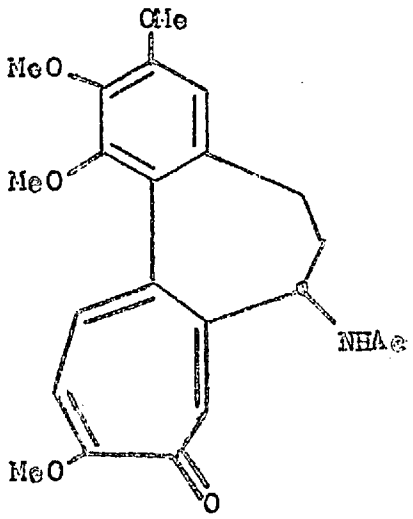
(45) (46)

This presumably occurs by way of the mechanism

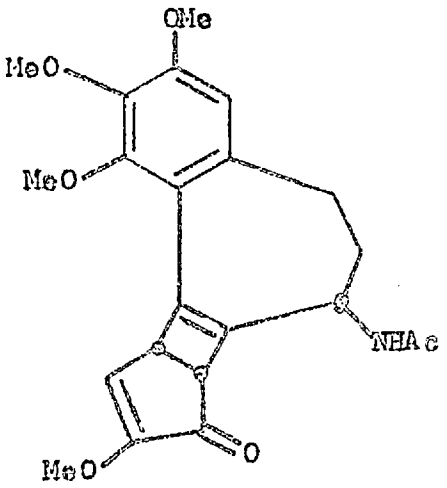


In the case of β-tropolone methyl ether, however, such a pathway would involve the formation of a three membered ring and as is to be expected, no bicyclic products have been found. Indeed, the product consists of a highly complex mixture of substances [95].

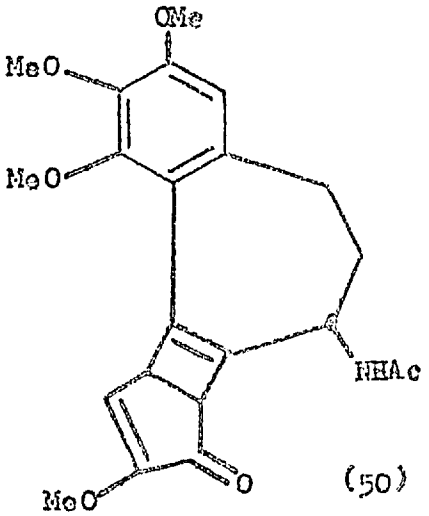
In addition to the simple structures discussed above, the alkaloid colchicine (47) is also photosensitive in a similar way. Aqueous solutions of this material on exposure to sunlight give [96, 97] varying quantities of three photoproducts α-, β- and γ-lumicolchicine (48, 49, 50 respectively).


OMe
MeO
MeO
NHAc
MeO
O

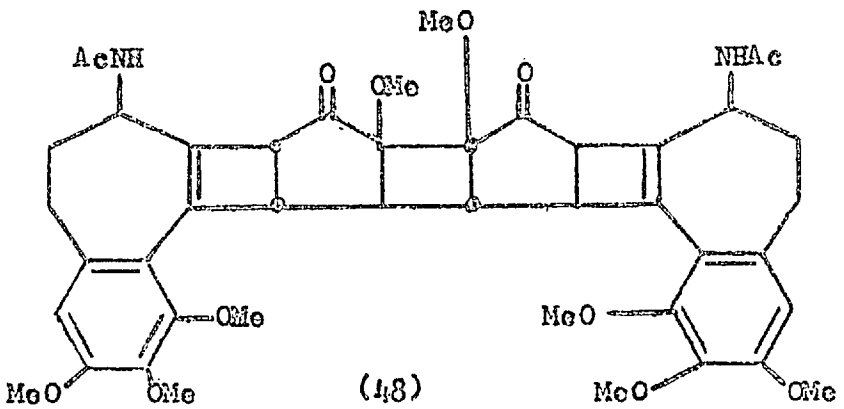
(47)


OMe
MeO
MeO
NHAc
MeO
O

(49)


OMe
MeO
MeO
NHAc
MeO
O

(50)


MeO
AcNH
O
OMe
O
NHAc
OMe
MeO
MeO
OMe
MeO
MeO
OMe

(48)

(iv) Olefinic and Aromatic Systems

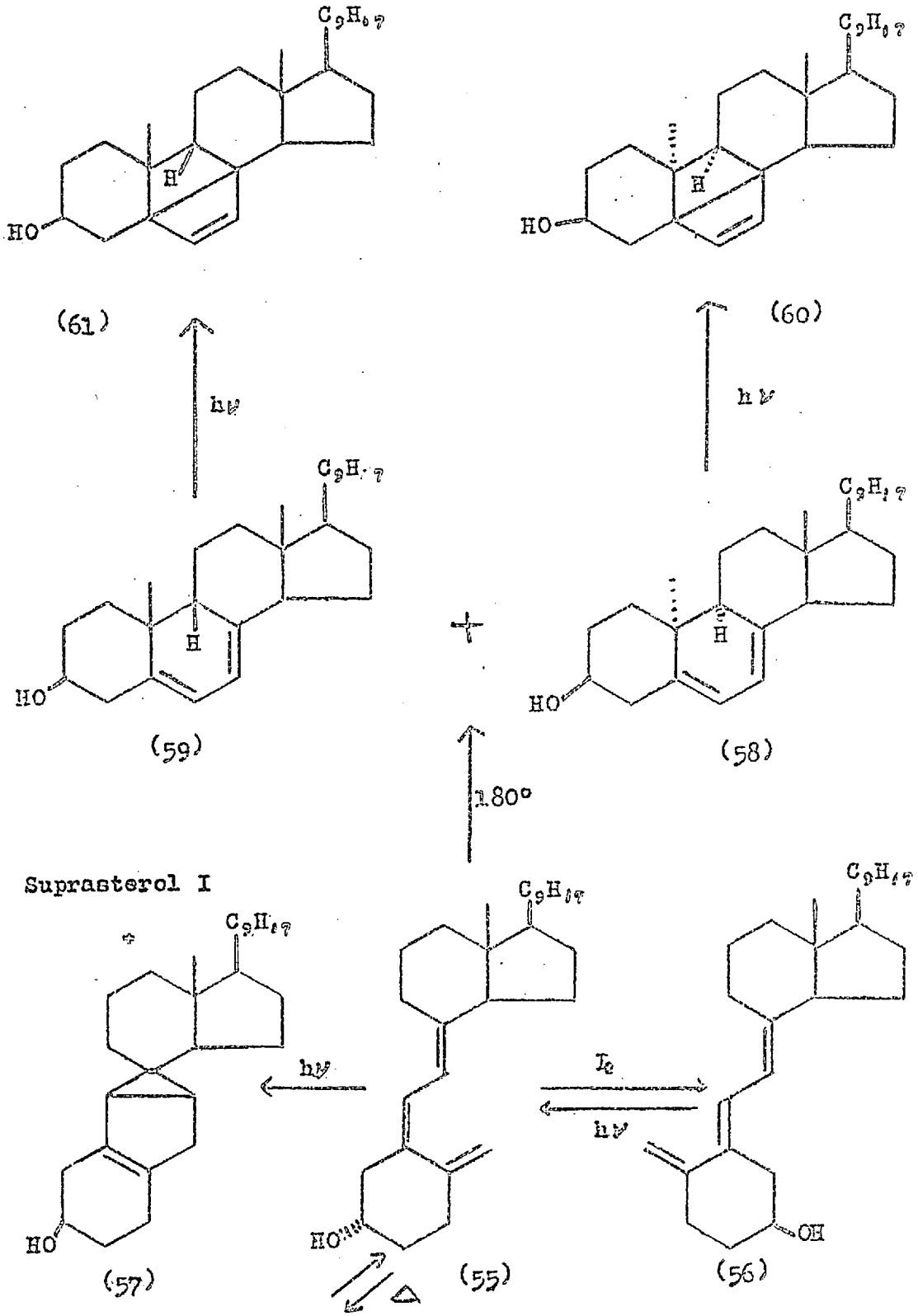
Investigations into the photochemistry of the vitamin D series have been extensive [99-107]. The more significant results are summarised in formulae (51) to (61) inclusive.

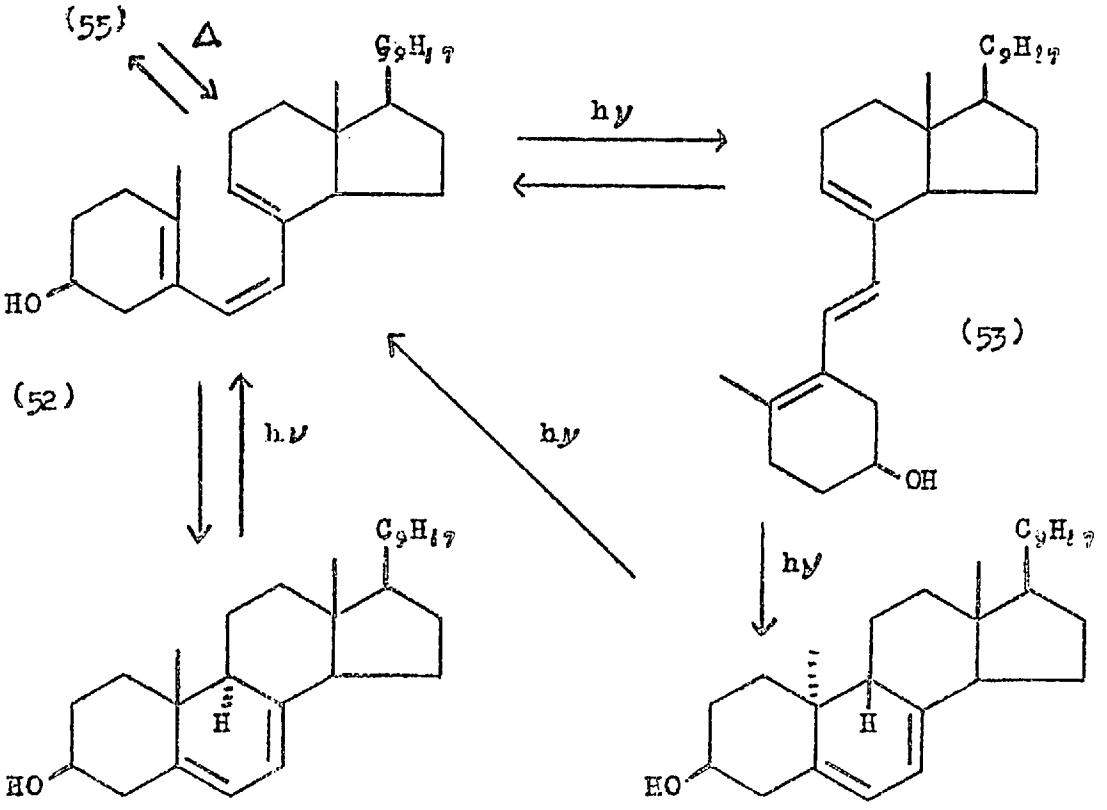
Irradiation of previtamin D_2 (52) gives as initial products tachysterol (53) and ergosterol (51). Tachysterol (53), on irradiation gives lumisterol (54), which itself can be transformed back into previtamin D_2 (52), and ergosterol (51). Likewise, ergosterol (51) also affords previtamin D_2 (52).

Previtamin D_2 (52) is equilibrated thermally with vitamin D_2 (55). Further, on treatment with iodine, a geometrical isomer (56) which can be reconverted into vitamin D_2 by irradiation, is obtained. Irradiation of vitamin D_2 itself produces suprasterol I (not yet characterised) and suprasterol II (57).

Vitamin D_2 is converted thermally in the absence of oxygen into a mixture of pyrocalciferol (58) and isopyrocalciferol (59). Irradiation of pyrocalciferol (58) gives a pentacyclic valence tautomer (60) and similarly, irradiation of isopyrocalciferol gives (61). These were the first reported examples of the cyclisation of a 1,3-diene to a cyclobutene.

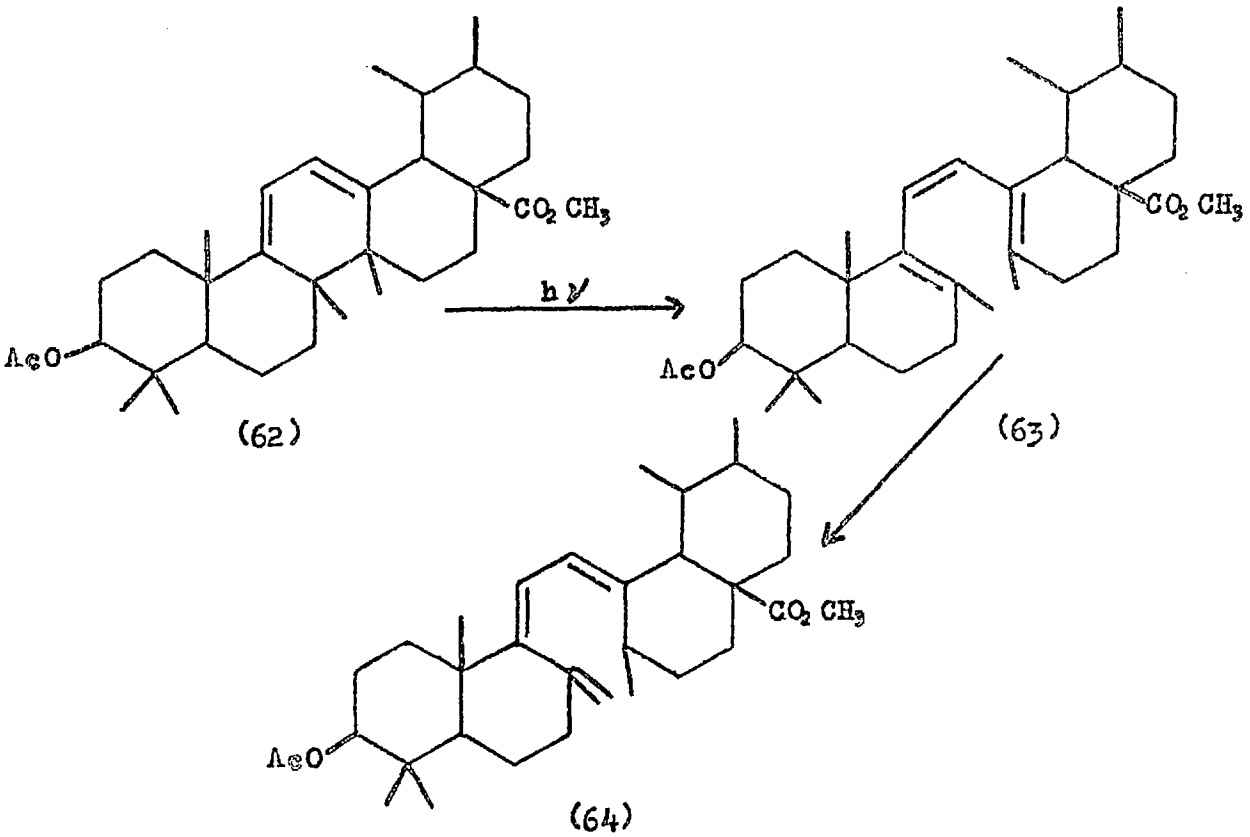
It is to be noted, that while 9,10-cis-stereochemistry (58,59) leads to valence tautomers, 9,10-trans-stereochemistry

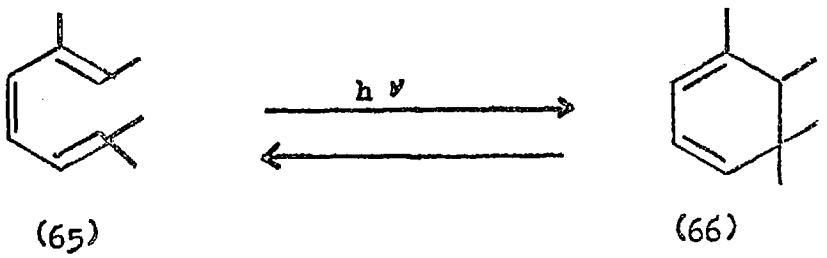

C_9H_{17}
HO
H
(61)
(60)
hν
hν
(59)
(58)
+
180°
Suprasterol I
(57)
(55)
(56)
hν
hν
Δ
OH



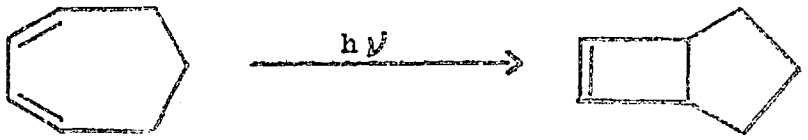
(51, 54) leads to ring cleavage.

Apart from the reactions described above, dienes and trienes are photosensitive generally. For example, methyl dehydroursolate acetate (62) undergoes photochemical opening to structure (63) followed by thermal isomerisation to (64)[108] Alloocimene (65) gives α-pyronene (66), the reaction being reversible.



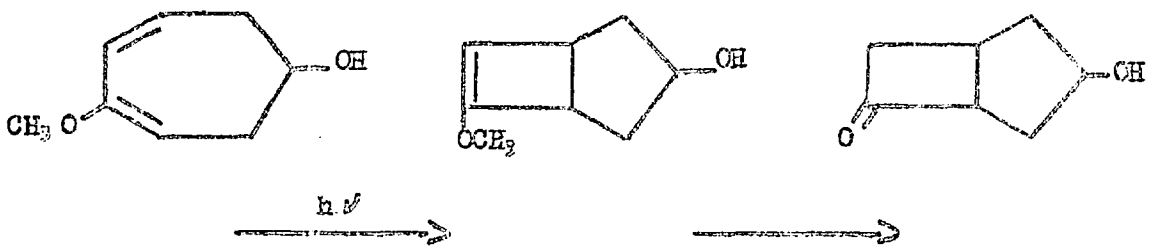


1,3-cycloHeptadienes undergo some interesting reactions. Irradiation of 1,3-cycloheptadiene itself(67) gives bicyclic photoisomer (68).

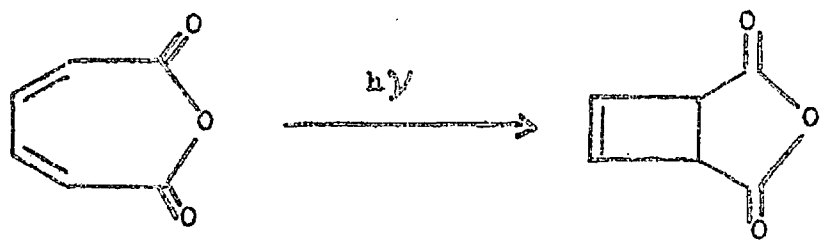


(67) (68)

Many other and analogous photocyclisations have been reported, often leading to compounds difficult to synthesise by alternative routes. Some of these are illustrated below.



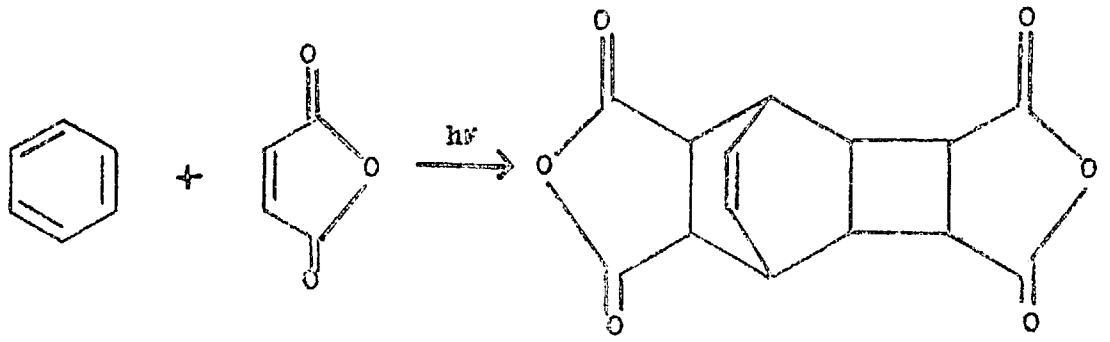
This represents a potentially general synthesis of cyclobutanone derivatives.



(69) (70)

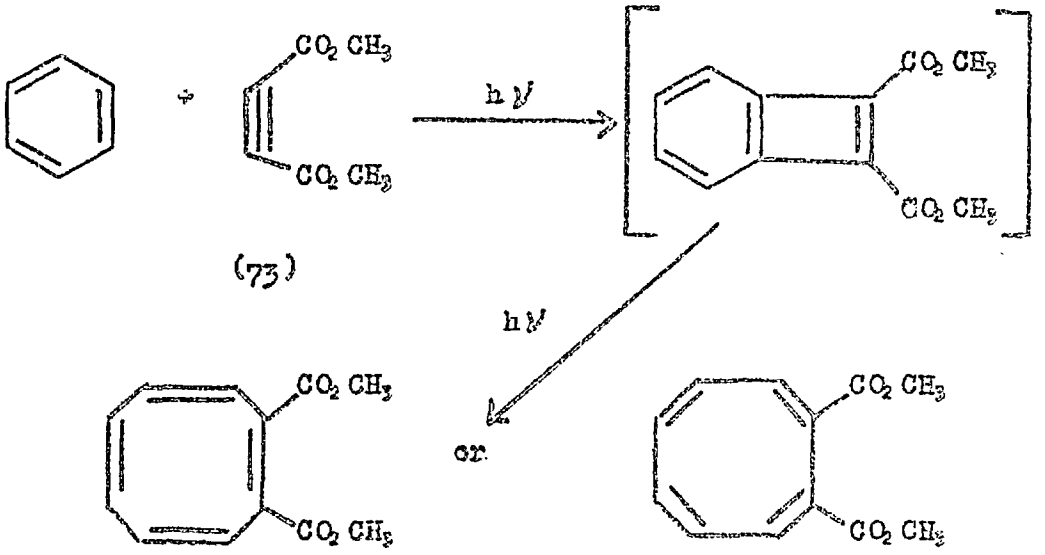
Formulae (69) to (70) show an elegant synthesis of cis-3-cyclobutene-1,2-dicarboxylic acid.

Benzene and its homologues have been believed until recently to be stable to photochemical excitation. However, it has been shown [109] that irradiation of benzene in the presence of maleic anhydride (71) gives rise to structure (72), produced formally by 1,2-addition followed by a Diels-Alder reaction.



(71) (72)

Similarly, from the irradiation of benzene in the presence of acetylenedicarboxylic dimethyl ester (73), either structure (74) or (75) is obtained [110,111].



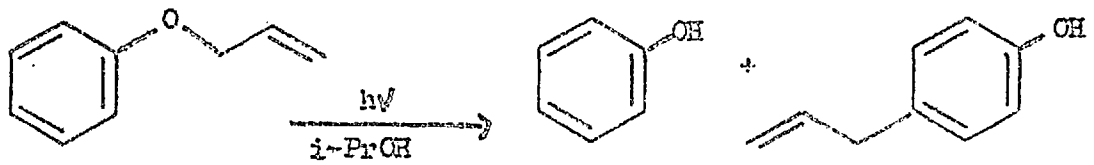
(73)

(74) (75)

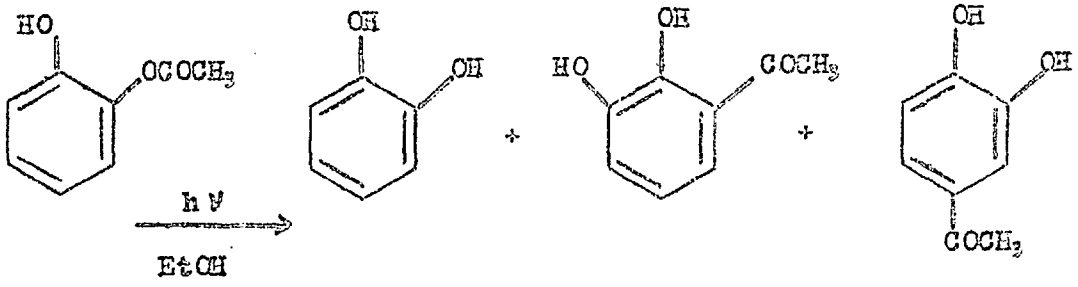
The irradiation of benzene itself has been reported [112] to give small amounts of fulvene (76).

(76)

Irradiation of aryl esters leads to products analogous to those obtained in the Claisen rearrangement [113].

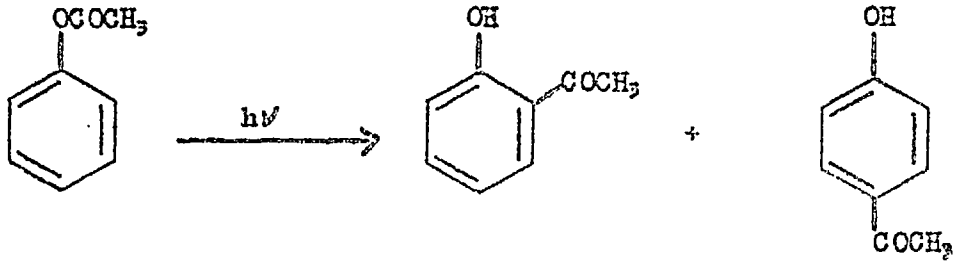


The Fries rearrangement also has its photochemical parallel. Irradiation of 2-hydroxyphenyl acetate (77) gives o-dihydroxybenzene (78), 2,3-dihydroxyacetophenone (79) and 3,4-dihydroxyacetophenone (80).



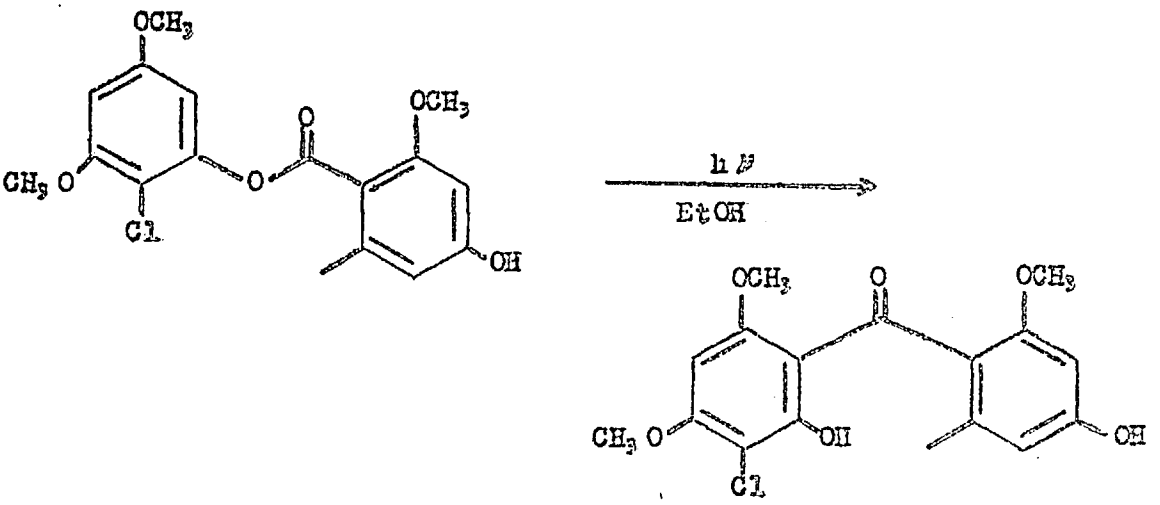
(77) (78) (79) (80)

Phenyl acetate (81) similarly produces 2-hydroxy-acetophenone (82) and 4-hydroxyacetophenone (83)



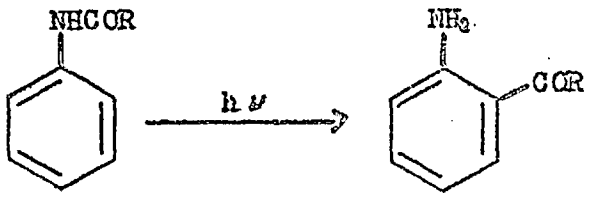
(81) (82) (83)

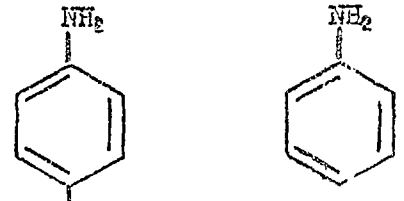
This reaction has been found useful in the griseofulvin synthesis [115].



The photochemical rearrangements of phenolic acetates have been studied in general and their synthetic possibilities revealed [116].

Recently, the photochemical rearrangement of N-acyl-anilines has been reported [117] viz:-



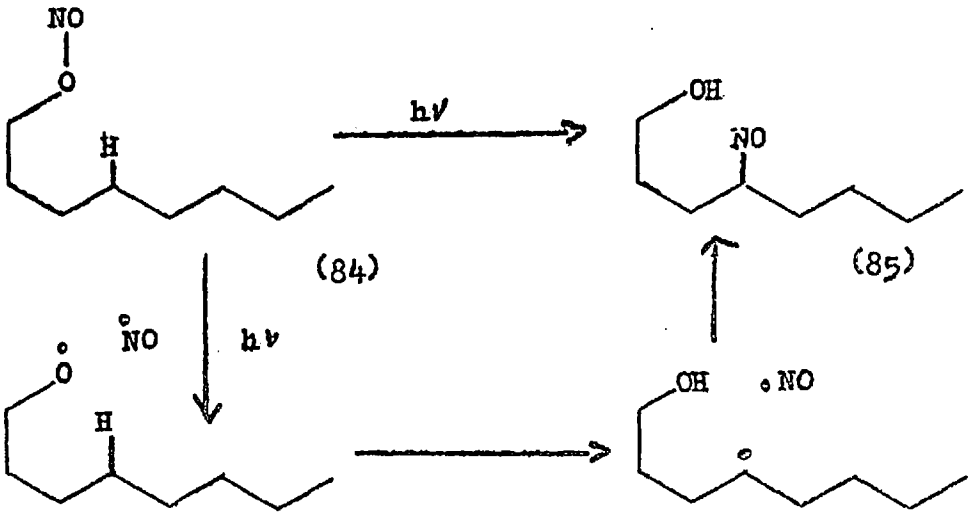


	%	%	%
R = CH_3	20	25	1(
R = Et	22	25	2(
R = n-C_3H_7	18	23	2:

(v) Nitrite Photolysis and Related Reactions

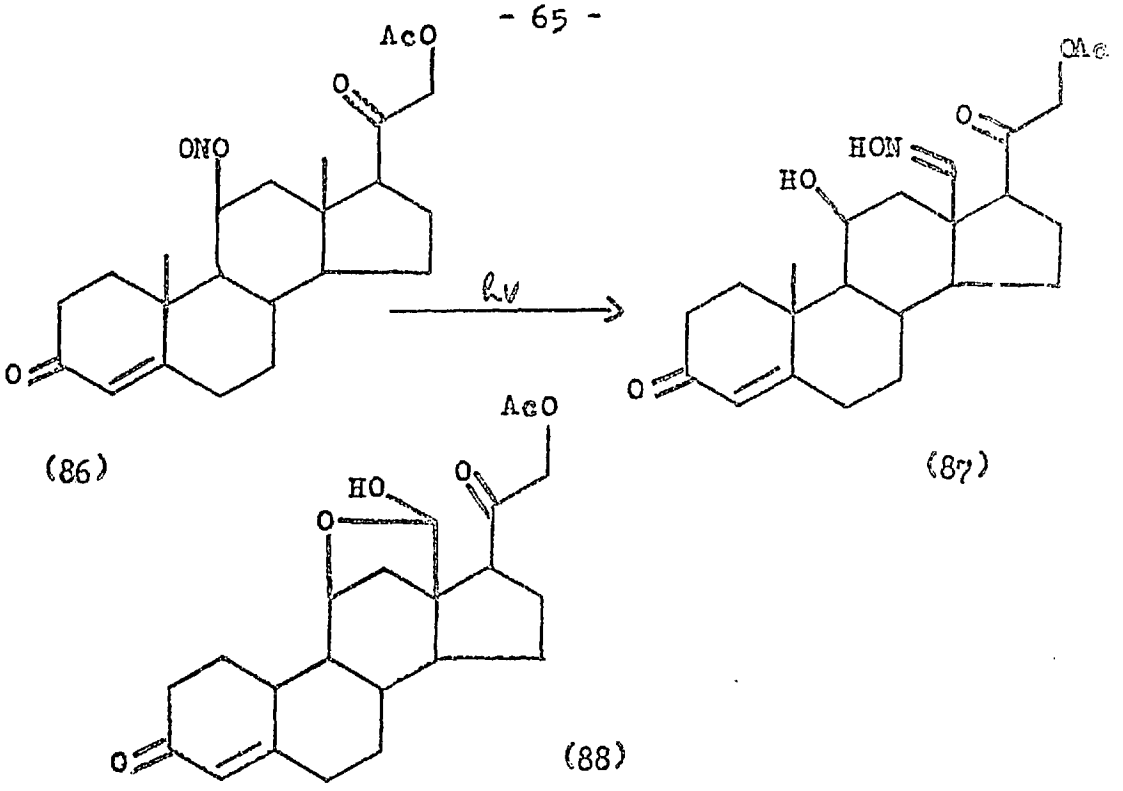
Nitrite photolysis is a long established reaction and has recently been reviewed [110] by Nussbaum and Robinson The real potential of nitrite photolysis, however, was only realised by the elegant work of Barton[65]. If an organic nitrite is photolysed, a hydrogen atom in a γ-relationship to the nitrite exchanges position with the nitroso group. This is called the Barton reaction. For example, irradiation of n-octyl nitrite (84) gives [119] principally 4-nitroso-1-octanol (85). The reaction involves fission of the N-O bond to give an alkoxy radical and nitric oxide, followed by shift of the γ-hydrogen to the alkoxy radical, thus generating a hydroxyl

group and an alkyl radical. The nitric oxide then combines with the alkyl radical giving nitroso derivative (85).



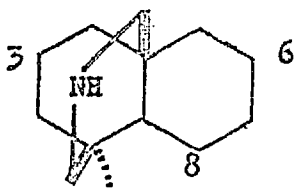
The mechanism of the Barton reaction has recently been the subject of some elegant work by Akhtar and Pechet [120].

Perhaps the most spectacular use of this reaction has been in the synthesis of aldosterone acetate [121]. Irradiation of corticosterone-21-acetate-11β-nitrite (86) gives, inter alia, aldosterone oxime acetate (87) in 21% yield. From this on hydrolysis can be obtained aldosterone acetate (88).



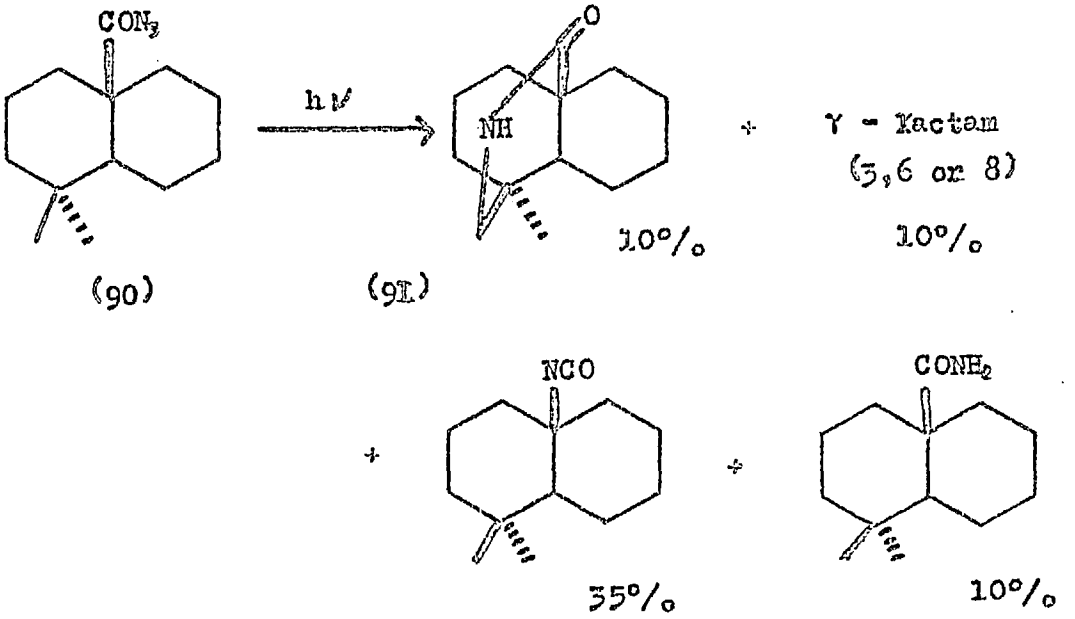
(86) (87) (88)

The photolysis of azides has also been investigated and has been dramatically used in the synthesis [122] of one of the major structural units in many diterpene alkaloids (89).



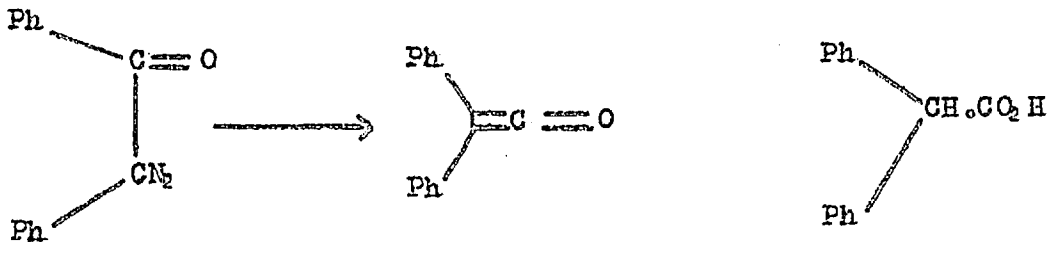
(89)

Irradiation of 1,1-dimethyl-trans-decalin-10-carbonyl azide (90) results in a 10% yield of the lactam (91) corresponding to this unit.

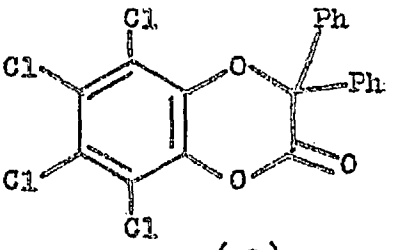


(vi) Diazoketones

Diazoketones are photosensitive and often their reactions may be interpreted as proceeding through a carbene. Thus rearrangements similar to the Arndt-Eistert reaction are frequently found [123, 124]. In some cases, the intermediate ketene may be trapped.



If this reaction is carried out in tetrachloro-o-quinone, a lactone (92) is formed [125].

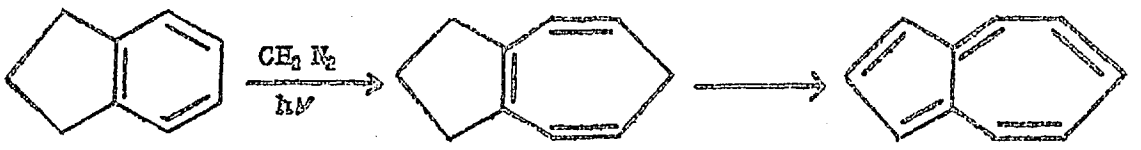


(92)

In contrast, diazoesters undergo addition reactions with unsaturated systems to give cyclopropane rings and further transformation products of these [126].

(vii) Diazoalkanes

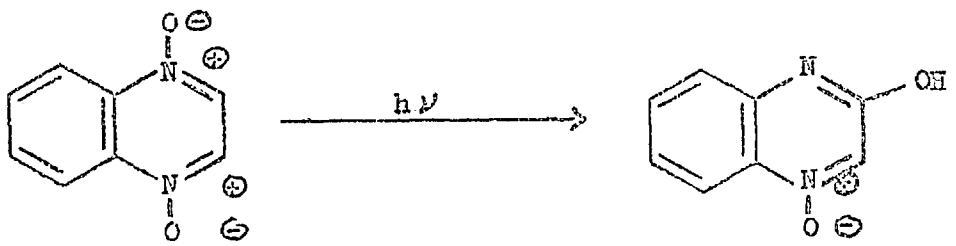
Of considerable synthetic usefulness has been the photolytic decomposition of diazomethane in a benzenoid solvent. This technique has been used in the synthesis of certain seven membered rings, for example, tropones, azulenes [127] and terpenes.



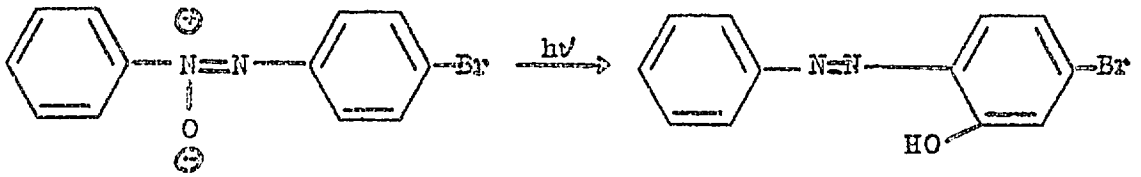
(viii) Oxygen Transfer Reactions

Nitrones photoisomerise to oxaziranes[128,129] which themselves often undergo thermal isomerisation to amides. In some cases, therefore, the amide is isolated directly from the irradiation. For example[128]

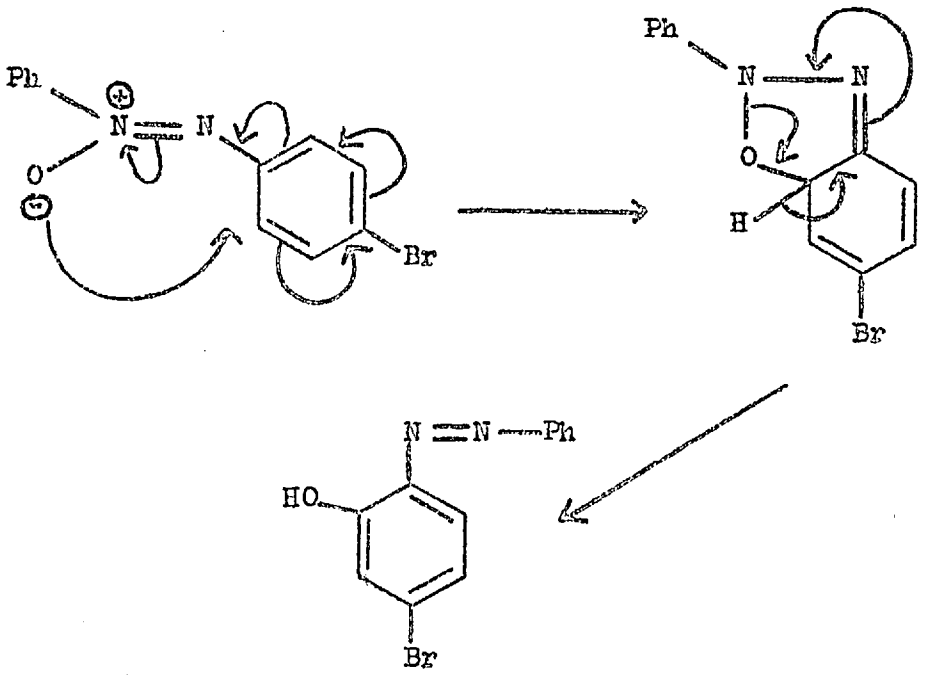
The enolic amide is occasionally isolated[130].



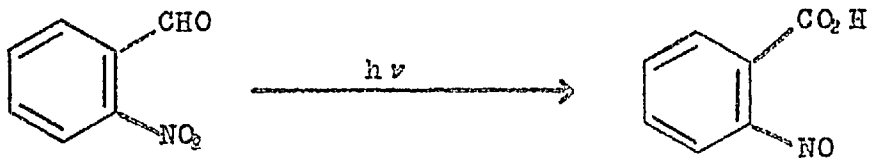
Azoxybenzenes undergo photoisomerisation to o-hydroxyazobenzenes[131].



The most likely mechanism [131] for such rearrangements is shown below.

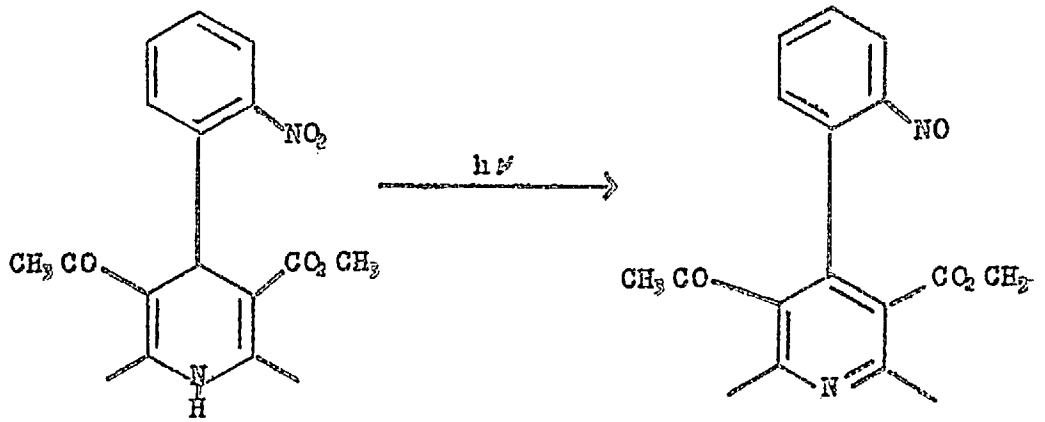


On irradiation, o-nitrobenzaldehyde (93) undergoes [132] an intramolecular disproportionation to o-nitrosobenzoic acid (94).



(93) (94)

Similarly, the dihydropyridine (95) affords [193] structure (96). Interestingly, if circularly polarised light is used, the phenylpyridyl (96) produced is optically active [194].



(95) (96)

DISCUSSION

The object of this research project was twofold. The field of photosensitive protecting groups was to be investigated generally, and an attempt was to be made to simulate the biogenesis of certain alkaloids arising by a phenol oxidative mechanism, for example, the amaryllidacae [1, 35] and morphine [1, 30] alkaloids. This was to be done by preparing a suitably protected phenol which on irradiation would cleave to give phenoxide radicals. If this protected phenol were held frozen in a glass, it was hoped that the radicals would couple preferentially in an intramolecular fashion, thus giving rise to the desired oxidation product. Such a photochemical procedure was obviously to be prefered over the more customary chemical procedures in that the yields of intramolecularly coupled products would be expected to be much higher, intermolecular reactions being kept to a minimum in the solid phase. Clearly, therefore, in any project whose ultimate aims are those stated above, it was necessary at the outset to establish that a phenoxide radical would preferentially couple with another such radical, rather than attack a phenol molecule or phenolate anion. Such an experiment is very difficult to devise since one is attempting to distinguish between two mechanisms, which in

the case of a simple phenol, give the same product[11,27].

The method used here was to oxidise[39,135] p-cresol with potassium ferricyanide in the presence of a large (x10 molar) excess of veratrole and to look for methoxylated products which had arisen from the radical substitution process, by the Zeisel method[136] in the usual way. Since negative evidence was being sought it was obviously very important to be quite sure that the procedures used were capable of giving results to the right degree of accuracy.

Initially, therefore, the Zeisel determination was calibrated by carrying out the determination on a representative sample of a mixture of p-cresol and $x10^{-3}$ its weight of veratrole. A positive result was obtained showing that the analysis was accurate to at least 1 part in 1,000. Next, the extraction procedure to be used to obtain the phenolic oxidation products free from unchanged veratrole was calibrated. p-Cresol was dissolved in Na_2CO_3 solution (a definite volume of standard solution) and a x10 molar excess of veratrole added. To this mixture was further added water (the volume later used to dissolve the ferricyanide) and ethanol (a definite constant volume) to make the mixture homogeneous. The mixture was now poured into a large volume of water and extracted with ether. The weight of extract was found to be exactly equal to the sum of the weights of the p-cresol and veratrole used.

The extract was now partitioned between 10N NaOH and ether, the aqueous layer being thoroughly washed several times with the organic solvent. A total recovery of 44% of the p-cresol was made. The reason for this low figure is that the mixture consistently formed an indefinite interface and since it was essential to be sure that the aqueous layer was quite free from veratrole, inevitably this resulted in a poor recovery.

A Zeisel determination on the p-cresol recovered from the basic extract gave a negative result. Finally, the mixture of p-cresol and veratrole (1:10 molar) was oxidised with potassium ferricyanide using the same volumes of solvents and solutions as above, and the phenolic fraction found to be entirely free from -OMe residues.

All the experiments in this series were repeated twice and identical results obtained in both cases.

Thus, in so far as -OMe could be equated with -OH for the process of radical coupling, a substitution mechanism seemed improbable. However, radical substitution into a phenolate anion could not be excluded.

With this established, it was then necessary to have a suitable phenol available for use as a model compound in the photochemical coupling experiments. To this end, 2,4'-dihydroxybibenzyl (9) was synthesised. This synthesis is outlined below.

Salicylaldehyde (1) was condensed [137] with p-hydroxyphenylacetic acid (2) in the presence of acetic anhydride and triethylamine in the hope of obtaining 2,4′-diacetoxystilbene-β-carboxylic acid (3). However, while some of this compound was in fact obtained (stereochemistry was not investigated) the bulk of the product was 3-(p-acetoxyphenyl)coumarin (4).

The salicylaldehyde was thus converted [138,139] to its benzyl ether (5) and this condensed in the same way [137] with p-hydroxyphenylacetic acid. The product, a mixture of cis-and trans-4-acetoxy-2′-benzyloxystilbene-β-carboxylic acids (6) was obtained as a crystalline solid which analysed correctly. Treatment [140] of this mixture with "copper chromite" catalyst [141] in quinoline at 210° for 1·25 hours gave a brown oil which could not be crystallised and whose I.R. spectrum indicated that decarboxylation and also partial deacetylation had occurred. Accordingly, the crude mixture was reacetylated using acetic anhydride in pyridine to give 4-acetoxy-2′-hydroxystilbene (7) of unknown stereochemistry. This product which again could not be crystallised was hydrogenated over palladium charcoal and 4-acetoxy-2′-hydroxybibenzyl (8) obtained. Hydrolysis with dilute alkali afforded 2,4′-dihydroxybibenzyl (9).

Another successful but more elegant route to this phenol was also investigated.

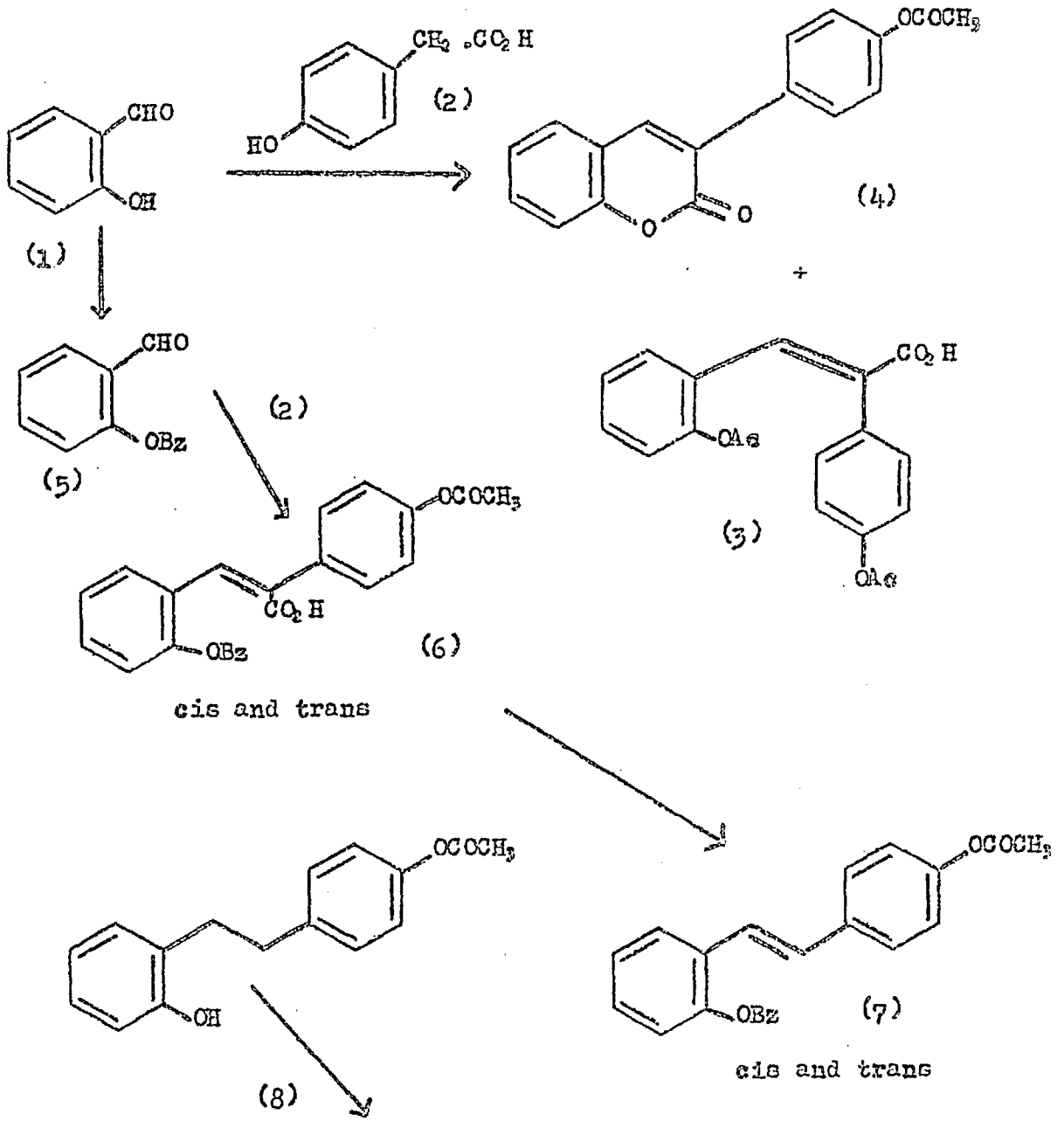
p-Hydroxybenzaldehyde (10) on treatment [139,142] with excess benzyl chloride in ethanolic alkali gave p-benzyloxybenzaldehyde (11) which was reduced [143] by potassium borohydride in suspension to give the alcohol (12). Treatment of this alcohol with thionyl chloride in boiling benzene containing a little pyridine gave the benzyl chloride (13).

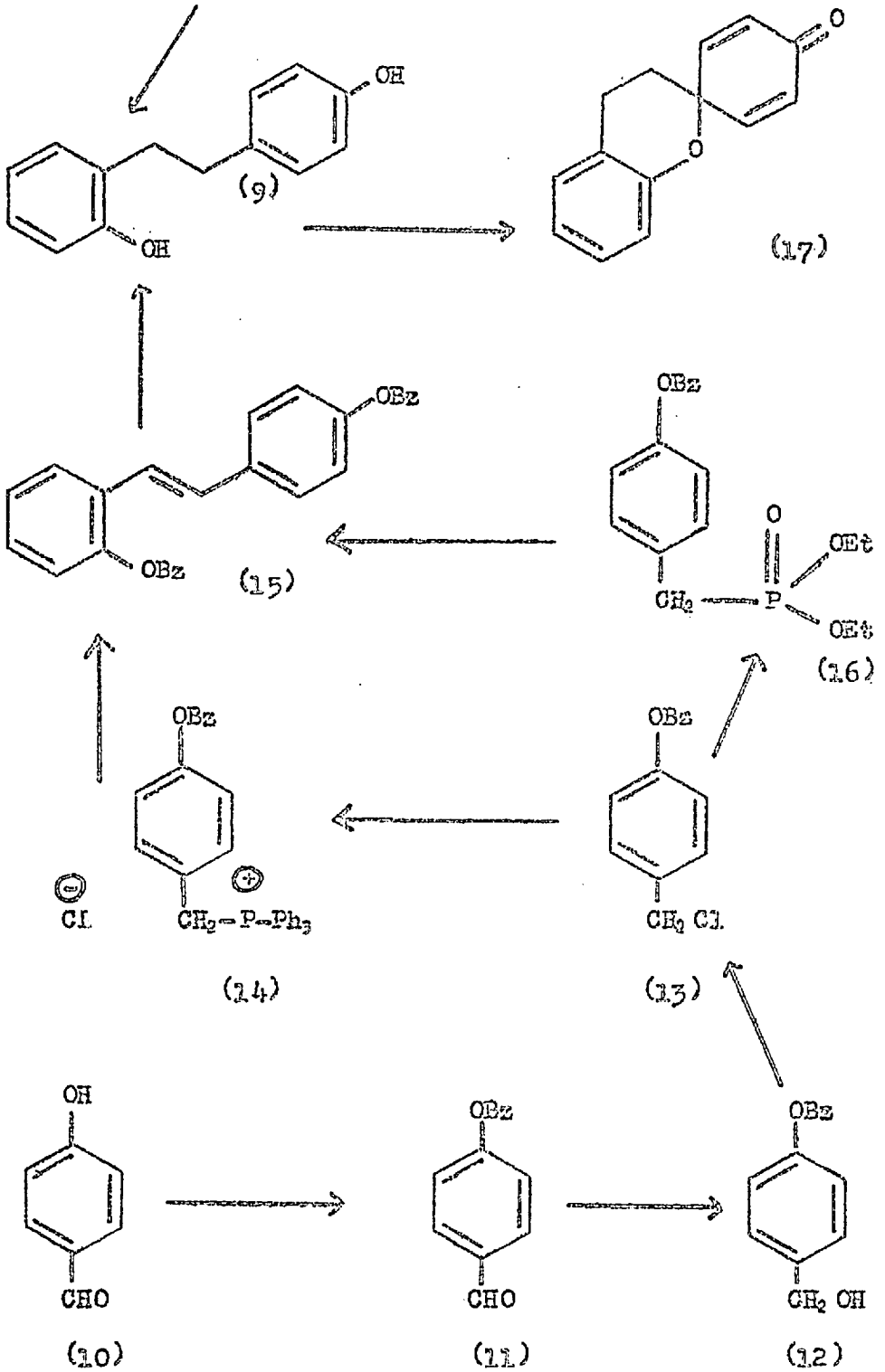
At this point, two alternative pathways were investigated. The benzyl chloride (13) was treated with triphenylphosphine in benzene and p-benzyloxybenzyltriphenylphosphonium chloride (14) precipitated almost quantitatively. A Wittig reaction was now carried out [144] on this material using salicylaldehyde benzyl ether (5), and 2,4'-dibenzyloxystilbene (15) obtained. Hydrogenation then gave 2,4'-dihydroxybibenzyl (9), identical in all respects with the material obtained by the earlier route.

The second pathway involved carrying out [145, 146, 147] a Michaelis-Arbuzov reaction on the benzyl chloride (13) by treating it with triethylphosphite at 160°. The p-benzyloxybenzyl diethyl phosphonate (16) produced was treated [145] with salicylaldehyde benzyl ether (5) and sodium methoxide in DMF, and 2,4'-dibenzyloxystilbene (15), identical in all respects with the material described above, obtained. Hydrogenation of this substance gave 2,4'-dihydroxybibenzyl (9) identical in all

respects with the material obtained by the first procedure.

Oxidation of this phenol with potassium ferricyanide in dilute sodium hydroxide solution gave a colourless crystalline solid m.p. 135-136° in 11·5% yield, $\nu_{max.}$ 1665 cm^{-1}. It was thus concluded to be the cross conjugated ketone (17).




OH
OH
(9)
O
O
(17)
OBz
OBz
(15)
OBz
O
OEt
CH2
P
OEt
(16)
OBz
Cl
CH2—P—Ph3
(14)
OBz
CH2 Cl
(13)
OH
CHO
(10)
OBz
CHO
(11)
OBz
CH2 OH
(12)

With this phenol now available, attention was turned to discovering a photosensitive group. Diagramatically, the object was to accomplish the transformation (18) to (19).

$$\underset{(18)}{ArO\sim X} \xrightarrow{h\nu} \underset{(19)}{ArO^{\circ} + X^{\circ}}$$

It was first inquired, however, what factors would be likely to favour this process and also what factors would be likely to favour its reversal so that Ar and X could be astutely chosen. Clearly, the more stable the radicals ArO° and X° were, the more readily would the photolysis proceed. However, such conditions would equally well favour the reverse reaction since the longer the radicals existed as such, the greater the chances of recombination taking place between them. To circumvent the difficulty, X was chosen so that it readily fragmented into two stable species Y° and Z°. The transformation then became,

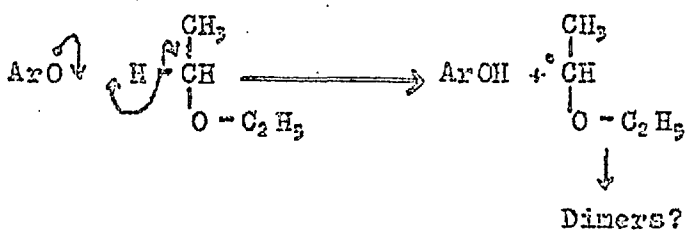
$$ArO\sim X \xrightarrow{h\nu} ArO^{\circ} + X^{\circ} \longrightarrow ArO^{\circ} + Y^{\circ} + Z^{\circ}$$

Obviously, the difficulty was not completely resolved, as products such as ArOY and ArOZ could arise, but at least it would be possible to say that some reaction had taken place.

As a first step it was felt that a suitable choice for X would be a carboxylic acid residue since the fragmentation process would then almost certainly involve the formation of carbon monoxide (a stable molecular species) and an alkyl radical (which could be chosen so that this would be stable also).

Moreover, a whole variety of aromatics esters were readily available with which to work.

The first carboxylic acids chosen was trichloracetic acid. β-Naphthyl trichloracetate was prepared [148] by acylating β-naphthol with trichloracetyl chloride [149,150]. Irradiation of the ester under standard conditions in a quartz flask and using ether as solvent gave β-naphthol in 22% yield as the only identifiable product. This presumably meant that the process



Ar = β-naphthol

was more highly favoured than the process

$$ArO^{\bullet} + \dot{C}Cl_3 \longrightarrow ArO\cdot CCl_3$$

Ar = β-naphthol

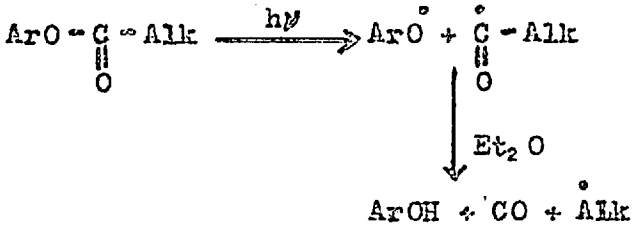
at least at the dilution and temperature employed. Since the yield of β-naphthol was low, the reaction time long, and since a quartz flask was necessary (the photolysis failed completely in pyrex) it was felt that a radical more stable than trichloromethyl was required. Attention was, therefore, turned to triphenylmethyl.

β-Naphthyl triphenylacetate was prepared by unexceptional means [150-155]. Irradiation of this ester under standard conditions in a quartz flask for 1 hour gave β-naphthol in 39% yield.

The use of another acid, fluorene-9-carboxylic acid was now investigated. It was prepared [156] by carrying out an internal Friedel-Crafts reaction on benzilic acid using aluminium chloride as catalyst. Treatment [157] of the acid with thionyl chloride gave fluorene-9-carbonyl chloride which readily acylated β-naphthol. In 4 hours in ether solution, β-naphthyl fluorene-9-carboxylate photolysed in a pyrex flask to give a 60% yield of pure β-naphthol.

In an exactly analogous manner, β-naphthyl xanthene-9-carboxylate was prepared from xanthene-9-carbonyl chloride [158] and β-naphthol. Irradiation of this ester again in ether solution and in a pyrex flask, gave, in 4 hours, a 60% yield of β-naphthol.

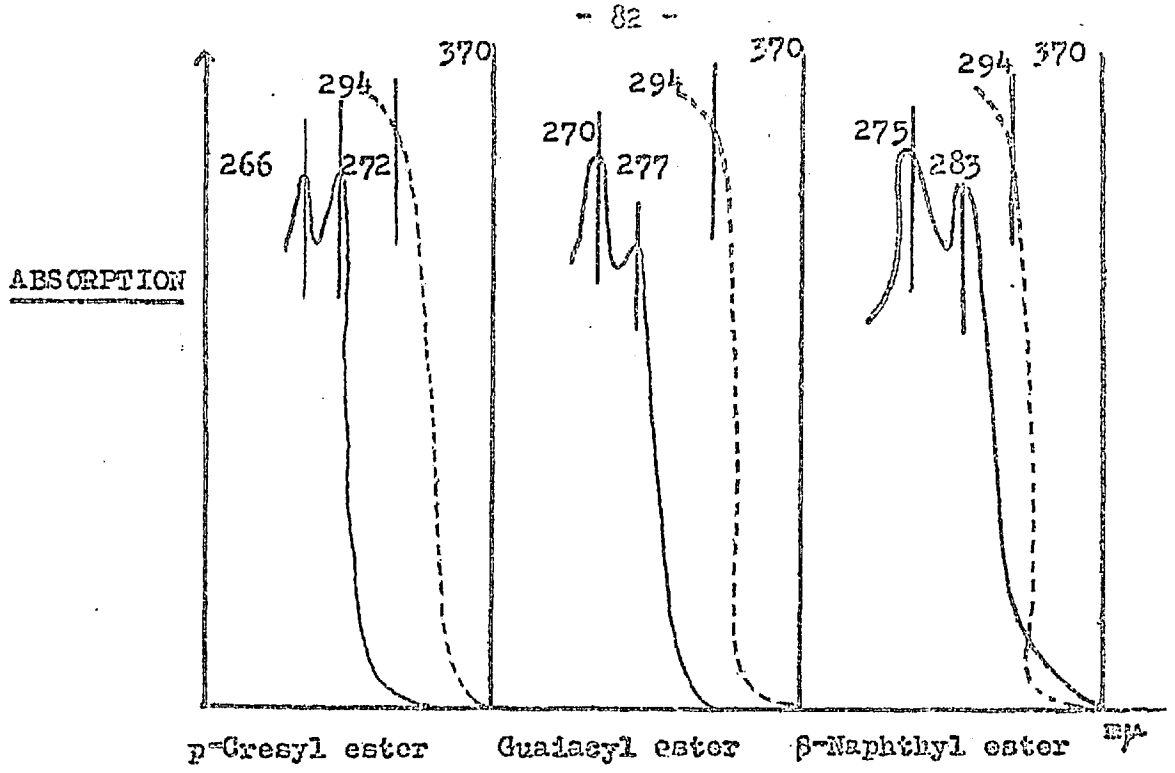
The reaction undergone by these esters on irradiation could, therefore, be represented by the scheme



Ar = β-naphthyl

Having estimated and characterised the β-naphthol it was now desirable first to prove that carbon monoxide was in fact being produced, and secondly to estimate it. These two experiments were combined as follows [59]. The exit gases from the apparatus were passed first through a U-tube containing a quantity of I_2O_5 maintained at 120° and then through two Dreschel bottles each containing saturated barium hydroxide solution. The free iodine liberated by oxidation of the carbon monoxide by the iodine pentoxide was estimated by titration giving a figure of 93%, and then the carbon dioxide estimated gravimetrically as barium carbonate (87%).

Two other phenolic esters of fluorene-9-carboxylic acid were also prepared, namely the p-cresyl ester and the guaiacyl ester and from a study of their U.V. spectra in conjunction with that of the corresponding β-naphthyl ester, and their behaviour on irradiation, a most interesting fact emerged. Neither of these two esters would photolyse in a pyrex vessel, but both of them cleaved readily in quartz (2 hours irradiation in each case gave about 60% of the pure phenol). Moreover, it appeared from their U.V. spectra that neither of them had any absorption in the pyrex region. In contrast, β-naphthyl fluorene-9-carboxylate had. These spectra are reproduced below.



The dotted line represents the pyrex "cut out".

Thus it seemed reasonable to conclude that it was the phenolic fragment of the molecule which was responsible for determining whether these esters would photolyse in a pyrex vessel or not.

In order to carry this investigation further, both cholesteryl fluorene-9-carboxylate and cholesteryl xanthene-9-carboxylate were prepared and irradiated. Now, while neither of these esters had absorptions in the pyrex region, both did have maxima at about 290 mμ due to the acid fragment, but surprisingly, neither ester would photolyse, recoveries of about 95% being made. In order to guard against the possibility

of cleavage taking place, followed by recombination of the radicals before they had left the solvent "cage", refluxing methylcyclohexane (b.p. 144°) was used as solvent, but the esters were still recovered unchanged. However, the experiment did reduce the weight of this possibility. Similar results were found in the case of methyl fluorene-9-carboxylate [160, 161]. The results of the photolyses carried out so far are summarised in Table I.

TABLE I

COMPOUND	IRRAD. TIME	BASE SOL. (%)	PURE PHENOL (%)
β-Naphthyl trichloracetate	3Q	40	22
β-Naphthyl triphenylacetate	1Q	66	39
β-Naphthyl fluorene-9-carboxylate	4P	74	60
β-Naphthyl xanthene-9-carboxylate	4P	52	60
p-Cresyl fluorene-9-carboxylate	2Q	71	58[X]
Guaiacyl fluorene-9-carboxylate	2Q	67	58

Q indicates a quartz flask was used.

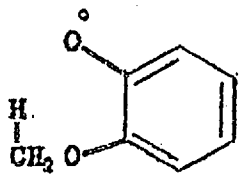
P indicates a pyrex flask was used.

[X] Isolated as 3,5-dinitrobenzoate.

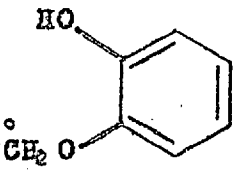
On the basis of the results so far, it is to be concluded that the energy responsible for photochemical break-down is absorbed by the phenolic fragment, and the acid moiety then determines the ease with which this break-down takes place.

Two other points are worthy of comment. First, fluorene-9-carboxylic acid has emerged as an excellent photosensitive protecting group for phenols. Moreover, in addition to the selectivity possible between phenols and alcohols, by varying the type of reaction vessel (either pyrex or quartz) a high degree of selectivity is possible between mononuclear and binuclear phenols.

Secondly, it has been suggested [62] that the methoxyl group can act as a source of the methylenedioxy group in alkaloids and direct evidence has been put forward [63] in support of this. One possible mechanism is via the generation of a phenoxide radical adjacent to a methoxyl group as in (20). Hydrogen abstraction from the methoxyl group would give the methylene radical (21), which by a further one electron oxidation could result in the methylenedioxy group (22).



(20)



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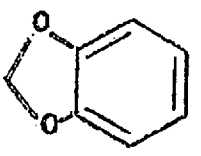


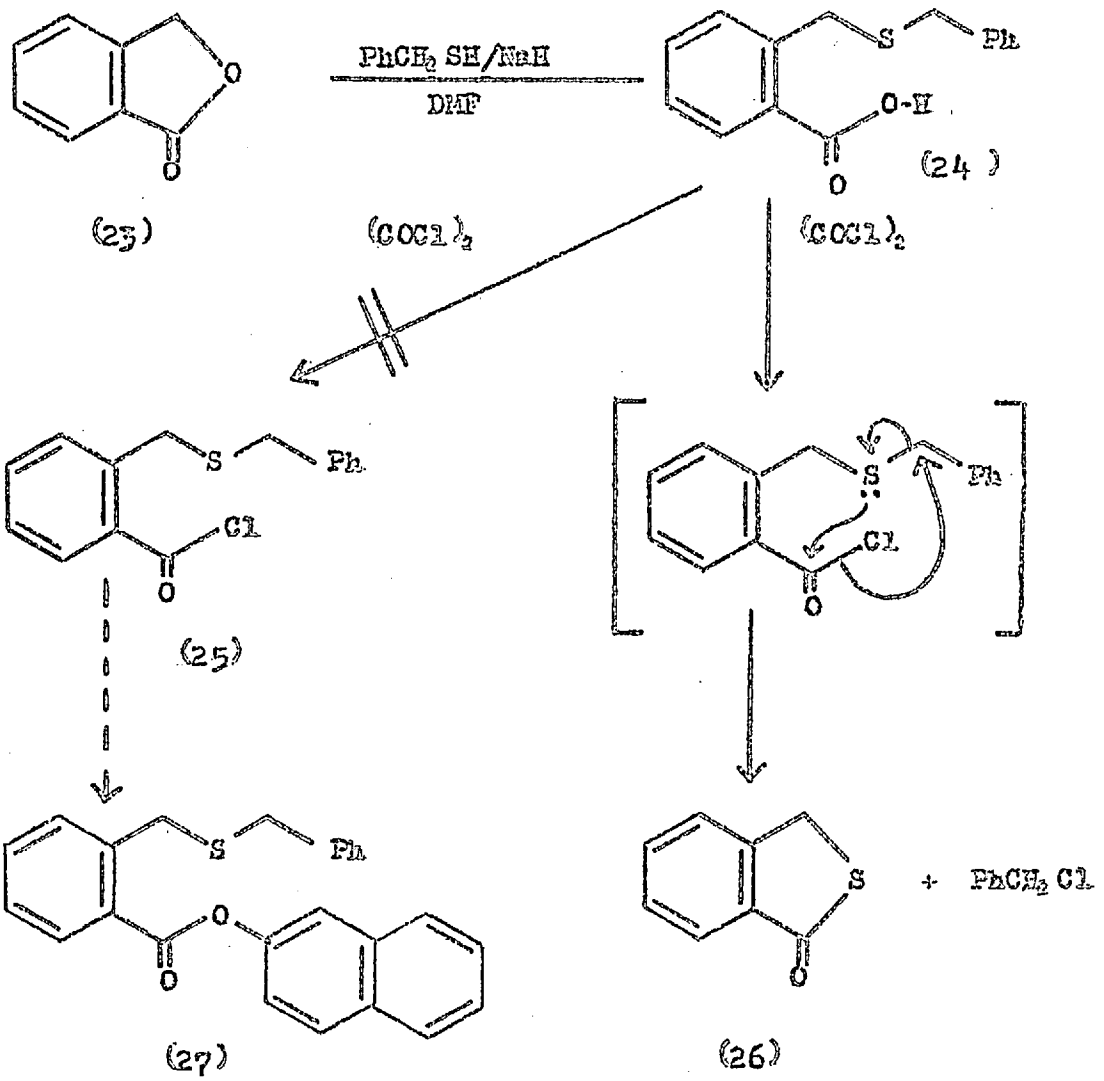
(22)

During the experiments on the photolysis of guaiacyl fluorene-9-carboxylate a search was made for methylenedioxybenzene in the reaction mixture by means of the chromotropic acid test and also by examination of the n.m.r. spectrum of the crude reaction mixture, but unfortunately no positive evidence was found. Chemical oxidation [164] of guaiacol has also met with no success in bringing about this cyclisation.

In view of the recent work by Martin and Bentrude [162], it was thought likely that the rate of homolysis of the C - O bond in an aryl ester could be considerably enhanced by the anchimeric effect of a sulphur or iodine atom attached to a methylene group in the ortho position relative to the ester carbonyl.

Thus an attempt was made to synthesise β-naphthyl o-(benzylthiomethyl)benzoate (27). This projected route is outlined below.

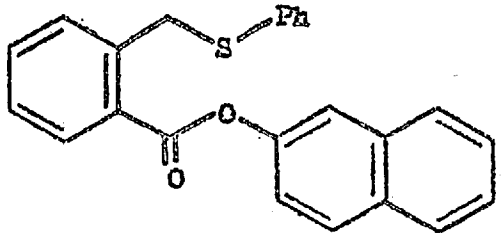
Phthalide was treated [166] with benzyl mercaptan in quinoline at 210° for 4 hours in an attempt to convert it to o-(benzylthiomethyl)benzoic acid (24). However, the organic base proved ineffective in catalysing the conversion and the phthalide was recovered unchanged. Accordingly, NaH in DMF was used in place of the quinoline and the substituted benzoic acid (24) obtained cleanly and in high yield. Reaction of this acid with oxalyl chloride at room temperature gave a yellow compound



which after recrystallisation from petrol had m.p. 59-60°, the I.R. spectrum showed a broad band at 1695 cm^{-1}. These facts were consistent with the deduction that the acid chloride (25) had undergone an internal cyclisation to give thiophthalide (26).

a compound already known [67] in the literature and melting at 60°. This reaction was again repeated, this time at 0°, but the same result was obtained. However, it was clearly a simple matter to strengthen the S - C bond which was being broken and at this stage it certainly appeared that the possibility of obtaining the anchimeric assistance that was hoped for was a very real one.

Thus, the above experiments were repeated using thiophenol in place of the benzyl mercaptan and β-naphthyl o-(phenyl-S-methyl)benzoate (28) obtained.



(28)

A sample of this ester was irradiated under standard conditions in a pyrex flask but found to photolyse only slowly. When a quartz flask was used, however, the photolysis was very rapid but unfortunately, only about 10% of the theoretical amount of the β-naphthol was produced.

In order to investigate this reaction in a little more detail, a sample of benzyl phenyl sulphide was made by treatment [68]

of a mixture of benzyl chloride and thiophenol with NaH/DMF as above and this irradiated. It was found to photolyse rapidly in a quartz though not a pyrex flask, to yield a tar which smelt very strongly of thiophenol. This clearly suggested that fission of the bond between the benzyl carbon and the sulphur atom was probably taking place and consequently, such a process would also have been occuring when ester (28) was irradiated.

The possibility of obtaining anchimeric assistance from an iodine atom was now investigated. β-Naphthyl o-iodobenzoate was synthesised by treatment [169,170] of o-iodobenzoyl chloride with β-naphthol.

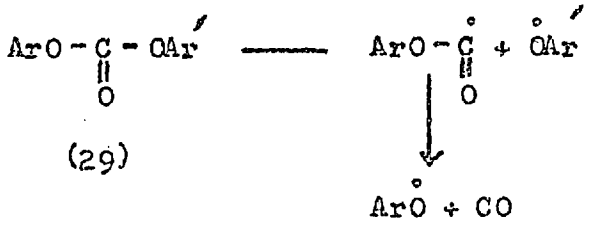
A sample of this ester was irradiated under standard conditions and a high rate of homolysis observed. However, the yield of β-naphthol was only 14%.

The results of these photolyses are summarised in Table II.

TABLE II

COMPOUND	IRRAD. TIME	BASE SOL. (%)	PURE PHENOL (%)
β-Naphthyl o-(phenyl-thiomethyl)benzoate	0·5	81	10
β-Naphthyl o-iodobenzoate	4	99	14

Of the esters discussed so far, the one which gave the highest yield of β-naphthol on photolysis in a pyrex vessel and in the shortest time was found to be β-naphthyl fluorene-9-carboxylate. Now as it has been pointed out, the phenolic fraction was the moiety concerned with absorption of the energy by the molecule and hence for activation of the molecule, while the acid fragment played little or no such part. Since it was clearly desirable to attain maximum efficiency in generating the phenoxide radicals, it was decided to investigated the possibility of photolysing a diphenolic carbonate (29) which it was expected would split according to the scheme



(29)

$\dot{ArO}$ was the radical required for the intramolecular coupling reaction and $\dot{Ar}$ a highly photosensitive species. The method for finding the best $\dot{Ar}$ unit was simply to take a series of phenols, esterify them with fluorene-9-carboxylic acid and then irradiate as before. The one giving the best result would then be reacted with β-naphthyl chloroformate to give the mixed carbonate (29).

The esters selected and the results of the photolyses are summarised in Table III.

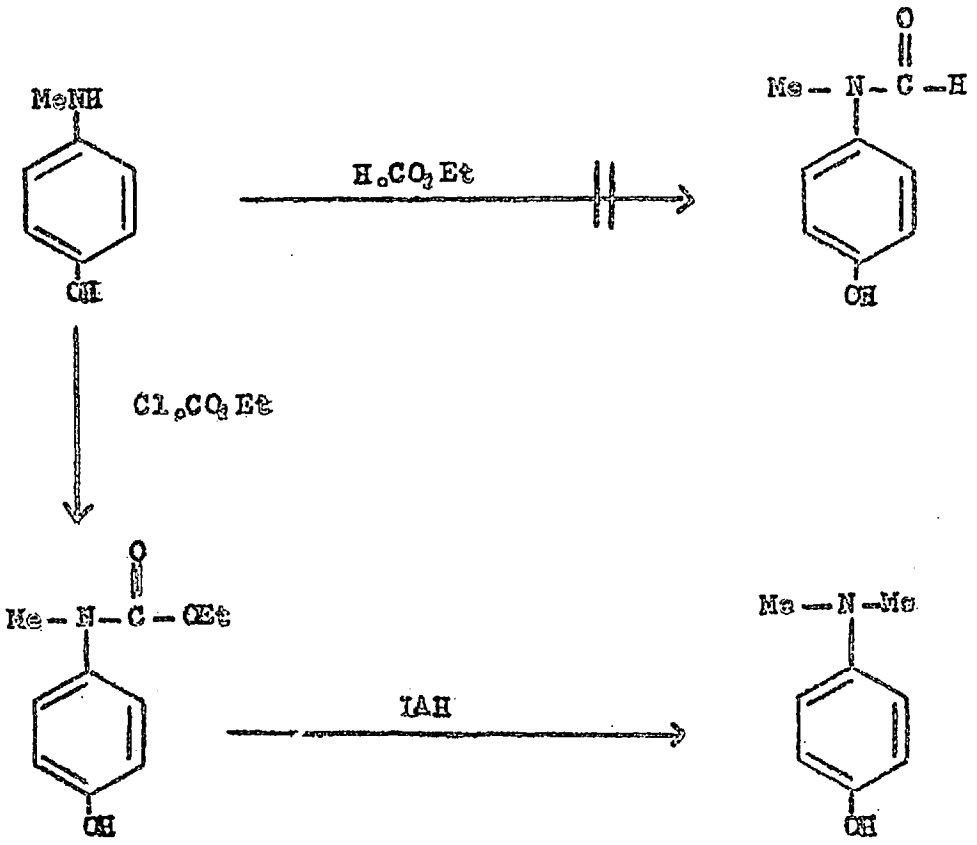
TABLE III

COMPOUND	IRRAD. TIME	BASE SOL. (%)	PURE PHENOL (%)
p-Acetophenyl fluorene-9-carboxylate	6Q	112	40
p-Benzeneazophenyl fluorene-9-carboxylate	4Q	85	15
p-Nitrophenyl fluorene-9-carboxylate	4Q	90	10
p-Dimethylaminophenyl fluorene-9-carboxylate	4Q	86	9

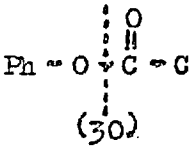
Q indicates a quartz flask was used.

All were made by treating fluorene-9-carbonyl chloride with the appropriate phenol, which with exception of the last one, prepared according to the scheme [7] shown below, were readily available.

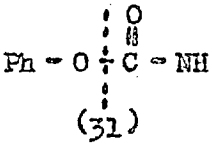
As can be seen from Table III a choice of phenols possessing both electron attracting and electron releasing groups was employed, but no dramatic effects were observed.



Having discussed the homolysis of the C - O bond in some compounds containing the fragment (30), attention was then turned to the study of compounds containing the unit (31).



(30)



(31)

These too after cleavage should readily decarbonylate as the species $-NH-\overset{\circ}{C}O$ was expected to be very unstable. β-Naphthyl N-phenylurethan and β-naphthyl N-α-naphthylurethan were both prepared in the usual way from the appropriate isocyanate, and β-naphthyl N,N-diphenylurethan from diphenylcarbamyl chloride. The results of photolysing these urethans are summarised in Table IV.

TABLE IV

COMPOUND		IRRAD. TIME	BASE SOL. (%)	PURE PHENOL (%)
β-Naphthyl N,N-diphenyl-urethan	(a)	4Q	73	67
	(b)	4Q	56	47.5
β-Naphthyl N-α-naphthyl-urethan	(a)	3P	83	75
	(b)	3P	71	64

Q indicates a quartz flask was used.

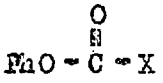
P indicates a pyrex flask was used.

(a) Solvent:- Et_2O/EtOH 9:1. (b) Solvent:- Dioxan.

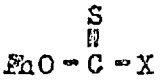
From Table IV it appears that while urethans of the type discussed above are excellent photosensitive protecting groups, particularly in the presence of ethanol as solvent, they

are of no use for generating phenoxide radicals which were required for the intramolecular coupling reaction.

It was now felt that having carried out irradiation experiments on some compounds containing the system (32) with only moderate success a more drastic variation in substitution pattern ought to be made and the carbonyl group replaced by the thione group to give the system (33).

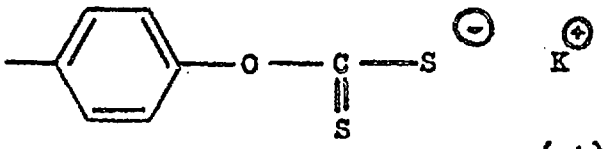


(32)



(33)

This group has pronounced ultraviolet absorption and thus could reasonably be expected to serve as a centre for energy absorption leading eventually to bond fission. The simplest and most obvious first choice of compound containing this group was the O-aryl xanthate (34).



(34)

Accordingly, following the original literature, potassium cresoxide was treated with carbon disulphide in ethanol at 50° for 6 hours. An orange coloured solid was obtained which was ill-defined and could not be recrystallised. A method of

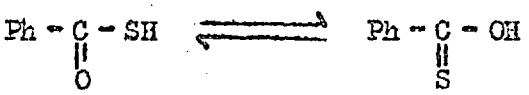
sulphur assay was, therefore, worked out which was capable of giving within 5% of the theoretical value for the sulphur content, potassium O-ethyl xanthate being used as the reference material. Determination of the sulphur content of the compound produced by the action of potassium p-cresoxide on carbon disulphide, indicated that there was less than 10% of the theoretical amount of sulphur present.

The reaction between p-cresol and carbon disulphide in the presence of triethylamine was carried out and the product of this reaction analysed as above for sulphur. Again a value of less than 10% of the theoretical was obtained.

A more rigorous investigation of the reaction between potassium cresoxide and carbon disulphide was carried out in the following way. The U.V. spectrum of potassium O-ethyl xanthate was first measured and a peak at 305mμ (4·25) was found. The U.V. spectrum of potassium cresoxide in water was measured and a peak at 295 mμ (3·42) found. On saturation of the solution with carbon disulphide, a new peak at 313 mμ (1·73) appeared, which gradually disappeared as the solution was aspirated. Aspiration of a solution of potassium O-ethyl xanthate produced no change in its U.V. spectrum. The experiments showed that the O-aryl xanthates of the type (34) , though

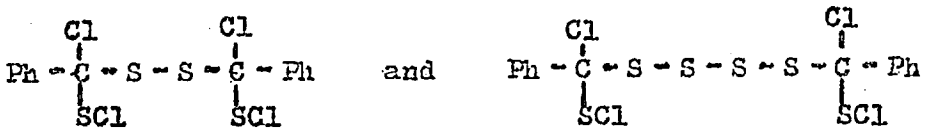
present in solution, were thermodynamically unstable and their investigation was, thus, discontinued.

The next step was clearly to make an ester of a thiobenzoic acid. The monothiobenzoic acid itself was of no use as it exists mainly in the thiol rather than the thione form.

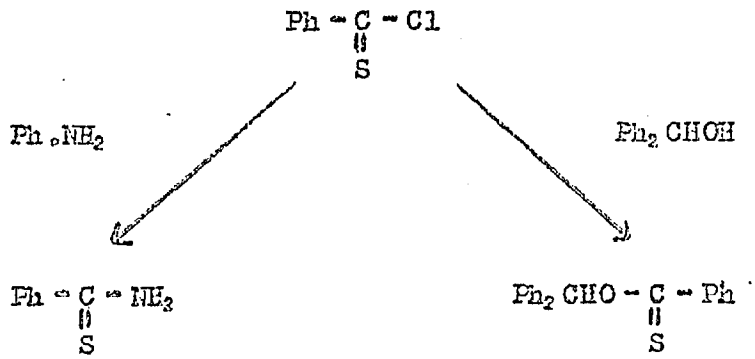


Indeed all known reactions of this acid give rise to derivatives of the thiol tautomer. Accordingly, dithiobenzoic acid was prepared [172] by reacting phenyl magnesium bromide with carbon disulphide. The free acid itself is far too easily oxidised to be isolated and so it was always used as its ethereal solution. This solution has an intense purple colour.

It is reported [173] that this ethereal solution of dithiobenzoic acid on treatment with thionyl chloride can be converted to the corresponding acid chloride, thiobenzoyl chloride. Following Staudinger's method, the reagent and substrate were simply refluxed for 7 hours under nitrogen, after which time a complex mixture, said to consist of products of the type



was produced. The solvent, the unchanged thionyl chloride and the sulphur monochloride (S_2Cl_2), generated in the reaction were then distilled off and then the apparatus set up for distillation under vacuum (0·2 mm). The temperature was gradually raised to 150° and then very cautiously to 240°. From about 200° upwards, a quantity of a deep purple material began to distil, the distillation being complete at 240°. On redistillation, the substance was founddto have b.p. 60-65° /0·2 mm. This material underwent reactions consistent with its formulation as thiobenzoyl chloride [173-175], viz:-

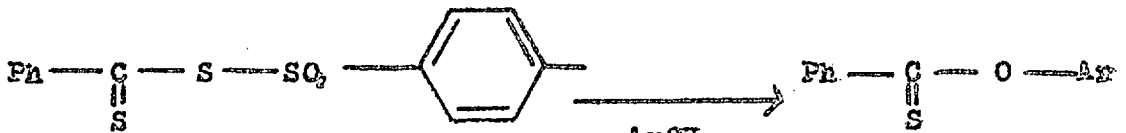


However, in the hands of the present author and another previous worker in this laboratory, the pyrolytic step necessary to crack the intermediate complexes was found to be unreliable, polymerisation to an unidentifyable brown tar often taking place. Consequently, an alternative method of

synthesising the desired thione ester was sought.

Recently, Overberger and Sarlo have prepared [176] several mixed sulphonic-carboxylic anhydrides such as benzoyl benzenesulphonate, and have found them to be active acylating agents, affording the acylated product in good yield and under mild conditions. Moreover, in no case was any sulphonylation observed.

Bearing this work in mind, the lead salt of dithiobenzoic acid (a dark reddish brown solid, m.p. 204-205°, recrystallisable from toluene) was prepared and this treated with tosyl chloride in refluxing DMF for 3 hours in an attempt to make the dithiobenzoic/p-toluenesulphonic mixed anhydride (35). It was then hoped to treat this with a phenol and so obtain the ester (36).



(35) (36)

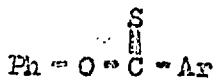
In the event, however, it was found that the lead dithiobenzoate and tosyl chloride did not react, the former being recovered almost quantitatively.

The reaction was now repeated using an ethereal solution of the free acid and triethylamine as base. On addition of this latter reagent, a white precipitate (triethylamine hydrochloride) was immediately thrown down. This was filtered off and the resulting dark reddish brown solution divided into two equal parts. To the first, an ethereal solution of aniline was added and an orange precipitate immediately formed. This was shown to be thiobenzamide. To the second, an ethereal solution of β-naphthol was added; no change was observed. The work up procedure simply involved removing the solvent (room temperature) followed by measurement of the I.R. spectrum. In all runs under a variety of conditions (reaction times of up to 3 hours in the refluxing solvent) a dark reddish gum was obtained which showed intense hydroxyl absorption. The thione ester was thus not being generated.

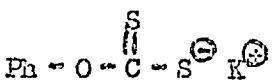
The conclusion to be drawn from these experiments is that the phenolate anion is a much weaker nucleophile than is the aniline molecule. This is, however, a well established phenomenon.

Since the procedures tried so far had not resulted in a satisfactory method of synthesising compounds of the type (36) and since ionic xanthates such as (37) had been shown to be thermodynamically unstable, the next most obvious series of

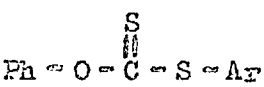
compounds to try was the diaryl xanthates (38).



(36)

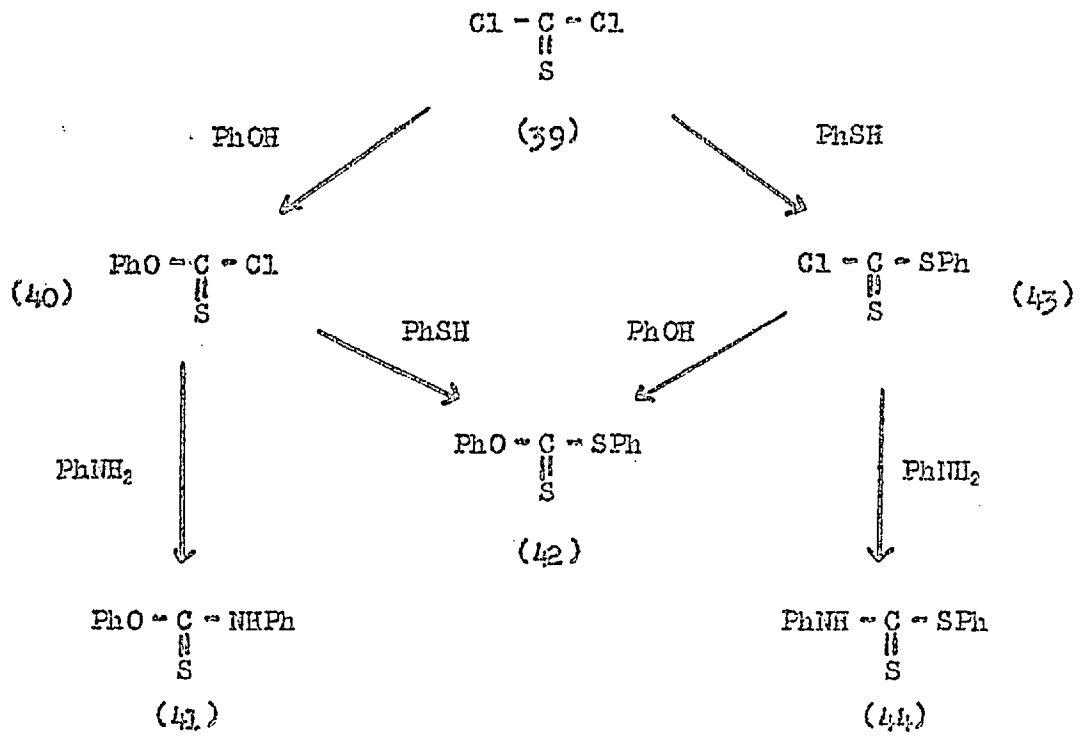


(37)



(38)

Thiophosgene (39) was treated [77] with phenol in the presence of sodium hydroxide solution and phenyl chlorothionformate (40) obtained in good yield. A small portion of this was converted [77] to its aniline derivative phenyl N-phenylthiourethan (41), while the rest, by reaction with thiophenol and sodium methoxide in methanol, gave [77] diphenyl xanthate (42) as a golden yellow solid, m.p. 49-51°.



Another route to this compound was also investigated. This was done by treating [178] thiophosgene with thiophenol, phenyl chlorodithioformate (43) being obtained. As in the case of the monothio derivatives, this was characterised [178] as its urethan, phenyl dithio-N-phenylurethan (44). Treatment [178] with phenol gave diphenyl xanthate (42). This route was investigated as it was clearly more desirable to use phenyl chlorodithioformate as a reagent rather than to convert the phenol required for the coupling reaction first to its bis-chlorothionformate and hence to its corresponding bis(diphenyl xanthate). The results of various photolytic experiments involving diphenyl xanthate are summarised in Table V.

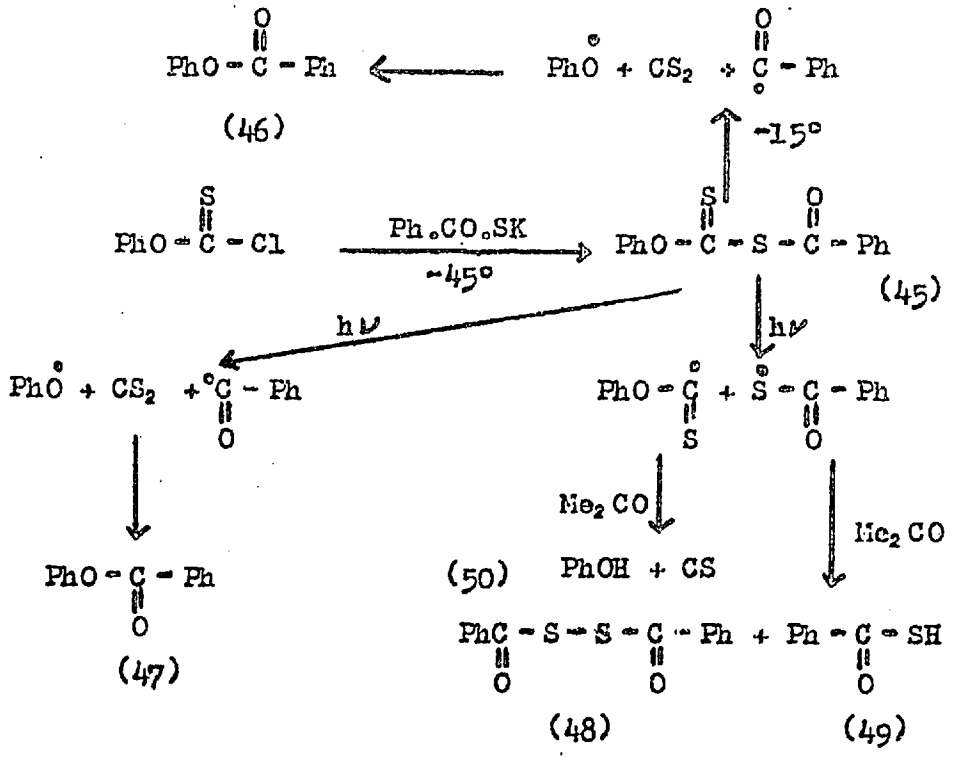
TABLE V

COMPOUND	IRRAD. TIME	BASE SOL. (%)	UNCHANGED STARTING MATERIAL (%)
Diphenyl xanthate	3P	2	76
Diphenyl xanthate	3Q	10	25
Diphenyl xanthate + 1 mol. Ph_2CO	3P	5	67
Diphenyl xanthate + 1 mol. Ph_2CO	3Q	14	20

P indicates a pyrex flask was used

Q indicates a quartz flask was used

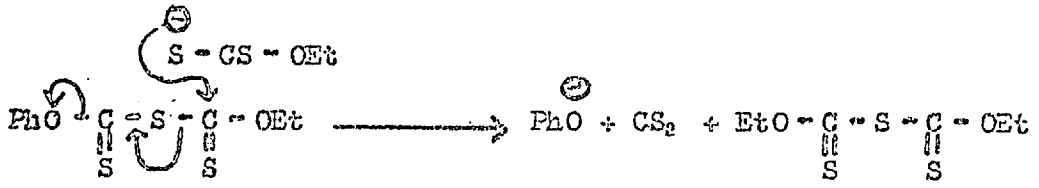
Clearly, the thione moiety alone did not appear to absorb sufficient energy for the photolytic process that was required and so it was decided to construct a molecule in which the carbonyl group, a group which had hitherto proved to be useful for this type of reaction, was incorporated. Accordingly, thiobenzoic acid was prepared [179] and the potassium salt allowed to react [180] with phenyl chlorothionformate at -45°. Attempts to isolate the expected product, S-benzoyl-O-phenyl xanthate (45), however, failed as it decomposed thermally at -15° into CS_2 (detected [180] as its piperidine derivative) and phenyl benzoate (46) (92%).



Irradiation of the reaction mixture at -60° for 1 hour gave phenyl benzoate (47) (78%) and a small amount of dibenzoyl disulphide (48) (by comparison with an authentic specimen [85]). Thiobenzoic acid (49) and phenol (50) were probably also produced.

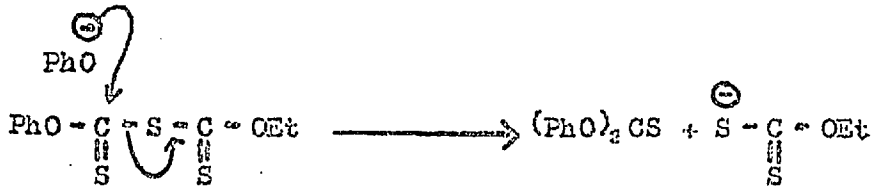
A similar reaction between phenyl chlorothionformate and the potassium salt of thioacetic acid gave [80] a less well defined result, the I.R. spectrum of the crude reaction product showing absorptions at 1770 cm^{-1}., 1740 cm^{-1}., 1710 cm^{-1}., and 1690 cm^{-1}. The 1770 cm^{-1}. peak could reasonably be assigned to phenyl acetate and the 1730 cm^{-1}. peak to diacetyl disulphide. Further weight for this conclusion was acquired from a study of the n.m.r. spectrum of the crude reaction product which showed a complex aromatic multiplet at about τ 2·8 and sharp singlets at τ 7·52 (diacetyl disulphide by comparison with an authentic specimen [82]) and τ 7·78 (phenyl acetate by comparison with an authentic specimen).

The reaction between phenyl chlorothionformate and potassium O-ethyl xanthate under the same conditions [80] followed a rather different course, however, diphenyl thionocarbonate [77] (51) being the only product characterised. This presumably arose in the following way:-



(52)

Then,



(51)

A deep yellow gum was also obtained which probably consisted largely of S-ethoxythiocarbonyl O-ethyl xanthate (52). Attempts to crystallise this material failed, the likely contaminant being ethyl phenyl thiocarbonate (53).

(53)

The next step was to ring the changes once again on the disposition of the oxygen and sulphur atoms in the molecule and prepare an O-ethyl S-aryloxycarbonyl xanthate such as (56).

p-Cresyl chloroformate (54, Ar = p-cresyl) was first prepared [183] by treating a benzene solution of p-cresol with excess phosgene in the presence of pyridine as base. Along with the desired product a small quantity of di-p-cresyl carbonate (55, Ar = p-cresyl) was also obtained, the former compound being readily separated by distillation.

The purified p-cresyl chloroformate was then reacted [180] with sodium O-ethyl xanthate [184] in acetone at -30° to give a yellow oil showing a strong peak in the I.R. spectrum at 1750 cm^{-1}. This was presumably O-ethyl S-p-cresyloxycarbonyl xanthate (56, Ar = p-cresyl). All attempts to crystallise this material, however, failed and it was thus decided to work with compounds higher in the homologous series which it was hoped would be more readily crystalline. To this end β-naphthyl chloroformate (54, Ar = β-naphthyl) was prepared [185] in the manner described above for p-cresyl chloroformate. Reaction [180] of this substance with sodium O-ethyl xanthate gave O-ethyl S-β-naphthyloxycarbonyl xanthate (56, Ar = β-naphthyl) as a yellow crystalline solid.

$$ArOH \xrightarrow{COCl_2} \underset{(54)}{ArO.CO.Cl} + \underset{(55)}{ArO.CO.OAr}$$

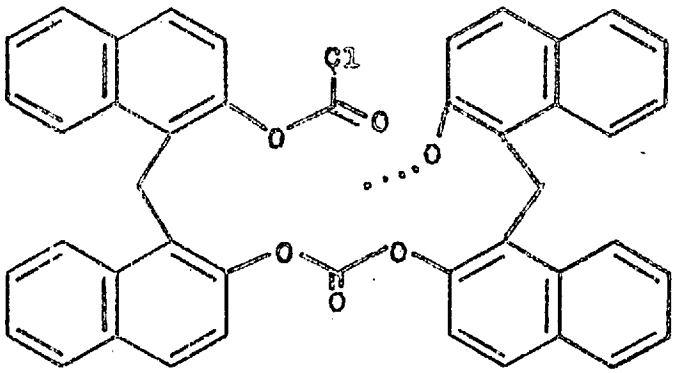
$$\downarrow -30^\circ \quad Na^{\oplus}\ {}^{\ominus}S.CS.OEt$$

$$ArO.CO.S.CS.OEt \qquad (56)$$

A sample of O-ethyl S-β-naphthyloxycarbonyl xanthate was irradiated under standard conditions in a pyrex flask and found to photolyse smoothly to give β-naphthol in 24% yield. The non-phenolic part of the product was a dark brown tar, the nature of which was not investigated.

It was now hoped to carry out an irradiation on a similar derivative of a binuclear dihydric phenol in order that the feasibility of the coupling concept could be tested. To this end, β,β'-dihydroxydinaphthylmethane (57) was synthesised [86] by treating β-naphthol with formaldehyde in the presence of sodium acetate. The next step was to make the dichloroformate (58). However, treatment [85] of a toluene solution of β,β'-dihydroxydinaphthylmethane with phosgene in the presence of quinoline did not give the desired compound but rather a complex mixture of products showing a strong but broad band at 1765 cm^{-1}. and a much weaker band at 1780 cm^{-1}. The general nature of the likely products consistent with these data is shown below.

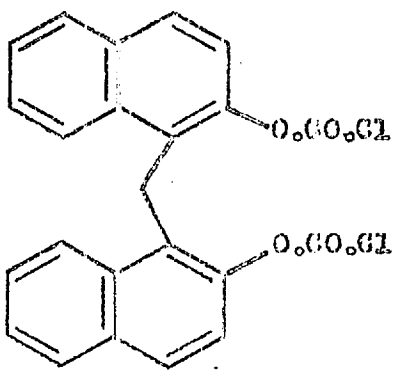
Variations in the experimental conditions failed to give any substantially different result.



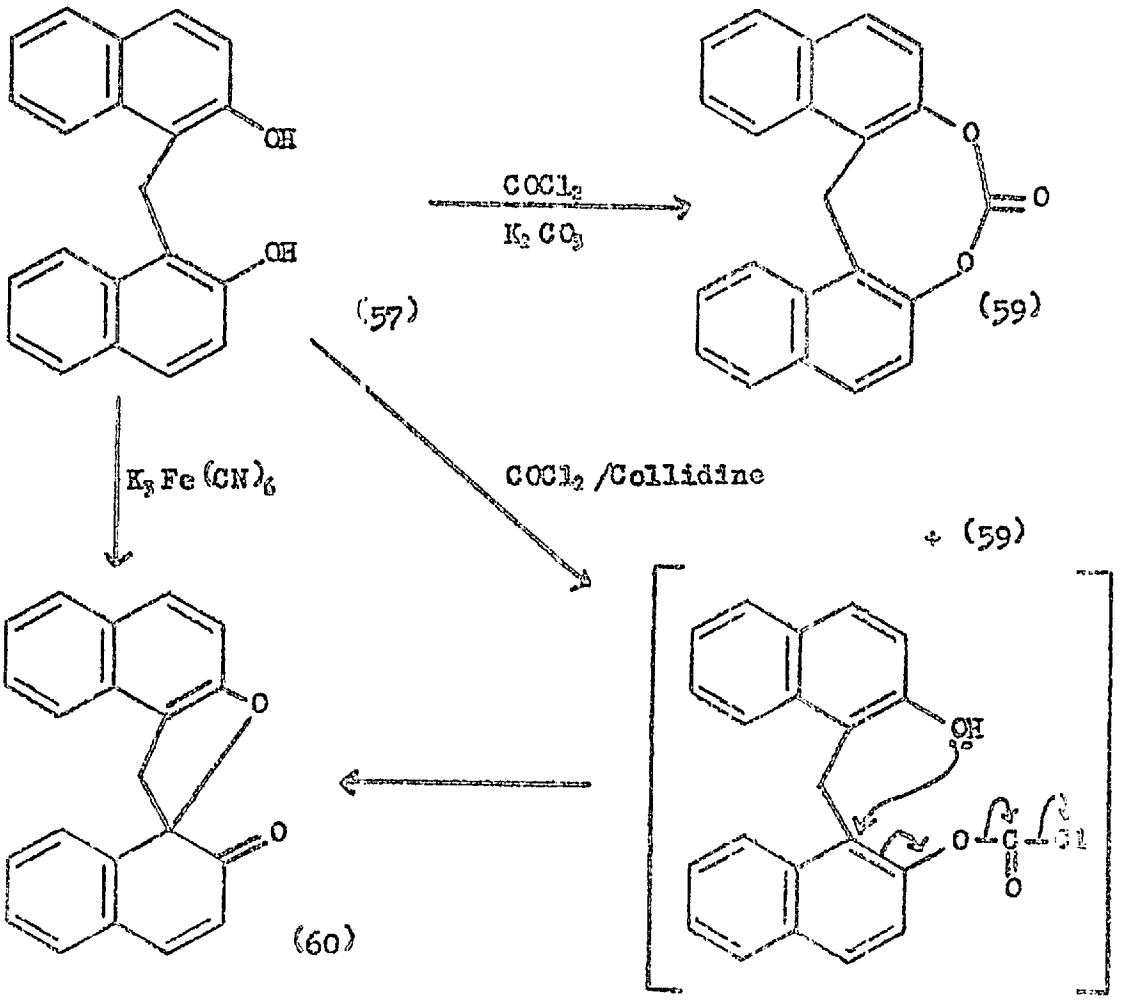
An attempt was now made to obtain the dichloroformate (58) by phosgenating β,β′-dihydroxydinaphthylmethane in benzene solution but using potassium carbonate as base. In this experiment, a white crystalline solid m.p.235-235·5° was readily isolated. Its I.R. spectrum showed an intense band at 1765 cm^{-1}. This strongly suggested that the cyclic carbonate (59) had been produced. Confirmation of this was obtained from the molecular weight determination which gave a value of 345·3 (calculated value 326).

A further attempt to prepare the dichloroformate (58) was made by phosgenating the dihydricphenol (57) in boiling benzene solution but using collidine (it was found in subsequent runs that quinoline was just as effective) as base. This base

was selected as it was felt that it would be unable, on steric grounds, to generate a large concentration of phenolate anions and so favour the formation of the dichloroformate. The product of this reaction showed two intense bands in the carbonyl region of the I.R. spectrum, one at 1765 cm^{-1}. and one at 1670 cm^{-1}. Chromatography on alumina readily effected a separation into two crystalline solids. The first was identified as the cyclic carbonate (59), while the second, a yellow solid, m.p. 171 - 172° surprisingly enough turned out to be the oxidation product of (80) of β,β'-dihydroxydinaphthylmethane. This conclusion was unambiguously confirmed by comparison (m.p., mixed m.p. and superimposable I.R. spectra) with an authentic sample prepared by oxidation of the phenol with potassium ferricyanide.



(58)



At this stage it was felt that if any great improvement was to be made in the photolytic generation of phenoxide radicals then a completely different series of compounds had to be investigated. So far all the work had been concerned with homolysing C = O bonds, the carbon being variously present as a carbonyl or thiocarbonyl group and variously substituted with

a carbon, oxygen or sulphur atom.

Now since diaryl disulphides (61) were well known in the literature, and since diaryl peroxides (62) were known to be unstable, it was considered likely that the mixed monothio-peroxides (63) i.e. the phenolic esters of sulphenic acids should, if it were possible to make them, homolyse readily on irradiation.

Ar - S - S - Ar	Ar - O - O - Ar	Ar - O - S - Ar
(61)	(62)	(63)

The relevant literature on these compounds was, however, confused [187], [188], one group of workers appearing to make a claim for the existence of such compounds and another finding no evidence for them. In order to attempt to clarify the position, therefore, the following experiments were carried out.

Phenol and β-naphthol were separately treated with 2,4-dinitrobenzenesulphenyl chloride [189] for periods ranging from 15 minutes to 6 hours and the reaction products, obtained simply by removal of the solvent under vacuum, always showed intense phenolic hydroxyl absorptions in the I.R. spectrum.

Bases, pyridine and triethylamine, were used in a

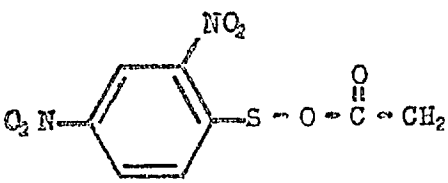
second series of experiments and in a third the mixtures were refluxed using either carbon tetrachloride or benzene as solvent. In all cases, the product, obtained as above and usually a non-crystalline yellow oil, showed intense phenolic hydroxyl absorptions in the I.R. spectrum.

In each case also, after the I.R. measurements had been taken, the product was dissolved in ether and quickly extracted with dilute sodium hydroxide solution. After removal of the ether, the base insoluble residue was found to be non-crystalline, all attempts to induce crystallisation failing.

It thus appeared that the phenolic esters of 2,4-dinitrobenzenesulphenic acid could not be formed. However, since the carboxylic/sulphenic mixed anhydrides (64) were well known it was decided to carry out an investigation of these compounds as they ought to cleave readily on irradiation.

2,4-Dinitrobenzenesulphenyl acetate (65, R = H) was prepared [90] by stirring a suspension of silver acetate in methylene dichloride containing 2,4-dinitrobenzenesulphenyl chloride at room temperature for 18 hours in the dark. The phenylacetate (65, R = Ph) and caproate (65, R = $CH_3(CH_2)_5$)

(64) $ArS-O-\overset{O}{\overset{\|}{C}}-CH_2R$

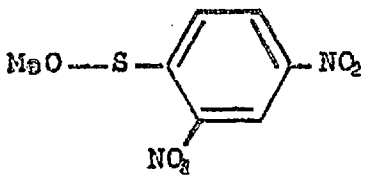
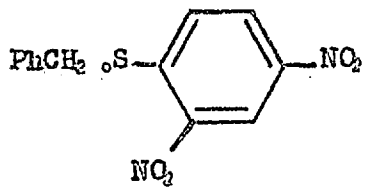
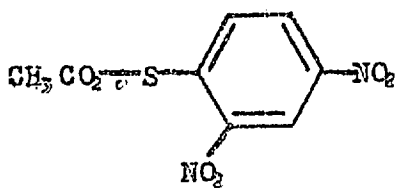


(65)

were similarly prepared.

In order to establish the structures of these mixed anhydrides unequivocally, the U.V. and n.m.r. spectra of the acetate have been measured. These are to be found with the corresponding spectra of some similar compounds, synthesised [191] in an unambiguous way, in Tables VI and VII

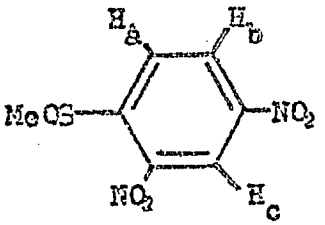
TABLE VI (U.V. data)

	in EtOH	330(4·06), 259(4·04), 209(4·12)
	in EtOH	333(4·13), 270(3·87), 207(4·42)
	in EtOH	329(4·03), 260(4·11), 209(4·17)
	in $CHCl_3$	323(4·05), 269(4·26)

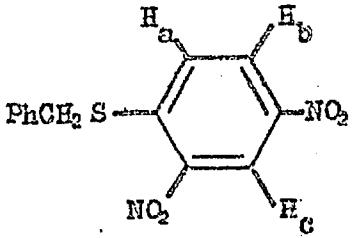
Along with Table VII these results show that 2,4-dinitrobenzenesulphenyl acetate is correctly formulated as (65, R = H).

TABLE VII

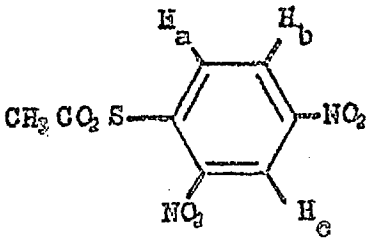
n.m.r. Data.



H(a).	Doublet	2·12	(J = 9)
H(b).	Quartet	1·52	(J = 9, J = 2)
H(c).	Doublet	0·96	(J = 2)
CH_3	Singlet	6·06	



H(a).	Doublet	2·5	(J = 9)
H(b).	Quartet	1·8	(J = 9, J = 2)
H(c).	Doublet	1·08	(J = 2)
Phenyl	Singlet	2·69	
CH_2	Singlet	5·72	

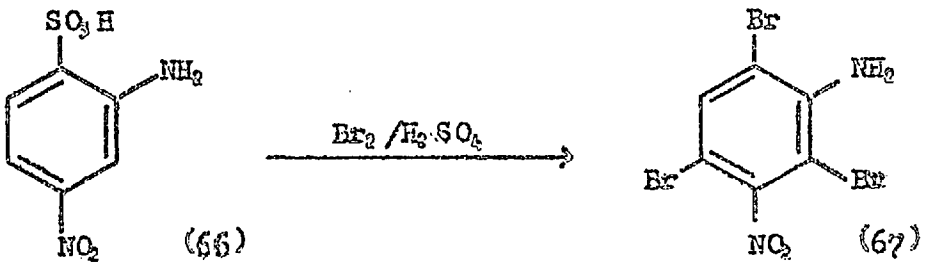


H(a).	Doublet	2·36	(J = 9)
H(b).	Quartet	1·54	(J = 9, J = 2)
H(c).	Doublet	0·94	(J = 2)
CH_3	Singlet	7·59	

On irradiation in benzene solution, the acetate is rapidly photolysed to give a mixture of products consisting of acetic acid (about 90%) identified as its p-bromophenacyl ester, 2,4-dinitrodiphenyl sulphide [93] (m.p., mixed m.p. and I.R. spectrum and by conversion to the corresponding sulphone [95]), 2,4,2',4'-tetranitrodiphenyl disulphide [94, 95] and a brown amorphous solid.

The I.R. spectrum of this brown solid was found to be

similar to that of 2-amino-4-nitrobenzenesulphonic acid (66), an authentic specimen being prepared [196] by the action of methanolic HCl on methyl 2,4-dinitrobenzenesulphenate, and furthermore, on treatment [197] with bromine in 50% sulphuric acid gave a flocculent precipitate which was identified as 2,4,6-tribromo-3-nitroaniline (67) (m.p., mixed m.p. and superimposable I.R. spectra).



(66) (67)

Thus it can be concluded that the material generated in the photolytic reaction is an impure form of the material generated by hydrolysis. This result was also indicated when the two compounds were run side by side on silica gel plates; the first streaked badly while the second moved as a single spot. Confirmation of this was obtained by treating both materials with bromine in acetic acid. While the substance obtained in the hydrolytic reaction took up 57% of the theoretical amount of bromine the "photolytic" consumed only 23%. (In this context the word "theoretical" refers to the bromine uptake

when 2-amino-4-nitrobenzenesulphonic acid is treated with this reagent in 50% sulphuric acid on the steam bath for 1 hour. Obviously, such a procedure could not be used when a quantitative estimation is required as loss of bromine would occur giving rise to a spurious result.)

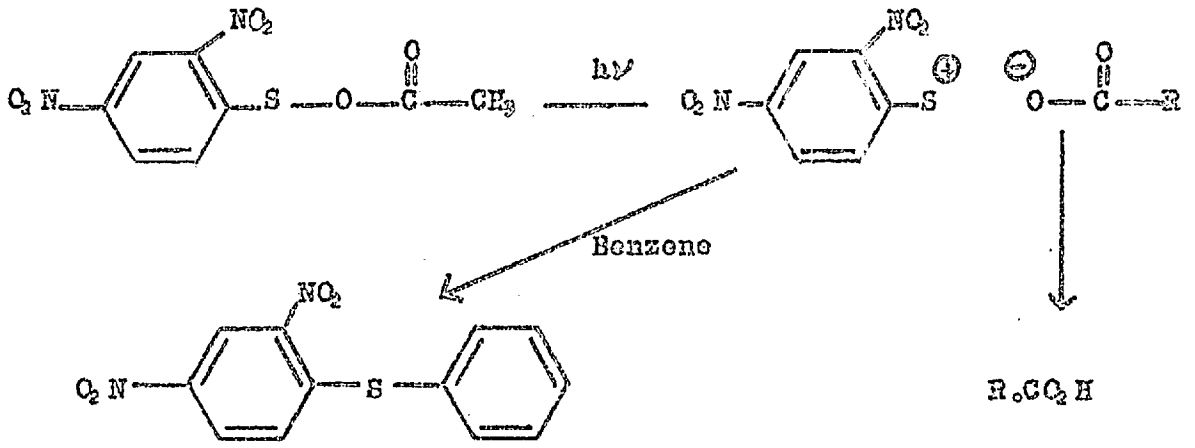
Furthermore, titration of the authentic sulphonic acid with standard NaOH gave a figure of 95% purity, while the material obtained from the photolysis gave a figure of only 36%.

A cognate experiment was carried out to determine whether p-toluenesulphinic acid could be oxidised to the sulphonic level by treatment with bromine in acetic acid. In the event, the reaction was instantaneous and quantitative.

In view of this result, it was clearly necessary to attempt to prove that the product of the photolysis was in fact the sulphonic and not the sulphinic acid. To this end, p-toluenesulphinic acid was irradiated in benzene in the presence of an excess of m-dinitrobenzene in order to attempt to oxidise it to the sulphonic level. After carrying out the experiment, 95% of the m-dinitrobenzene was recovered unchanged showing that such a conversion was not possible. The question of the oxidation level of the sulphur atom in the product is, therefore, still in doubt.

A further experiment was carried out to try to decide whether the product of the reaction was a mixture of the free sulphonic and carboxylic acids or their mixed anhydride. In order to determine this, dry cyclohexylamine was added to the total crude reaction product and the mixture warmed for 10 minutes. After this time the free acetic acid was isolated and found to amount to 89% of the theoretical, showing that no acetylation of the cyclohexylamine had taken place, and hence that the free acid was present at the time this reagent was added.

The next problem to be considered was that of the mechanism of the reaction. Immediately, the isolation of 2,4-dinitrodiphenyl sulphide as a product, suggested an ionic mechanism of the type

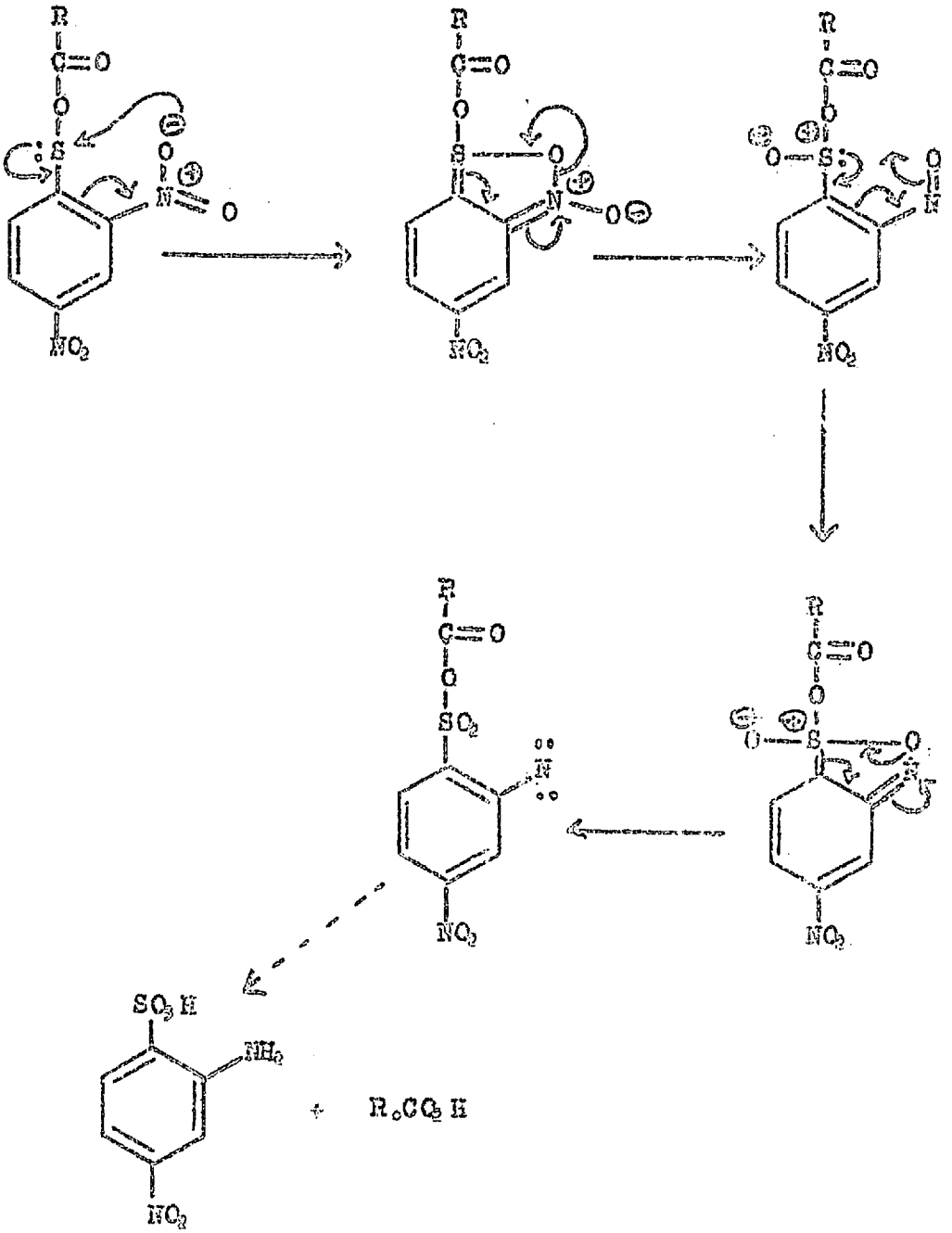


This was an attractive scheme since the existence of the 2,4-dinitrobenzenesulphenic cation and its tendency to undergo Friedel-Crafts reactions is well established and moreover, the generation of the acetate anion would nicely account for the high yield of acetic acid.

The photolysis was, therefore, carried out again in the presence of 1 mol. of anisole and 2,4-dinitro-4'-methoxydiphenyl sulphide isolated (74%). This is conclusive proof that the mechanism is ionic since the rate of electrophilic attack on anisole is about $\times 10^{9}$ faster than on benzene, whereas the rate of radical attack is practically the same [98].

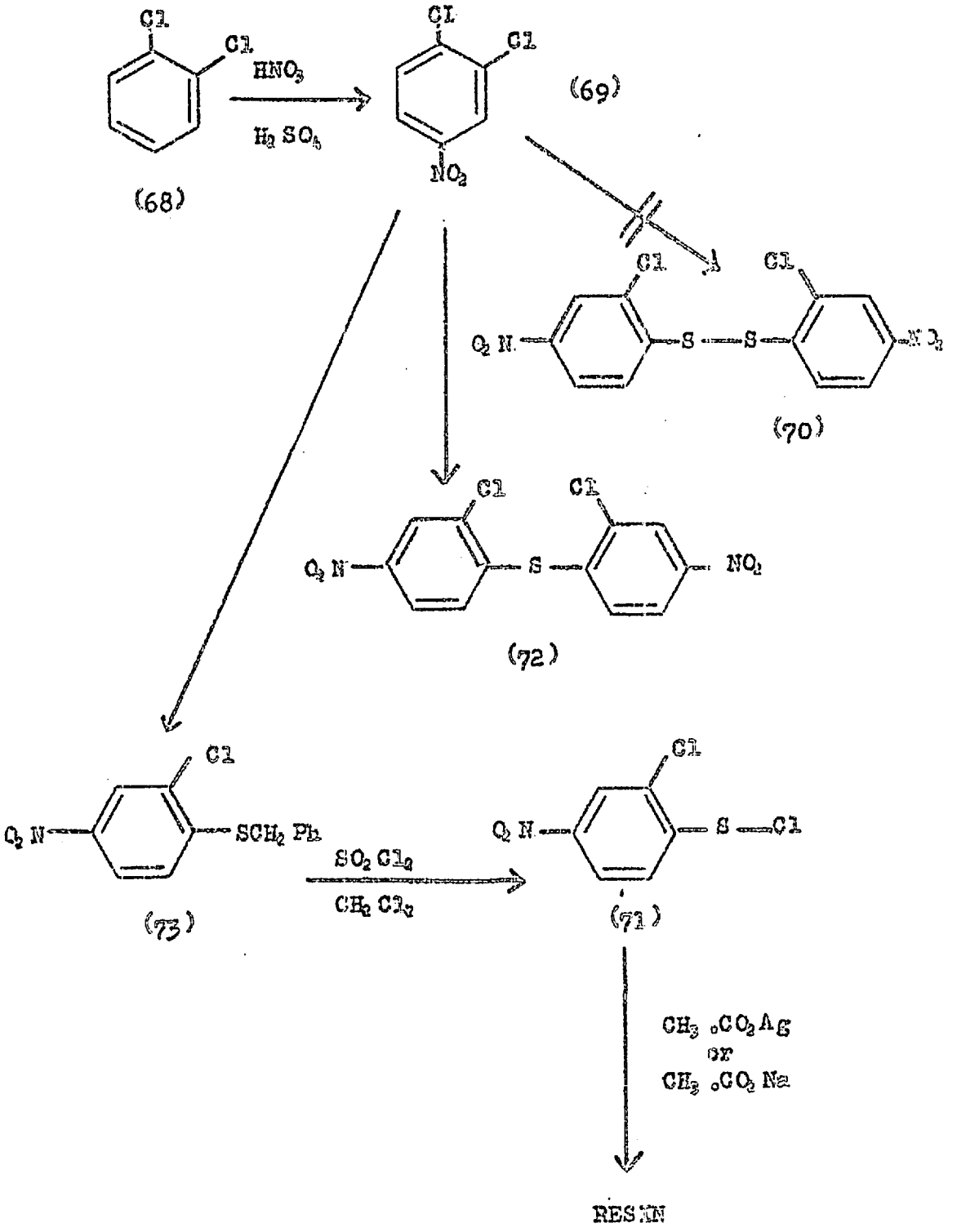
This mechanism, however, cannot account for the formation of the sulphonic acid, and so a second mode of break-down must be operative. One reasonable suggestion for this second mechanism is illustrated below.

Obviously such a process depends upon the presence of the o-nitro substituent and so in order to test the mechanism, it was clearly desirable to synthesise a sulphenyl halide not possessing this group.


R
C=O
O
S
O
N
O
NO2
SO2
NH2
+ R.CO2H

To this end the following series of reactions has been carried out. o-Dichlorobenzene (68) was nitrated [199] to give 1,2-dichloro-4-nitrobenzene (69) which on treatment [195] with sodium disulphide gave not the desired organic disulphide (70) (which was to have been converted to the sulphenyl halide (72) by chlorinolysis [200]) but rather the monosulphide (72). Accordingly, the 1,2-dichloro-4-nitrobenzene was treated [201] with S-benzylthiouronium chloride in alcoholic KOH to give the benzyl 1-chloro-4-nitrophenyl sulphide (73). This on treatment [189] with sulphuryl chloride in methylene dichloride gave the desired 1-chloro-4-nitrobenzenesulphenyl chloride (71). After purification as far as was possible by recrystallisation from petrol, estimation by titration [202] showed it to be only 73% pure. All attempts to raise this figure failed.

This sulphenyl halide was then reacted with silver acetate in methylene dichloride in the way already described [190] in order to convert it to the mixed sulphenic/acetic anhydride. However, none of the desired product was obtained, a resinous material and a small amount of a yellow oil containing no carbonyl band being the only products.


Cl
Cl
HNO_3
H_2SO_4
NO_2
(68)
(69)
O_2N
S
S
(70)
(72)
SCH_2Ph
SO_2Cl_2
CH_2Cl_2
(73)
(71)
$CH_3 \cdot CO_2Ag$
or
$CH_3 \cdot CO_2Na$
RESIN

EXPERIMENTAL

Unless otherwise stated, melting points were determined on a Kofler block, infrared spectra measured on a Unicam SP 200, ultraviolet spectra on a Unicam SP 500 or SP 700 spectrophotometer, and nuclear magnetic resonance spectra on a Varian A60 instrument. Microanalyses were carried out by the Organic Microanalytical Laboratory of the Imperial College. Petroleum ether refers to the fraction of b.p. 40-60°.

Attempted substitution of the p-cresyl radical into veratrole[155,156]

1. Calibration of the Zeisel Method

(a) p-Cresol (100 mg.) was thoroughly admixed with veratrole (1 mg.) and a Zeisel determination carried out on the whole. A positive result was obtained.

(b) The above experiment was repeated with the same result using p-cresol (100 mg.) and veratrole (0·1 mg.).

2. Calibration of the extraction procedure

p-Cresol (0·01 mol., 1·08 g.) was dissolved in Na_2CO_3 solution (100 ml. of M/5) and veratrole (0·1 mol., 13·8 g.) added. To this mixture was further added, water (30 ml.) and ethanol (50 ml.).

(a) The mixture was poured into a large volume of water and extracted with ether. The ether was dried (Na_2SO_4), the solvent removed and the weight (14·88 g.) of extract found to be equal to the sum of the weights of the p-cresol and the veratrole used.

(b) This extract was strongly basified (10 $\bar{N}$ NaOH) and repeatedly extracted with ether. The basic layer was then acidified, extracted with ether, the ether dried (Na_2SO_4) and evaporated. The weight (0·324 g.) of the phenolic material so obtained was found to be equal to 30% of the p-cresol used.

(c) The ether washings from (b) were then extracted with sodium hydroxide solution (10 N), acidified, extracted with ether, the ether dried (Na_2SO_4) and evaporated. The weight (0·119 g.) of phenolic material so obtained was found to be equal to a further 11% of the weight of the p-cresol used.

(d) A Zeisel determination on 100 mg. of the combined phenolic fractions was carried out and a negative result obtained.

3. Oxidation of p-cresol in the presence of veratrole

p-Cresol (0·01 mol.) was dissolved in Na_2CO_3 solution (100 ml. of M/5) and veratrole (0·1 mol.) added. To this was further added ethanol (50 ml.) and then the whole oxidised by running in an aqueous solution of potassium ferricyanide (6·58 g. in 30 ml. of water). Procedures 2(a), 2(b) and 2(c) were then repeated. Again a negative Zeisel determination was obtained.

All the experiments in this series were repeated twice, identical results being obtained in both cases.

3-(p-Acetoxyphenyl)coumarin and 2,4'-diacetoxystilbene-β-carboxylic acid [39]

p-Hydroxyphenylacetic acid (1·124 g.) and redistilled salicylaldehyde (0·576 ml.) were dissolved in acetic anhydride

(3·2 ml.) and triethylamine (0·8 ml.) added. The whole was refluxed for 5 hours.

On cooling, a compound separated out. This was collected at the pump and on recrystallisation from an ethanol/acetone mixture gave 3-(p-acetoxyphenyl)coumarin as needles, m.p. 181-182·5° (57%), $\nu_{max.}$ 1720 and 1770 cm^{-1}.
(Found: C, 73·19; H, 4·17. $C_{17}H_{12}O_4$ requires: C, 72·9; H, 4·28%).

The filtrate obtained after separation of the above crystals was poured into water and extracted with ether. The ethereal solution was extracted with sodium bicarbonate solution, the extract acidified and extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal solution gave a colourless solid which on recrystallisation from aqueous ethanol gave 2,4'-diacetoxystilbene-β-carboxylic acid (of unknown stereochemistry) as needles, m.p. 177-178° (14%), $\nu_{max.}$ 1695 and 1760cm^{-1}.
(Found: C, 66·59; H, 5·32. $C_{19}H_{16}O_6$ requires: C, 67·1; H, 4·7%).

Salicylaldehyde benzyl ether

This compound was prepared by the method of Hey and Hobbs [39] and obtained as needles from ethanol, m.p. 46-47° (87%).

4-Acetoxy-2'-benzyloxystilbene-α-carboxylic acid [57]

p-Hydroxyphenylacetic acid (0·75 g.) and salicyl-aldehyde benzyl ether (1·05 g.) were dissolved in acetic anhydride (3·2 ml.) and triethylamine (0·7 ml.) added. The whole was refluxed for 5 hours.

The reaction mixture was cooled and poured into a large volume of water. The product was extracted with ether and then the ethereal layer washed with sodium bicarbonate solution and water, and dried (Na_2SO_4). Evaporation of the solvent gave a crystalline product which on recrystallisation from petrol/ethanol gave needles, m.p. 163-175°,(54%), $\nu_{max.}$ 1770 and 1670 cm^{-1}., suggesting that a mixture of the two possible stereoisomers had been obtained.

(Found: C, 74·42; H, 5·10. $C_{25}H_{20}O_5$ requires: C, 74·21; 5·19%).

Copper Chromite catalyst

This compound was prepared by the method described in Organic Syntheses [48].

4-Acetoxy-2'-benzyloxystilbene [40]

4-Acetoxy-2'-benzyloxystilbene-α-carboxylic acid (236·4 mg.) was dissolved in redistilled quinoline (2·5 ml.) and "copper chromite" catalyst (23·6 mg.) added. This mixture

was heated at 210-220° for 1·25 hours and then cooled and poured into dilute HCl solution. The product was extracted with ether, dried (Na_2SO_4) and the solvent evaporated. A brown oil was obtained whose I.R. spectrum showed weak bands at 1770 and 3590 cm^{-1}. and total absence of a band at 1670 cm^{-1}., indicating that decarboxylation had taken place together with some deacetylation. Both trituration with solvents and chromatography on alumina (grade 5) using benzene as eluant failed to induce crystallisation.

The material was, therefore, dissolved in dry pyridine (10 ml.) and acetic anhydride (5 ml.) added and the mixture a allowed to stand overnight at room temperature.

The whole was poured into water, extracted with ether and the ethereal layer washed successively with dilute HCl solution, sodium bicarbonate solution and water and then dried (Na_2SO_4). Evaporation of the solvent gave a gum whose I.R. spectrum showed a strong band at 1770 cm^{-1}. and absence of a band at 3590 cm^{-1}., indicating that reacetylation had taken place. Both trituration with solvents and chromatography on alumina (grade 3) using benzene as eluant failed to induce crystallisation.

4-Acetoxy-2'-hydroxybibenzyl

Crude 4-acetoxy-2'-benzyloxystilbene (110 mg.) was dissolved in ethanol (25 ml.) and hydrogenated over a 10% palladium/carbon catalyst (10 mg.). After 5 hours all absorption of hydrogen had ceased and the total uptake corresponded to 2·27 double bond equivalents. The catalyst was removed by filtration and the solvent evaporated. Recrystallisation of the solid residue from petroleum ether/benzene gave needles, m.p. 93-95° (91%).

(Found: C, 74·98; H, 6·31. $C_{16}H_{16}O_3$ requires: C, 74·98; H, 6·29%).

2,4'-Dihydroxybibenzyl

4-Acetoxy-2'-hydroxybibenzyl (250 mg.) was boiled under reflux with 10% aqueous sodium hydroxide solution (50 ml.) for 1·5 hours, at the end of which time all the solid had dissolved.

The reaction mixture was poured into cold water (100 ml.) and acidified with dilute HCl solution. The product was extracted with ether and the ethereal solution washed successively with dilute sodium bicarbonate solution and water, dried (Na_2SO_4) and finally evaporated. There remained a white crystalline solid which on recrystallisation from benzene/petrol gave colourless needles, m.p. 132-133° (93%).

(Found: C, 77·41; H, 6·48. $C_{14}H_{14}O_2$ requires: C, 78·48; H, 6·59%).

p-Benzyloxybenzaldehyde

This compound was prepared by the method of Hey and Hobbs [39] and obtained as needles from aqueous ethanol m.p. 72° (73%).

p-Benzyloxybenzyl alcohol

This compound was prepared by the method of Shelton et al.[45] and obtained as plates from benzene/petroleum ether, m.p. 87·5-88° (93%).

p-Benzyloxybenzyl chloride

This compound was prepared by the procedure due to Taylor (Ph.D. Thesis, London, 1962) and obtained as plates from petroleum ether, m.p. 78-79° (70%).

p-Benzyloxybenzyltriphenylphosphonium chloride

p-Benzyloxybenzyl chloride (0·82 g.) was dissolved in benzene and treated with a solution of triphenylphosphine (0·83 g.) in benzene. p-Benzyloxybenzyltriphenylphosphonium chloride was immediately precipitated. It was separated at the pump and recrystallised from benzene and obtained in a micro-

crystalline state, m.p. 242-245°, in almost quantitative yield. (Found: ionic Cl, 7·0. $C_{32}H_{29}ClOP$ requires: ionic Cl, 7·2%).

2,4'-Dibenzyloxystilbene [144, 145]

To a solution of sodium (0·046 g.) in ethanol (50 ml.), p-benzyloxybenzyltriphenylphosphonium chloride (0·99 g.) was added under nitrogen. A yellow colour was produced. Salicylaldehyde benzyl ether (0·424 g.) in ethanol (25 ml.) was now run in and the mixture stirred for 24 hours. The precipitate was removed at the pump and recrystallised from petrol/benzene to give needles, m.p. 124·5-125·5° (53%).
(Found: C, 85·31; H, 6·10. $C_{28}H_{24}O_2$ requires: C, 85·68; H, 6·16%).

2,4'-Dihydroxybibenzyl

2,4'-Dibenzyloxystilbene (250 mg.) was dissolved in ethanol (50 ml.) and hydrogenated over a 10% palladium/carbon catalyst (25 mg.). After 5 hours all absorption of hydrogen had ceased, the total uptake corresponding to 3·13 double bonds. The catalyst was removed by filtration and the solvent evaporated. Recrystallisation of the product from benzene/petrol gave needles, m.p. 132-133° (93%), identical in all respects with the material obtained by the earlier procedure.

p-Benzyloxybenzyldiethyl phosphonate [145, 146, 147]

A mixture of p-benzyloxybenzyl chloride (0·67 g.) and triethyl phosphite (0·472 ml.) were heated at 160° until the reaction was complete as evidenced by the cessation of the ethyl chloride evolution (about 90 minutes). Distillation under reduced pressure gave a colourless liquid, b.p. 185°/0·4 mm. (85%).

2,4'-Dibenzyloxystilbene [145]

p-Benzyloxybenzyldiethyl phosphonate (0·345 g.) was treated with salicylaldehyde benzyl ether (0·219 g.) and sodium methoxide (0·796 g.) in dry DMF and left to stand overnight at room temperature.

The mixture was poured into ice/water and the solid obtained filtered at the pump. Recrystallisation from petrol/benzene gave needles, m.p. 132-133° (75%). The material was found to be identical (m.p., mixed m.p. and superimposable I.R.) with the material made by the alternative procedure previously discussed.

Oxidation of 2,4'-dihydroxybibenzyl

A solution of 2,4'-dihydroxybibenzyl (0·533 g.) in 2N NaOH solution (300 ml.) was added dropwise over a period of

90 minutes to an agitated mixture of ether (200 ml.) and water (600 ml.) in which had been dissolved potassium ferricyanide (6 g.) and which was maintained under an atmosphere of nitrogen.

The ether was separated, dried (Na_2SO_4) and evaporated. Chromatography of the residue on alumina (grade 3) using benzene as eluant gave a crystalline product which after recrystallisation from petroleum ether/benzene was obtained as needles, m.p. 135-136° (11·5%).

(Found: C, 79·30; H, 5·92. $C_{18}H_{12}O_2$ requires: C, 79·22; H, 5·70%).

Trichloroacetyl chloride

This compound was prepared according to the method of Brown[150], and obtained as a colourless liquid b.p. 116-119° (51%).

β-Naphthyl trichloroacetate

This compound was prepared according to the method of Houben and Fischer [146] and obtained as needles from benzene/petrol, m.p. 86-87° (67%), $\nu_{max.}$ 1775 cm^{-1}.

General Procedure for Irradiation

A solution was made up from the compound (usually about 0·5 millimole) and a dry oxygen and peroxide free solvent

(usually ether, cyclohexane or dioxan - about 125 ml.) in a 250 ml. round bottomed flask (pyrex or quartz) equipped with a Herschberg stirrer (Fieser, "Experiments in Organic Chemistry" 3 rd. Ed., Heath and Co., Boston, 1955, p. 265.), a nitrogen inlet and a double-walled reflux condenser. Immediately beneath the flask was situated a Phillips 125 watt, high pressure mercury arc lamp (57236F/21).

At intervals during the photolysis, samples were withdrawn and U.V. and/or I.R. spectroscopic measurements taken to follow the course of the reaction. For the U.V. measurements the sample was properly diluted with the solvent in which the reaction was being carried out. In the case of the I.R. measurements, the sample was evaporated under vacuum and the residue dissolved in a finite amount of chloroform.

Blank reactions were run by refluxing the compound in the same solvent for about 5 hours in the dark. In every case the U.V. and/or I.R. spectra of the solutions were found to be identical to those of the starting material.

The solvents were freed from peroxides by washing with alkaline ferrous sulphate solution or, in the case of dioxan, by treatment with stannous chloride. They were dried by distillation from sodium and then stored in the dark over sodium. Immediately before use, they were boiled for a few

minutes under vacuum to remove any dissolved oxygen. Solvents more than two weeks old were always repurified before use.

Irradiation of β-naphthyl trichloroacetate

β-Naphthyl trichloroacetate (0·5 millimole) dissolved in dry ether (125 ml.) was irradiated in the usual way in a quartz flask. After 3 hours the reaction was complete (as evidenced by the disappearance of the strong band at 1775 cm^{-1}.) giving a deep yellow solution.

The ether was extracted with $2\bar{N}$ NaOH solution, the basic layer acidified, extracted with ether and then the ethereal solution washed with water and dried (Na_2SO_4). The solvent was removed giving a brown solid (29 mg., 40·3%) which after chromatography on alumina (grade 3, using benzene/20% ether as eluant) gave colourless plates (20·9 mg., 29%). This material was then recrystallised from benzene and shown to be β-naphthol (22%) (m.p., mixed m.p. and superimposable I.R. spectrum).

Triphenylmethyl chloride

This compound was prepared by the method described in Organic Syntheses [151].

Triphenylacetic acid

This compound was prepared by the method of Schmidlin [152, 153, 154] and obtained as colourless plates from acetic acid m.p. 264-265° (80%).

Triphenylacetyl chloride

This compound was prepared by the method of Jones and Hurd [155] and obtained as prisms, m.p. 127°, without recrystallisation, in almost quantitative yield.

β-Naphthyl triphenylacetate

Triphenylacetyl chloride (1 millimole) was dissolved in dry benzene (15 ml.) and a solution of β-naphthol (1 millimole) in dry benzene (10 ml.) added. Dry pyridine (1 ml.) was added and the mixture boiled under reflux for 3 hours. The whole was poured into water, washed with 2N NaOH solution, dilute HCl solution, dilute Na_2CO_3 solution, water and finally dried (Na_2SO_4).

Evaporation of the solvent followed by filtration through an alumina column (grade 3, benzene as eluant) gave β-naphthyl triphenylacetate which on recrystallisation from benzene/petrol gave needles, m.p. 169·5-170·5° (56·5%), $\nu_{max.}$ 1750 cm^{-1}.

(Found: C, 86·88; H, 5·69. $C_{30}H_{22}O_2$ requires: C, 86·93; H, 5·35%)

Irradiation of β-naphthyl triphenylacetate

This compound was irradiated in a quartz flask for 1 hour as already described for β-naphthyl trichloroacetate, and β-naphthol obtained (39%).

Fluorene-9-carboxylic acid

This compound was prepared by the method described in Organic Syntheses [156].

Fluorene-9-carbonyl chloride

This compound was prepared by the method of Stolle and Wolf [157] and obtained as needles from ether, m.p. 77° (64%), $\nu_{max.}$ 1785 cm^{-1}.

β-Naphthyl fluorene-9-carboxylate

Fluorene-9-carbonyl chloride (136.2 mg.) was dissolved in dry benzene (15 ml.) and a solution of β-naphthol (86.4 mg.) in dry benzene (10 ml.) added. Dry pyridine (1 ml.) was added and a white precipitate immediately formed. The mixture was allowed to stand for 1 hour. The whole was poured into water, washed with 2N NaOH solution, dilute HCl solution, dilute Na_2CO_3 solution, water and finally dried (Na_2SO_4).

Evaporation of the solvent followed by filtration

through an alumina column (grade 3, benzene as eluant) gave β-naphthyl fluorene-9-carboxylate which on recrystallisation from petrol/benzene gave needles, m.p. 143-144° (65%), $\nu_{max.}$ 1755 cm^{-1}.

(Found: C, 85·76; H, 4·73. $C_{24}H_{16}O_2$ requires: C, 85·69; H, 4·79%).

Irradiation of β-naphthyl fluorene-9-carboxylate

This compound was irradiated in a pyrex flask for 4 hours as already described for β-naphthyl trichloroacetate and β-naphthol obtained (60%).

In a further experiment, the exit gases were passed first through a U-tube containing a quantity of I_2O_5 maintained at 120°, and then through two Dreschel bottles each containing saturated barium hydroxide solution (100 ml.).

The free iodine liberated by oxidation of the CO generated in the photolysis was estimated by titration giving a figure equivalent to 93% of the theoretical amount of carbon monoxide, and then the carbon dioxide estimated gravimetrically as $BaCO_3$ (87%).

Xanthene-9-carbonyl chloride

This compound was prepared by the method of Cusic [156] and obtained as needles from ether, m.p. 81° (61%), $\nu_{max.}$ 1785 cm^{-1}.

β-Naphthyl xanthene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as needles from acetone, m.p. 168-169·5° (68%), $\nu_{max.}$ 1760 cm^{-1}.
(Found: C, 81·72; H, 4·47. $C_{21}H_{16}O_3$ requires: C, 81·80; H, 4·58%).

Irradiation of β-naphthyl xanthene-9-carboxylate

This compound was irradiated in a pyrex flask for 4 hours as already described for β-naphthyl trichloroacetate, and β-naphthol obtained (60%).

p-Cresyl fluorene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as prisms from cyclohexane, m.p. 114-115° (67%), $\nu_{max.}$ 1755 cm^{-1}.
(Found: C, 83·95; H, 5·24. $C_{21}H_{16}O_2$ requires: C, 83·98; H, 5·37%).

Irradiation of p-cresyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 2 hours as already described for β-naphthyl trichloroacetate, and β-naphthol obtained (58%, as 3,5-dinitrobenzoate).

Guaiacyl fluorene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as large prisms from carbon tetrachloride/petroleum ether, m.p. 116-117° (66%), $\nu_{max.}$ 1760 cm^{-1}.

(Found: C, 80·13; H, 5·05. $C_{21}H_{16}O_3$ requires: C, 79·73; H, 5·10%).

Irradiation of guaiacyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 2 hours as already described for β-naphthyl trichloroacetate, and β-naphthol obtained (58%).

In another similar experiment the crude reaction mixture was evaporated and the n.m.r. spectrum of the residue measured. No peak about τ 6·0 was observed indicating absence of any methylenedioxy residue.

Cholesteryl fluorene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as needles fo from petroleum ether/benzene, m.p. 179-180° (61%), $\nu_{max.}$ 1730 cm^{-1}.

(Found: C, 85·07; H, 9·30. $C_{41}H_{64}O_2$ requires: C, 85·07; H, 9·40%).

Irradiation of cholesteryl fluorene-9-carboxylate

Cholesteryl fluorene-9-carboxylate (289 mg.) dissolved in dry ether (125 ml.) was irradiated in the usual way in a quartz flask. After 6 hours the strong band at 1730 cm^{-1}. showed no diminution in its intensity and so the bulk of the reaction mixture was evaporated. Recrystallisation of the solid obtained from petrol/benzene gave unchanged starting material (m.p., mixed m.p. and superimposable I.R.) (96%).

This experiment was now repeated using dry methyl-cyclohexane as solvent. Again no photolysis took place and the starting material was recovered (94%).

Cholesteryl xanthene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as plates from ethyl acetate, m.p. 165-166° (68%), $\nu_{max.}$ 1720 cm^{-1}. (Found: C, 82·75; H, 9·00. $C_{41}H_{54}O_3$ requires: C, 82·78; H, 9·15%).

Irradiation of cholesteryl xanthene-9-carboxylate

Cholesteryl xanthene-9-carboxylate (297 mg.) dissolved in dry ether (125 ml.) was irradiated in the usual way in a quartz flask. After 6 hours the strong band at 1720 cm^{-1}. showed no diminution in its intensity and so the bulk of the

reaction mixture was evaporated. Recrystallisation of the solid obtained from ethyl acetate gave unchanged starting material (93%).

Methyl fluorene-9-carboxylate

This compound was prepared by the method of Tucker [60, 61] and obtained as needles from methanol, m.p. 63° (91%), $\nu_{max.}$ 1730 cm^{-1}.

Irradiation of methyl fluorene-9-carboxylate

Methyl fluorene-9-carboxylate (117 mg.), dissolved in dry ether (125 ml.), was irradiated in the usual way in a quartz flask. After 6 hours, the strong band at 1730 cm^{-1}. showed no diminution in its intensity and so the bulk of the reaction mixture was evaporated. Recrystallisation of the solid obtained from methanol gave unchanged starting material (m.p., mixed m.p. and superimposable I.R.) (94%).

Attempted preparation of o-(benzyl-S-methyl)benzoic acid [66]

Phthalide (307 mg.) was dissolved in quinoline (15 ml.) and benzyl mercaptan (0·3 ml.) added. The mixture was refluxed for 4 hours.

After cooling, the solution was poured into water and

extracted with ether. This extract was washed with dilute HCl solution, Na_2CO_3 solution, water and finally dried (Na_2SO_4). Evaporation of the solvent gave a brown solid which after recrystallisation from water gave needles, m.p. 75°. Mixed m.p. with an authentic specimen of phthalide showed no depression.

o-(Benzyl-S-methyl)benzoic acid

Phthalide (297 mg.) was dissolved in dry DMF (25 ml.) and sodium hydride (106 mg.) added. Benzyl mercaptan (0·3 ml.) was then run in and the mixture refluxed for 4 hours.

After cooling, the solution was poured into water and extracted with ether. This extract was washed with dilute HCl solution, Na_2CO_3 solution, water and finally dried (Na_2SO_4).

Evaporation of the solvent gave a brown solid which on recrystallisation from petrol (80-100°)/CCl_4 gave large colourless prisms, m.p. 108-110° (73%), $\nu_{max.}$ 1710 cm^{-1}.
(Found: C, 69·77; H, 5·42. $C_{15}H_{14}O_2S$ requires: C, 69·84; H, 5·24%).

Attempted preparation of o-(benzyl-S-methyl)benzoyl chloride

o-(Benzyl-S-methyl)benzoic acid (46·5 mg.) was dissolved in dry benzene (2 ml.) and oxalyl chloride (0·0465 ml.) was added at room temperature. An immediate effervescence took place which subsided after about 15 minutes. The mixture was then heated

on the water bath for a further 15 minutes. Removal of the solvent afforded a yellow cheese-like solid which on recrystallisation from petrol (80-100°) gave pale yellow needles, m.p. 59-60°, $\nu_{max.}$ 1695 cm^{-1}, (broad). This experiment was then repeated at 0° and the same result obtained.

o-(Phenyl-S-methyl)benzoic acid

Phthalide (108·7 mg.) was dissolved in dry DMF (25 ml.) and sodium hydride (60 mg.) added. Thiophenol (0·089 ml.) was then run in and the mixture refluxed for 4 hours.

After cooling, the solution was poured into water and extracted with ether. This extract was washed with dilute HCl solution, Na_2CO_3 solution, water and finally dried (Na_2SO_4).

Evaporation of the solvent gave a brown solid which on recrystallisation from cyclohexane/petrol (60-80°) gave plates, m.p. 109-110° (71%), $\nu_{max.}$ 1710 cm^{-1}.
(Found: C, 68·85; H, 4·91. $C_{14}H_{12}O_2S$ requires: C, 69·07; H, 5·01%).

o-(Phenyl-S-methyl)benzoyl chloride

o-(Phenyl-S-methyl)benzoic acid was dissolved in dry benzene (2 ml.) and oxalyl chloride (0·05 ml.) was added. The whole was refluxed on the steam bath for 30 minutes.

The solvent was evaporated to give a non-crystalline

product ($\nu_{max.}$ 1765 cm^{-1}.) indicating an aromatic acid chloride. The material was not further purified.

β-Naphthyl o-(phenyl-S-methyl)benzoate

This compound was prepared as already described for β-naphthyl trichloroacetate using a reaction time of 12 hours, and obtained as needles from cyclohexane/petrol, m.p. 84-85° (69%), $\nu_{max.}$ 1740 cm^{-1}.

(Found: C, 78·14; H, 4·79. $C_{24}H_{18}O_2S$ requires: C, 77·84; H, 4·79%).

Irradiation of β-naphthyl o-(phenyl-S-methyl)benzoate

This compound was irradiated in a quartz flask for 30 minutes as already described for β-naphthyl trichloroacetate, and β-naphthol obtained (9%).

Benzyl phenyl sulphide [68]

Sodium hydride (567·8 mg.) was added to dry DMF (20 ml.) and benzyl chloride (1·1 ml.) and thiophenol (1·5 ml.) run in. The mixture was refluxed for 2 hours.

The whole was poured into water and extracted with ether. The ether layer was washed with dilute HCl solution, Na_2CO_3 solution, water and finally dried (Na_2SO_4). Removal of solvent followed by recrystallisation of the residue solid from

alcohol gave leaflets, m.p. 44° (87%).

Irradiation of benzyl phenyl sulphide

This compound was irradiated in a quartz flask for 30 minutes as already described for β-naphthyl trichloroacetate. Evaporation of the solvent gave a brown gum which smelt strongly of thiophenol and from which no benzyl phenyl sulphide could be isolated by chromatography.

o-Iodobenzoyl chloride

This compound was prepared by the method of Raiford and Lankelma [169,170] and obtained as colourless needles, m.p. 35-38° (92%).

β-Naphthyl o-iodobenzoate

This compound was prepared by the method already described for β-naphthyl fluorene-9-carboxylate and obtained as colourless prisms from ethylacetate/petrol, m.p. 85-86°, $\nu_{max.}$ 1740 cm^{-1}.

(Found: C, 54·19; H, 2·92. $C_{17}H_{11}IO_2$ requires: C, 54·54; H, 2·94%)

Irradiation of β-naphthyl o-iodobenzoate

This compound was irradiated in a quartz flask for

4 hours as already described for β-naphthyl triphenylacetate and β-naphthol obtained (14%).

p-Acetophenyl fluorene-9-carboxylate

This compound was prepared by the method described for β-naphthyl fluorene-9-carboxylate and obtained as needles from cyclohexane/benzene, m.p. 156-157° (72%), $\nu_{max.}$ 1745 and 1680 cm^{-1}. (Found: C, 80·61; H, 4·89. $C_{22}H_{16}O_3$ requires: C, 80·47; H, 4·91%).

Irradiation of p-acetophenyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 6 hours as already described for β-naphthyl trichloroacetate and p-hydroxyacetophenone obtained (40%).

p-Benzeneazophenyl fluorene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as orange needles from acetone, m.p. 177-178° (70%), $\nu_{max.}$ 1760 cm^{-1}. (Found: C, 79·71; H, 4·43. $C_{26}H_{18}N_2O_2$ requires: C, 79·98; H, 4·65%).

Irradiation of p-benzeneazophenyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 4 hours as already described for β-naphthyl trichloroacetate and

p-hydroxyazobenzene obtained (15%).

p-Nitrophenyl fluorene-9-carboxylate

This compound was prepared by the method described for β-naphthyl fluorene-9-carboxylate and obtained as needles from cyclohexane/benzene, m.p. 152-153° (69%), $\nu_{max.}$ 1745 cm^{-1}. (Found: C, 72·85; H, 3·98, $C_{20}H_{13}NO_4$ requires: C, 72·5; H, 3·96%).

Irradiation of p-nitrophenyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 4 hours as already described for β-naphthyl trichloroacetate and p-nitrophenol obtained (10%).

Isolation of N-p-methylaminophenol from metol

Metol (N-p-hydroxyphenylmethylammonium sulphate) was simply converted to its free base, N-p-methylaminophenol, by treating the salt with an excess of Na_2CO_3 solution and extracting with ether. The ethereal solution was dried (Na_2SO_4) and evaporated to yield the free base which on recrystallisation from benzene gave colourless needles, m.p. 87°.

Attempted preparation of N-p-hydroxyphenyl-N-methylformamide[97]

N-p-Methylaminophenol (0·105 g.) was treated with ethyl

formate (0·07 ml.) and dioxan (5 ml.) added. The mixture was refluxed for 1 hour.

After this time the solvent was evaporated to yield a colourless solid, the I.R. spectrum of which was measured. No band at about 1680 cm^{-1}. was observed, indicating the absence of a formamide. Furthermore, recrystallisation of the solid from benzene gave colourless crystals which were shown to be identical with the starting material (m.p., mixed m.p. and superimposable I.R. spectra).

N-Carbethoxy-N-methyl-p-aminophenol

N-p-Methylaminophenol (104 mg.) was dissolved in dry benzene (10 ml.), treated with ethyl chloroformate (0·0815 ml.) and the whole refluxed for 2 hours. The mixture was cooled and extracted first with dilute HCl solution and then dilute NaOH solution. This latter extract was acidified and extracted with ether, the ethereal solution dried (Na_2SO_4) and then evaporated to yield a colourless oil. The I.R. spectrum showed an intense band at 1670 cm^{-1}. indicating the presence of the grouping $>N-CO.O$. However, repeated chromatography on alumina failed to crystallise it.

p-Dimethylaminophenol

Lithium aluminium hydride (1·5 g.) was dissolved in dry ether (250 ml.) and crude N-carbethoxy-N-methyl-p-aminophenol (200 mg.), dissolved in dry ether, gradually added. The mixture was then heated under reflux for 3 hours.

After carefully destroying any excess lithium aluminium hydride with ethyl acetate, water was added and then the precipitated aluminium hydroxide filtered off. The ethereal solution was dried (Na_2SO_4) and the solvent evaporated to yield a white crystalline solid which on recrystallisation from benzene gave p-dimethylaminophenol, m.p. 74-76° (87%).

p-Dimethylaminophenyl fluorene-9-carboxylate

This compound was prepared as already described for β-naphthyl fluorene-9-carboxylate and obtained as a colourless oil (67%), $\nu_{max.}$ 1740 cm^{-1}. which could not be crystallised.

Irradiation of p-dimethylaminophenyl fluorene-9-carboxylate

This compound was irradiated in a quartz flask for 4 hours as already described for β-naphthyl trichloroacetate and p-dimethylaminophenol obtained (9%).

β-Naphthyl N-phenylurethan and β-naphthyl N-α-naphthylurethan

β-Naphthol (0·01 mol.) was dissolved in phenyl isocyanate (0·01 mol.) and dry triethylamine (1 drop) added. The mixture was heated on the water bath under anhydrous conditions for 5 minutes and then cooled. Colourless crystals quickly separated which were then filtered at the pump and extracted with hot carbon tetrachloride. The crystals which subsequently separated on cooling, were recrystallised from the same solvent to give needles, m.p. 155-156°. In an exactly analogous manner, β-naphthyl N-α-naphthylurethan was prepared from α-naphthyl isocyanate (m.p. 157-158° ex CCl_4).

β-Naphthyl N,N-diphenylurethan

β-Naphthol (0·01 mol.) was dissolved in dry triethylamine (3 ml.) and diphenylcarbamyl chloride (0·01 mol.) added. The mixture was heated under reflux for 1 hour and then poured into water. The product was filtered, washed with Na_2CO_3 solution, dried and finally recrystallised from carbon tetrachloride/petroleum ether (60-80°) to give needles, m.p. 141-142°.

Irradiation of β-naphthyl N-phenylurethan

β-Naphthyl N-phenylurethan (131 mg.), dissolved in dry dioxan (125 ml.) was irradiated in the usual way in a quartz flask.

After 6 hours, the strong band at 1730 cm^{-1}. showed no diminution in its intensity and so the bulk of the reaction mixture was evaporated. Recrystallisation of the solid obtained from carbon tetrachloride gave unchanged starting material (94%).

Irradiation of β-naphthyl N,N-diphenylurethan

This compound was irradiated in a quartz flask for 4 hours using ether/ethanol 9:1 as solvent as described for β-naphthyl trichloroacetate and β-naphthol obtained (67%).

After base extraction of the reaction mixture, it was then extracted with dilute HCl solution, the acidic layer made alkaline, extracted with ether, and then the ethereal solution washed with water and dried (Na_2SO_4). The solvent was removed giving a brown solid which readily formed a tosylate (58%), m.p. 142° (diphenylamine tosylate m.p. 142°, mixed m.p. showed no depression).

This photolysis was repeated in dry dioxan (125 ml.) giving pure β-naphthol (47.5%) and pure diphenylamine tosylate (46%).

Irradiation of β-naphthyl N-α-naphthylurethan

This compound was irradiated in a pyrex flask for 3 hours using ether/ethanol 9:1 as solvent as described for

β-naphthyl trichloroacetate and β-naphthol obtained (75%).

After base extraction of the reaction mixture, evaporation of the ether gave a brown solid, (111 mg. 97%) which after chromatography on alumina (grade 3, using benzene/ 10% ether as eluant) followed by recrystallisation from carbon tetrachloride gave colourless prisms (74 mg., 64.3%) m.p. 79° (ethyl N-α-naphthylurethan m.p.79°, mixed m.p. showed no depression).

This photolysis was repeated in dry dioxan (125 ml.) giving β-naphthol (64%).

Attempted preparation of potassium p-cresyl xanthate

(Chem. Abs., 1949, 43, 8604g.)

A mixture of potassium hydroxide (90 g.), ethanol (200 ml., 95%), p-cresol (25 g.) and carbon disulphide (25 g.) were boiled under reflux for 5 hours. An orange/yellow solid was quickly produced. This was filtered at the pump, washed with ethanol, dried and analysed for sulphur by the method later described and was found to contain only 8.9% of the theortical amount, a result in direct contrast to that in the literature cited.

General procedure for estimation of sulphur in xanthates

The xanthate (about 0·5 g.) was dissolved in water (15 ml.) and potassium hydroxide pellets (1 g.) added. After boiling the mixture under reflux for 30 minutes it was acidified with 50% HCl and nitrogen passed through until all the hydrogen sulphide liberated had been swept out of the reaction flask and slowly bubbled through three Dreschel bottles each containing I_2/KI solution (100 ml. of 0·1 $\bar{N}$). The unreacted iodine was then estimated by titration with 0·1 $\bar{N}$ sodium thiosulphate solution. In all cases the titre obtained for the the third bottle corresponded exactly to the amount of iodine present in it initially.

The procedure was standardised by using potassium O-ethyl xanthate and was found to be capable of giving a value within 5% of the theoretical amount of sulphur present.

Attempted preparation of potassium p-cresyl xanthate

p-Cresol (1 g.) was dissolved in dry dioxan (10 ml.) and redistilled triethylamine (2 ml.) and carbon disulphide (1 ml.) were added. A yellow colour was produced and the mixture refluxed for 2 hours.

The solvent was evaporated to give a dark orange oil. A sulphur estimation was carried out on this on this material

and a value of only 7·9% of the theoretical was obtained.

Thermodynamic instability of potassium p-cresyl xanthate

The U.V. spectrum of potassium O-ethyl xanthate was first measured in the usual way in ethanol and a peak at 305 mμ (4·25) found. The U.V. spectrum of potassium cresoxide in water was measured and a peak at 295 mμ (3·42) found.

Five drops of carbon disulphide were then added to the solution of potassium cresoxide to saturate it, and a new peak at 313 mμ (1·73) appeared in the U.V. This gradually disappeared as the solution was aspirated.

Aspiration of the solution of potassium O-ethyl xanthate produced no change in its U.V. spectrum.

Dithiobenzoic acid

An ethereal solution of this compound and also its lead salt (purple needles from toluene, m.p. 204-205°, 70%) were prepared by the method described in "Houben-Weyl" [172].

Thiobenzoyl chloride [173]

A mixture of dithiobenzoic acid (53 g.) in ether (50 ml.) and thionyl chloride (8 g.) was refluxed on the steam bath for 7 hours. The ether and unchanged thionyl chloride were distilled

off and then the apparatus set up for distillation under vacuum (0·2 mm.). The temperature was gradually raised to 240°, when the thiobenzoyl chloride began to distil. The product was redistilled to give a violet liquid b.p. 60-65°/0·2 mm., (57%). This preparation was found to be unreliable, polymerisation often taking place at 200-245° before any product had been obtained.

Thiobenzamide

This compound was prepared by the method of Staudinger and Siegmant [173] and obtained as orange prisms from cyclohexane, m.p. 96-97° (67%).

Benzhydryl thionbenzoate

This compound was prepared by the method of Smith [174, 175] and obtained as yellow needles from petroleum ether, m.p. 68-69° (59%)

Attempted preparation of the tosylate of dithiobenzoic acid [176]

Tosyl chloride (56 mg.) was dissolved in acetonitrile (20 ml.) and lead dithiobenzoate (513 mg.) added. The suspension was stirred for 2 hours at room temperature. After this time no dissolution of the lead salt had taken place, and accordingly,

DMF (30 ml.) was added. A clear dark red solution resulted. This was stirred at room temperature for a further 4 hours.

The solvent was removed under vacuum and the residue washed free from tosyl chloride with ether. There remained lead dithiobenzoate in almost quantitative recovery.

The above experiment was repeated using the same weights of starting materials in refluxing DMF for 3 hours. Again the lead salt was recovered unchanged.

Attempted preparation of the tosylate of dithiobenzoic acid

Dithiobenzoic acid (69 mg.)* in solution in ether was treated with tosyl chloride (85 mg.) and triethylamine (45·5 mg.). A white precipitate was produced. This was filtered off and the solution divided into two equal parts.

To one half of the above solution was added a solution of aniline (50 mg.) in ether (10 ml.) and the precipitate of thiobenzamide which was immediately formed, isolated and characterised as in an earlier experiment.

To the other half was added a solution of β-naphthol (64·5 mg.) in ether (10 ml.). After 90 minutes, the solvent was removed at room temperature and the I.R. spectrum of the product (a dark reddish gum) showed intense hydroxyl absorption.

* The solution of dithiobenzoic acid was obtained as

follows:- lead dithiobenzoate (900·5 mg.) was suspended in ether and dilute HCl solution added. The mixture was vigorously agitated until all the organic acid had been liberated. The ethereal layer was separated and made up to 140 ml. In the above experiment, 20 ml. of this solution were used.

Phenyl chlorothionformate

This compound was prepared by the method of Rivier [77] and obtained as a pale yellow liquid, b.p. 91°/10 mm., (66%).

Phenyl N-phenylthionurethan

This compound was prepared by the method of Rivier [77] and obtained as colourless needles from ethanol, m.p. 140-141° (76%).

Diphenyl xanthate

This compound was prepared by the method of Rivier [77] and obtained as golden yellow prisms from ethanol, m.p. 49-51° (69%).

Phenyl chlorodithioformate

This compound was prepared by the method of Rivier [78] and obtained as a pale orange liquid, b.p. 135°/15 mm., (75%).

Phenyl dithio-N-phenylurethan

This compound was prepared by the method of Rivier [78] and obtained as colourless prisms from ethanol, m.p. 116-117° (71%).

Diphenyl xanthate

This compound was prepared by the method of Rivier [78] and obtained as golden yellow prisms from ethanol, m.p. 48-50° (56%).

Irradiation of diphenyl xanthate

Diphenyl xanthate (123 mg.), dissolved in dry cyclohexane (125 ml.) was irradiated in the usual way in a pyrex flask for 3 hours.

The cyclohexane was extracted quickly with 2N NaOH solution, the basic layer acidified, extracted with chloroform and the chloroform solution washed with water and dried (Na_2SO_4). The solvent was removed giving a brown tar (2%).

The cyclohexane solution was dried (Na_2SO_4) and evaporated to give a light brown gum which after chromatography on alumina (grade 5 using 40-60° petrol as eluant) gave a non-crystalline yellow compound (76%) whose I.R. spectrum was superimposable on that of diphenyl xanthate.

The experiment was then repeated using a quartz flask. In this case, the yield of the phenolic material was 10% and that of unchanged starting material 25%.

Both the above experiments were repeated with the addition of benzophenone (1 mol.) to the reaction mixture. With the use of a pyrex flask the yield of phenolic material was 5% and that of unchanged starting material 67%, while with a quartz flask, the yield of phenolic material was 14% and that of unchanged starting material 20%.

Thiobenzoic acid

This compound was prepared by the method described in Organic Syntheses [79].

S-Benzoyl-O-phenyl xanthate [100]

Potassium thiobenzoate (176 mg.) dissolved in dry acetone (100 ml.) was gradually run into a solution of phenyl chlorothionformate (172 mg.) in dry acetone (50 ml.) at -45° over a period of about 30 minutes. The mixture was then allowed to react for a further 30 minutes, at the end of which time a deep yellow colour had developed.

The solution was gradually allowed to warm to room temperature and at about -15° it was observed that the yellow

colour was rapidly discharged to give a practically colourless solution.

Evaporation of the solvent at room temperature gave a mass of almost colourless needles, m.p. 64-65° (ex EtOH) (92%), $\nu_{max.}$ 1730 cm^{-1}. Mixed m.p. with authentic phenyl benzoate showed no depression and the I.R. spectrum of the two substances were superimposable.

This experiment was then repeated and as the colour began to fade at -15°, the solution was gently aspirated with dry nitrogen. The exit gases were passed into an ethereal solution of piperidine and a precipitate gradually formed. This precipitate was identified as its 1-dithiocarboxy derivative (m.p., mixed m.p. and I.R. spectrum). It was thus concluded that CS_2 had been evolved.

Irradiation of S-benzoyl-O-phenyl xanthate

S-Benzoyl-O-phenyl xanthate was prepared as described earlier from phenyl thiobenzoate and phenyl chlorothionformate (536 mg.) in acetone at -60°. The deep yellow solution was then irradiated at this temperature for 1 hour at the end of which time it was almost colourless.

The solution was allowed to warm to room temperature and evaporated. The residue was extracted with ether to separate

the organic material from potassium chloride and then the ethereal solution extracted with NaOH solution. The basic layer was acidified, extracted with ether, the ethereal solution washed with water, dried (Na_2SO_4) and the solvent evaporated to give a non-crystalline brown tar (114 mg.) which smelt strongly of thiobenzoic acid. The I.R. spectrum showed strong bands at 3600 cm^{-1}. and 3350 cm^{-1}., and a weaker band at 1660 cm^{-1}. indicating it to be a mixture of phenol and thiobenzoic acid.

The base insoluble fraction was dried (Na_2SO_4) and evaporated to give a pale yellow gum. Chromatography on alumina (grade 5) gave on elution with a 50% petroleum ether/benzene mixture, phenyl benzoate (383 mg., 78%) (m.p., mixed m.p. and I.R. comparison), and on elution with benzene alone gave dibenzoyl disulphide (3 mg., 7%) (m.p., mixed m.p. and I.R. comparison)

Dibenzoyl disulphide

This compound was prepared by the method described in Organic Syntheses [81] and obtained as prisms from ethanol, m.p. 128° (73%), $\nu_{max.}$ 1690 cm^{-1}.

S-Acetyl-O-phenyl xanthate [80]

Potassium thioacetate (192 mg.), dissolved in dry acetone (100 ml.), was gradually run into a solution of phenyl

chlorothionformate (172 mg.) in dry acetone (50 ml.) at -45° over a period of about 30minutes. The mixture was then allowed to react for a further 30 minutes, at the end of which time a deep yellow colour had developed.

The solution was gradually allowed to warm to room temperature and at about -25° it was observed that the yellow colour was rapidly lost to give a practically colourless solution.

The mixture was filtered to remove potassium chloride and evaporation of the solvent at room temperature gave a yellow gum whose I.R. spectrum showed absorptions at 1770 cm^{-1}., 1740 cm^{-1}., 1730 cm^{-1}., 1710 cm^{-1}. and 1690 cm^{-1}. The 1770 cm^{-1}. peak could reasonably be assigned to phenyl acetate and the 1730 cm^{-1}. peak to diacetyl disulphide. Further weight for this conclusion was acquired from an examination of the n.m.r. spectrum of the crude reaction product which showed a complex aromatic multiplet at about τ 2·8 and sharp singlets at τ 7·52 (diacetyl disulphide by comparison with an authentic specimen) and τ 7·78 (phenyl acetate by comparison with an authentic specimen).

Diacetyl disulphide [82]

Potassium thioacetate (700 mg.) was dissolved in water

(50 ml.) and an ethanolic solution of iodine added until a slight permanent brown colour persisted. The mixture was poured into a large volume of water and the product extracted with ether. The ether layer was washed with an aqueous solution of sodium thiosulphate, water and finally dried (Na_2SO_4). The solvent was removed to give a colourless gum which crystallised with difficulty and which on recrystallisation from aqueous ethanol gave needles, m.p. 20-21° (63%)

O-Ethyl S-phenyloxythiocarbonyl xanthate [80]

Potassium O-ethyl xanthate (333 mg.) dissolved in dry acetone (200 ml.) was gradually run into a solution of phenyl chlorothionformate (400 mg.) in dry acetone (100 ml.) at -45° over a period of about 30 minutes. The mixture was then allowed to react for a further 30 minutes, at the end of which time a deep yellow colour had developed.

The solution was gradually allowed to warm to room temperature and then the solvent evaporated at room temperature to give a deep yellow gum. This gum was extracted with boiling petroleum ether (40-60°) and afforded an almost colourless oil (insoluble) and a deep yellow solution. On trituration with ethanol, the colourless oil crystallised, and recrystallisation from the same solvent gave colourless needles, m.p. 106-107°

(23%). This was shown to be diphenyl thioncarbonate (m.p., mixed m.p. and I.R. spectrum)

Evaporation of the petrol fraction gave a yellow oil which failed to crystallise. Chromatography on alumina (grade 5 using petrol/benzene 9:1 as eluant) also failed to induce crystallisation.

Diphenyl thioncarbonate

This compound was prepared by the method of Rivier [177] and obtained as needles from ethanol, m.p. 106-107° (67%).

p-Cresyl chloroformate [185]

Dry benzene (500 ml.) was saturated with phosgene and a solution of p-cresol (50 g.) in benzene (100 ml.) and pyridine (40 ml.) gradually added. The mixture was allowed to stand for 30 minutes and then the solvent removed. The residual liquid was distilled under reduced pressure, the major fraction b.p. 46°/0·6 mm. being obtained in 61% yield, $\nu_{max.}$ 1780 cm^{-1}.

After distillation, there remained in the flask a solid which on recrystallisation from ethanol had m.p. 111-111·5° (21%). This was di-p-cresyl carbonate (lit. m.p. 112°) ν_{max} 1770 cm^{-1}.

Sodium O-ethyl xanthate

This compound was prepared as described in "Vogel" [84] and obtained as fine yellow needles from ethanol.

O-Ethyl S-p-cresyloxycarbonyl xanthate [180]

Sodium O-ethyl xanthate (0·337 g.) dissolved in dry acetone (25 ml.) was gradually added to p-cresyl chloroformate (0·4 g.) in dry acetone (25 ml.) at -30° with stirring. After 1 hour, the mixture was allowed to warm to room temperature the solvent removed *in vacuo*, water (50 ml.) added to the residue and the product extracted with methylene dichloride. The extract was washed with aqueous Na_2CO_3 solution (1%), and water and finally dried (Na_2SO_4). The solvent was removed at room temperature to yield a yellow gum (84%), $\nu_{max.}$ 1750 cm^{-1}, which could not be crystallised.

β-Naphthyl chloroformate

This compound was prepared by the method of Einhorn and Rothlauf [185] and obtained as prisms from petroleum ether, m.p. 65-66° (62%), $\nu_{max.}$ 1780 cm^{-1}.

O-Ethyl S-β-naphthyloxycarbonyl xanthate

Sodium O-ethyl xanthate (0·132 g.) dissolved in dry

acetone (25 ml.) was gradually added to β-naphthyl chloroformate (0·238 g.) in dry acetone (25 ml.) at -30° with stirring. After 1 hour, the mixture was allowed to warm to room temperature, the solvent removed in vacuo, water (50 ml.) added to the residue and the product extracted with methylene dichloride. The extract was washed with aqueous Na_2CO_3 solution (1%) and water and finally dried (Na_2SO_4). The solvent was removed at room temperature to give a yellow crystalline solid which on recrystallisation from petrol gave needles, m.p. 73-74° (87%), $\nu_{max.}$ 1750 cm^{-1}. (Found: C, 57·44; H, 4·41; S, 21·69. $C_{18}H_{12}O_3S_2$ requires: C, 57·50; H, 4·12; S, 21·90%)

This experiment was repeated at room temperature and a yellow gum was obtained which could not be crystallised. The I.R. spectrum showed intense bands at 1750 cm^{-1}. and 1700 cm^{-1}. presumably due to the phenyloxyformic thioanhydride and a much weaker band at 1770 cm^{-1}. presumably due to di-β-naphthyl carbonate.

Irradiation of O-ethyl S-β-naphthyloxycarbonyl xanthate

This compound was irradiated in a pyrex flask for 2 hours as already described for β-naphthyl trichloroacetate and β-naphthol obtained (24%).

β,β'-Dihydroxydinaphthylmethane

This compound was prepared by the method of Fries and Müber and obtained as needles from glacial acetic acid, m.p.196-198° (74%).

Attempted preparation of methylene-bis-β-naphthyl chloroformate [185]

Dry toluene (100 ml.) was saturated with phosgene and a solution of methylene-bis-β-naphthol (1·78 g.) in dry toluene (50 ml.) and quinoline (1·78 g.) gradually added with vigorous stirring. The mixture was allowed to react for 30 minutes and then the solvent removed. The solid residue obtained was ill-defined and attempts to recrystallise it from nonhydroxylic solvents failed. Its I.R. spectrum showed a strong but broad band at 1765 cm^{-1}. and a much weaker band at 1780 cm^{-1}. This experiment was repeated using a reaction time of 3 hours with an identical result.

Phosgenation of methylene-bis-β-naphthol using K_2CO_3 as base

Methylene-bis-β-naphthol (0·25 g.) was dissolved in dry toluene (100 ml.) in which was suspended anhydrous K_2CO_3 (1 g.). The mixture was refluxed for 5 hours with the continous passage of phosgene. Removal of the solvent gave a crystalline solid which on recrystallisation from benzene gave prisms, m.p. 235-235.5° (67%), $\nu_{max.}$ 1765 cm^{-1}. A molecular weight

determination by the freezing point method gave a value of 343·3.

(Found: C, 80·63; H, 4·23. $C_{22}H_{14}O_3$ requires: C, 80·97; H, 4·30%) Molecular weight by calculation 326.

This compound was thus concluded to be the cyclic carbonate, 2,8-dioxa-3,4,6,7-dinaphtho(2′,3′,2″,3″)octan-1-one.

Phosgenation of methylene-bis-β-naphthol

Dry benzene (75 ml.) was saturated with phosgene at its boiling point and then a steady stream of the gas continuously bubbled through. A solution of methylene-bis-β-naphthol (201·8 g.) and collidine (0·1735 ml.) in dry benzene (50 ml.) was gradually added. After the addition of the phenol/collidine mixture the reaction was allowed to proceed for a further 15 minutes.

The solution was filtered and evaporated to dryness on the steam bath. Chromatography of the product on alumina (grade 5 using 50% petrol/benzene as eluant) gave a white crystalline solid, m.p. 235-235·5° (ex benzene) (46%), and, using benzene as eluant, a yellow solid, m.p. 171-172° (ex ethanol) (24%).

On admixture with authentic 1-oxaspiro[4,5]-6,7-benzo-2,3-naphtho(2′,1′)-decan-8-en-10-one this material showed no

m.p. depression and further, the I.R. spectra of these compounds were superimposable.

The former compound on admixture with authentic 2,8-dioxa-3,4,6,7-dinaphtho(2',3',2'',3'')octan-1-one showed no m.p. depression, and the I.R. spectra of these compounds were also superimposable.

Oxidation of methylene-bis-β-naphthol

This compound was oxidised by the method of Pummerer and Cherbuliez [41] and the product obtained as yellow needles from ethanol, m.p. 171-172° (13%), $\nu_{max.}$ 1670 cm^{-1}.

Attempted preparation of phenyl esters of 2,4-dinitrobenzene sulphenic acid [87, 88]

Phenol (94 mg.) dissolved in dry carbon tetrachloride (100 ml.) was treated with 2,4-dinitrobenzenesulphenyl chloride (235 mg.) for 15 minutes at room temperature. After this time, the solvent was removed at room temperature to give a non-crystalline yellow residue. The I.R. spectrum showed strong bands at 3610 cm^{-1}, and 3520 cm^{-1}. This experiment was repeated with reaction times up to 6 hours with the same result. β-Naphthol also gave the same result.

In each case after the I.R. measurements had been taken,

the product was dissolved in ether and quickly extracted with dilute NaOH solution. After removal of the ether, the base insoluble residue was found to be non-crystalline, all attempts to induce crystallisation failing.

In a second series of experiments, pyridine (79 mg.) or triethylamine (101 mg.) were added to the reaction mixture, but the same results were again obtained.

In a third and final series, the solvent, either carbon tetrachloride or benzene, was refluxed but again the same result was obtained.

Benzyl 2,4-dinitrophenyl sulphide

2,4-Dinitrochlorobenzene (20·2 g.) dissolved in hot ethanol (100 ml.) was treated with benzyl mercaptan (12·4 g.). Dry triethylamine (10·1 g.) was now added and an immediate precipitation of a mixture of the benzyl 2,4-dinitrophenyl sulphide and triethylamine hydrochloride took place. This was filtered at the pump and then digested with cold water in order to remove the salt. The insoluble material was collected, dried and recrystallised from $CHCl_3$/petrol to give large yellow prisms, m.p. 128° (80°/$_o$).

2,4-Dinitrobenzenesulphenyl chloride

This compound was prepared by the method of Kharasch and Langford [89] and obtained as yellow needles from carbon tetrachloride, m.p. 95-96° (86%).

2,4-Dinitrobenzenesulphenyl acetate

This compound was prepared by the method of Putnam and Sharkey [90] and obtained as bright yellow needles, m.p. 89-90° dec. (86%), $\nu_{max.}$ 1780 cm^{-1}.

Methyl 2,4-dinitrobenzenesulphenate

This compound was prepared by the method of Perold and Snyman [91] and obtained as yellow needles from methanol, m.p. 124-125° (63%).

Irradiation of 2,4-dinitrobenzenesulphenyl acetate

2,4-Dinitrobenzenesulphenyl acetate (250 mg.) dissolved in dry benzene (125 ml.) was irradiated in the usual way in a pyrex flask. The outlet of the condenser was attached to two wash-bottles connected in series and each containing 0·1$\bar{N}$ NaOH solution (25 ml.). After 1 hour, the reaction was complete (as evidenced by the disappearance of the band at 1780 cm^{-1}.) giving a pale yellow solution and a dark brown precipitate. The

precipitate was filtered and freed from a small amount of admixed yellow material by dissolution in ethanol followed by filtration and subsequent reprecipitation with benzene, to give a dark brown amorphous powder (19%). The I.R. spectrum of this compound was found to be very similar to that of authentic 2-amino-4-nitrobenzenesulphonic acid. However, thin layer chromatography on silica gel plates (50/50 EtOH/EtOAc as solvent) showed the material obtained in the photolysis to be impure.

Confirmation that it did contain some 2-amino-4-nitrobenzenesulphonic acid was obtained by treatment with bromine in 50% sulphuric acid [57] when a flocculent precipitate identified as 2,4,6-tribromo-3-nitroaniline (m.p., mixed m.p. and superimposable I.R. spectra) was obtained.

Further, treatment of an authentic specimen of the acid with bromine in acetic acid at room temperature showed by back titration of the excess bromine in the usual way that 57% of the theoretical amount was consumed. The material obtained in the photolysis, however, consumed only 23% in an identical experiment.

Estimation of the total acid content by titration with 0·1$\bar{N}$ NaOH solution gave figures of 95% and 36% for the authentic and "photolytic" materials respectively.

The I.R. spectrum of the aforementioned yellow

precipitate (6%) was found to be superimposable on that of authentic 2,4,2',4'-tetranitrodiphenyl disulphide.

The pale yellow solution was extracted with 2N NaOH solution, heated briefly on the steam bath to free it from dissolved ether, acidified with sulphuric acid and finally steam distilled until about 200 ml. of the distillate had been obtained. This distillate was divided into two equal parts, and each part titrated with 0·1N NaOH solution using phenolphthalein as indicator. The combined titres (which were equal) were found to be equivalent to an 87% yield of acetic acid.

To the neutralised solution was added a few ml. of 4N NaOH solution and the whole concentrated to about 10 ml. A p-bromophenacyl ester was prepared in the usual way and found to have m.p. 84-86°, identical with that of p-bromophenacyl acetate (m.p. and mixed m.p.).

Titration of the NaOH solution through which the exit gases from the photolysis had passed, against 0·1N HCl solution showed that there had been no evolution of carbon dioxide.

Evaporation of the filtrate after separation of the 2-amino-4-nitrobenzenesulphonic acid gave a yellow solid which after chromatography on alumina (grade 3 using 50% petrol/benzene as eluant) followed by recrystallisation from ethanol/benzene gave bright yellow needles, m.p. 121-122° (73%). Its

I.R. spectrum was superimposable on that of authentic 2,4-dinitrodiphenyl sulphide and its n.m.r. spectrum showed a singlet (τ = 2·39, 5 protons), two doublets (τ = 3·04, J = 9, 1 proton and τ = 1·03, J = 2, 1 proton), and a quartet (τ = 1·94, J = 9, J = 2, 1 proton).

Another irradiation experiment performed in the presence of anisole gave identical results except that the compound isolated on evaporation of the filtrate after separation of 2-amino-4-nitrobenzenesulphonic acid was 2,4-dinitro-4'-methoxydiphenyl sulphide (m.p., mixed m.p.). The n.m.r. showed a singlet (τ = 6·05, 3 protons), two doublets (τ = 3·05, J = 9, 1 proton and τ = 1·02, J = 2·5, 1 proton), a double doublet (τ = 2·98, J = 9, τ = 2·51, J = 9, J = 28, 4 protons) and a quartet (τ = 1·90, J = 9, J = 2·5, 1 proton).

In another experiment in this series, the acetate was irradiated as above in benzene for one hour and then excess cyclohexylamine added. The mixture was gently warmed for 10 minutes after which time the acetic acid was isolated and estimated as above. It was obtained in 89% yield showing that it had been present originally as the free acid and not as a mixed carboxylic/sulphonic anhydride.

2,4-Dinitrodiphenyl sulphide [92]

2,4-Dinitrochlorobenzene (13·3 g.) was dissolved in hot ethanol (100 ml.) and thiophenol (7·25 ml.) added. Dilute NaOH solution (33 ml. of 2N) was now gradually added with vigorous stirring and a yellow precipitate thrown down. This was collected at the pump, washed with a little ethanol and then digested with cold water to remove the NaCl. The insoluble material was filtered off and recrystallised from an ethanol/benzene mixture to give bright yellow needles, m.p. 121-122° (84%).

p-Anisyl mercaptan

This compound was prepared according to the method of Suter and Hansen [203] and obtained as a colourless oil (67%).

2,4-Dinitro-4'-methoxydiphenyl sulphide

p-Anisyl mercaptan (3·84 g.) was dissolved in ethanol (50 ml.) and a solution of 2,4-dinitrochlorobenzene (5·55 g.) in ethanol (50 ml.) added. Dilute NaOH solution was now added dropwise with agitation until the solution became just alkaline, followed by 1 drop of dilute HCl solution.

The yellow precipitate was filtered and digested with cold water to remove the NaCl and then dried. Recrystallisation from benzene/ethanol gave needles, m.p. 116-117° (84%). (Found: C, 51·40; H, 3·38. $C_{13}H_{10}N_2O_5S$ requires: C, 50·98; H, 3·29%).

2,4,2',4'-Tetranitrodiphenyl disulphide

This compound was prepared by the method of Claasz [194, 195] and obtained as a bright yellow microcrystalline solid, m.p. 240-280° dec. in almost quantitative yield.

2,4-Dinitrodiphenyl sulphone

This compound was prepared by the method of Gilman and Broadbent [195] and obtained as colourless needles from ethanol/benzene, m.p. 157-158° (95%).

2-Amino-4-nitrobenzenesulphonic acid

This compound was prepared by the method of Kharasch et al. [196], and obtained as almost colourless needles (70%).

Action of bromine on sodium p-toluenesulphinate

Sodium p-toluenesulphinate (392·3 mg.) was dissolved in water (100 ml.) and an excess of a standard solution of bromine in acetic acid added. The mixture was allowed to stand for 10 minutes.

After this time, an excess of a standard I_2/KI solution was added and the excess iodine estimated by back titration with 0·1N $Na_2S_2O_3$ solution. The estimation showed that the oxidation of the sulphinate by bromine was quantitative.

A cognate experiment was carried out in which a dilute solution of bromine in acetic acid was added dropwise to a solution of sodium p-toluenesulphinate in water. Decolorisation took place immediately showing that the oxidation was instantaneous.

Irradiation of p-toluenesulphinic acid in the presence of m-dinitrobenzene

A solution of p-toluenesulphinic acid (372·8 mg.) and m-dinitrobenzene (400 mg.) in dry benzene (125 ml.) was irradiated for 90 minutes under standard conditions.

After this time, the solution was extracted with saturated $NaHCO_3$ solution, washed with water and dried (Na_2SO_4). Evaporation of the solvent followed by recrystallisation of the solid from ethanol gave m-dinitrobenzene (m.p., mixed m.p. and I.R. spectrum).

3,4-Dichloronitrobenzene

This compound was made by the method of Hodgson and Kershaw [99] and obtained as colourless needles, m.p. 45° (67%).

Attempted preparation of 2,2'-dichloro-4,4'-dinitrodiphenyl disulphide [99]

Crystalline sodium sulphide (8.27 g.) was dissolved in 95% ethanol (30 ml.) by gently warming, and finely powdered sulphur (1.14 g.) added. The heating was continued until all the sulphur had dissolved to give a brown/red solution of sodium disulphide.

This mixture was then gradually added to a solution of 3,4-dichloronitrobenzene (8.82 g.) in ethanol (20 ml.). A violent reaction set in. After the addition was complete, the whole was refluxed for 2 hours on the steam bath and then the product separated by filtration. It was washed with water to remove NaCl and then recrystallised from methanol to give needles, m.p. 176-177° (10%). (2,2'-Dichloro-4,4'-dinitrodiphenyl sulphide, m.p. 176-177°, mixed m.p. showed no depression.)
(Found: C, 41.75; H, 1.74. Calc. for $C_{12}H_6Cl_2N_2O_4S$: C, 41.86; H, 1.85%)

Benzyl 2-chloro-4-nitrophenyl sulphide

This compound was prepared by the method of Baker et al.[201], and obtained as yellow needles from ethanol, m.p. 110-111° (81%).

2-Chloro-4-nitrobenzenesulphenyl chloride

This compound was prepared by the method due to

Kharasch [199], and obtained as yellow needles which after recrystallisation from petrol had m.p. 77-82° (84%). Repeated recrystallisations failed to raise the melting point. The compound was thus estimated for active chlorine [202] and a figure of only 73% of the theoretical obtained.

Attempted preparation of 2-chloro-4-nitrobenzenesulphenyl acetate[190]

2-Chloro-4-nitrobenzenesulphenyl chloride (0.448 g.) was dissolved in dry methylene dichloride (10 ml.) and silver acetate (3.34 g.) added. The mixture was shaken in the dark for 18 hours.

The precipitate of silver salts was removed by filtration and found to contain a quantity of resinous matter. Evaporation of the solvent yielded a small amount (32 mg.) of yellow gum which possessed no carbonyl absorption in the I.R.

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