THE PHOTOLYSIS OF THIONØESTERS

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ABSTRACT

The preparation and photochemistry of the thionobenzoates of a range of alcohols is described. When the necessary structural requirements are met, a facile elimination of thiolbenzoic acid occurs leading to the formation of olefins. Evidence for the existence of a biradical intermediate is produced. Other thionobenzoates potentially capable of undergoing the photo-elimination reaction were prepared and their photochemistry examined.

ACKNOWLEDGEMENTS

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Whiffen Laboratory.

CONTENTS

REVIEW

The Nature of Excited States in the Carbonyl Group

A few of the fundamental concepts are as follows [1, 2]:
When light is absorbed by a chromophore, electronic transitions which involve a change in multiplicity are forbidden. Most organic molecules have singlet ground states (all electrons paired). Thus absorption of ultraviolet light results in singlet-singlet transitions. Electronic transitions are considered to be rapid with respect to frequency of vibration and thus should occur without change in molecular geometry (Franck-Condon principle). If the energy of the photon absorbed by the molecule is slightly in excess of that required to excite the molecule from the ground electronic state, S_0, to some upper excited singlet state, the excess energy will appear as vibrational excitation in the upper excited state. In solution, thermal equilibration of the excited molecule with its environment will be very rapid. Consequently, conversion of upper excited singlet states to the lowest excited singlet state, S_1, is quite rapid. Rate constants for this process are of the order of 10^{11} to 10^{13} sec^{-1}. This conversion is generally a non-radiative process. Conversion of the S_1 state to the ground state S_0 is somewhat slower. Typical fluorescence (emission of light from S_1 with return to S_0) rate constants for organic molecules are 10^7 to 10^8 sec^{-1}. This means that the lifetime of even the longest-lived lowest excited singlet state is very short. Inversion of spin in an excited state (intersystem-crossing) leads to the lowest energy triplet state, T_1. Intersystem-crossing rates are of the order 10^8 to 10^{10} sec^{-1}. Typical

phosphorescence (emission of light from T_1 with return to S_0) rate constants are 1 to 10^3 sec^{-1}. The lowest triplet state, T_1, thus has a lifetime greater than 10^{-3} sec, (lifetimes measured in seconds are known). The longer lifetime of the low-lying triplet is a consequence of the spin forbidden transition $T_1 \longrightarrow S_0$. Reactions of excited states in solution usually involve either the S_1 or T_1 states because of their longer lifetimes. The fact that T_1 states have a lifetime 10^4 or more times that of S_1 state strongly favours the T_1 state in intermolecular reactions.

The carbonyl chromophore in simple aliphatic aldehydes and ketones exhibits three bands: a weak band around 280nm., a more intense band around 190nm. and a still more intense band around 150nm.[3] Theoretical analysis of these electronic transitions have been made by many spectroscopists notably Kasha[4], Mulliken[5] and Sidman[6]. However, while a reasonably satisfactory treatment of the nature and energy of the lowest excited states is available, the status of more complex compounds is derived more from analogy with formaldehyde and from semi-empirical correlations.

Two molecular orbitals make up the carbonyl band: a σ-M.O. and a π-M.O. Two pairs of unshared electrons in the oxygen atom occupy n-orbitals: one of the two pairs is believed to be in an sp-hybrid orbital in which the electrons are firmly held, the other pair is in a 2p-orbital from which an electron may be easily excited.

The weak long-wavelength absorption band of simple aliphatic ketones and aldehydes is thought to be due to the forbidden n,π^* transition[4, 5]. The second absorption band is related to an allowed n,σ^* transition, while the third strong absorption band is due to an allowed π,π^* transition. Since the n,π^* state in general has the lowest energy it is therefore the photochemically active singlet and triplet state. In terms of M.O's., both S_1 (n, π^*) & T_1 (n,π^*) may be pictured as a system containing 2π electrons, one n electron and one π^* electron. A simple model which makes the same qualitative predictions as the M.O. description may be given in terms of the atomic orbitals on the carbon and oxygen on the carbonyl group[4, 7]. Both of these descriptions predict that the n,π^* state should be a "bipolar" species in the sense that the carbonyl oxygen is a radical-like electrophilic species which has its main electron deficiency as a half-vacant orbital in the plane of the carbonyl function. The carbonyl carbon atom, on the other hand, should behave as a radical-like nucleophilic species which derives its reactivity from the presence of three electrons in the pi-system which is located above and below the plane of the carbonyl function[8]. This is opposite direction to the dipole moment in the ground state and has been used to explain certain hydrogen-abstracting properties of various carbonyl compounds[7, 9, 10].

An increase in solvent polarity generally causes a blue shift in the n,π^* bands and a red shift in the π,π^* bands[11]. The reason for the shifts of the n,π^* bands is that hydrogen bonding with the unshared electron-pair lowers the ground-state energy in polar solvents, so that excitation requires additional energy

to overcome the hydrogen bond. For example in acetone the n,π* band is located at 265nm. in aqueous solution, while in hexane it is shifted to 279nm[12]. Other causes of shifts may be due to the formation of charge-transfer complexes or π-complexes between solute and solvent. In all cases the net effect is alteration in effective dipole moment of the solute[11].

Effect of Structure on Absorption Spectra of Aliphatic Aldehydes and Ketones

Replacing the aldehyde hydrogen on formaldehyde by alkyl groups causes the n, π* transition to shift to shorter wavelength (blue shift). For example, in the series formaldehyde, acetaldehyde and acetone the λ_{max} for the n, π* transitions is 354nm.[13], 339nm.[14], and 275nm.[15], respectively. The reason being that as mentioned above[8], the n, π* transition involves transfer of negative charge from the oxygen to the carbon atom; substituent groups that donate charge to the carbonyl carbon raise the energy of the antibonding π-orbital causing a blue shift. Owing to resonance interaction between π-electron system and substituent, the π,π* absorption is shifted to longer wavelengths. This is demonstrated by the π, π* absorption for the above series having λ_{max} at 156nm.[16], 165nm.[17, 18], and 188nm.[18]. Substitution of the aldehydic hydrogen by a group such as OH, NH_2, or Cl gives a shift to shorter wavelengths in the n, π* transition. These groups are more electronegative than carbon; and the lone pairs on the carbonyl oxygen are held more firmly than they would be in the absence of an inductive effect. The result is a lowering of the n level and thus a blue shift on going from acetaldehyde (λ_{max} = 339nm.)[14] to, e.g., acetyl chloride (λ_{max} = 240nm.)[19].

Effect of Structure on Absorption Spectra of Unsaturated and Aromatic Aldehydes and Ketones.

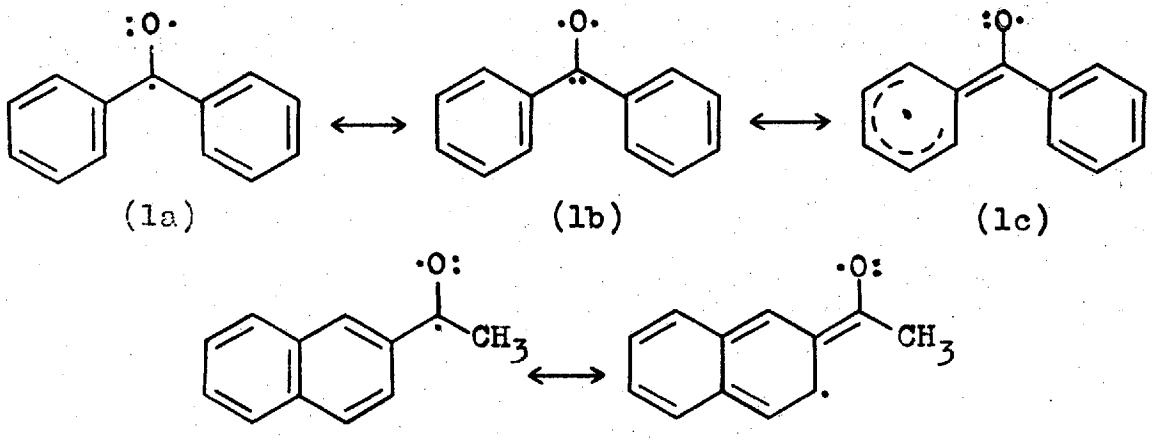
If the carbonyl bond is conjugated with a double bond or with a conjugated system, the n, π^* transitions will shift to longer wavelengths (red shift); e.g. the shift is 9.1nm. for the singlet -triplet transition and 32.2nm. for the singlet-singlet transition on going from formaldehyde to acrolein[13, 20, 21]. The π, π^* transition is also shifted to longer wavelengths but much more so than the n,π^*. This is because, as well as the π^* orbital being lowered in energy, the π orbital is raised in energy.

In general, the model for the n,π^* state alkyl aldehydes and ketones should suffice for the description of the photochemistry of aldehydes and ketones possessing lowest n,π^* states. We should expect that, although the primary processes should remain similar for aliphatic and aromatic carbonyl systems with lowest n,π^* states, the rate constants for these primary processes should vary with the nature of the aromatic moiety. However, if an excited state associated with the aromatic group is strongly "mixed" into lowest singlet or triplet of the carbonyl group, we expect the photochemistry typical of the n,π^* state to be modified or disappear entirely. For example, if a π,π^* aromatic state is lower in energy than the carbonyl n,π state, reactivity may be more like that of a π,π^* state of a carbonyl function because of interaction of the π, π^* aromatic and n,π^* carbonyl states.

For aryl ketones the energies of n,π^* and π, π^* configurations are much closer than for alkyl ketones so that the corresponding

S_1 or T_1 states may not be so clearly described in terms of either configurations. Indeed for certain substituted benzophenones and all naphthyl ketones and aldehydes, the lowest triplet is better classified as π,π^*. This implies that (a) the excited carbonyl oxygen is not as electron deficient as it is in the n,π^* state, (b) the excitation energy is delocalised into the system and may not be available to overcome activation energies for reaction at the carbonyl moiety and (c) primary processes involving the π-system may occur. For some aryl ketones possessing strong electron-releasing groups, a configuration which involves nearly complete transfer of an electron from the substituent to the carbonyl is required to describe the excited state. This has the effect of reducing the electrophilicity of the carbonyl oxygen in the excited state and making it nucleophilic. Such states are best described as charge transfer states.

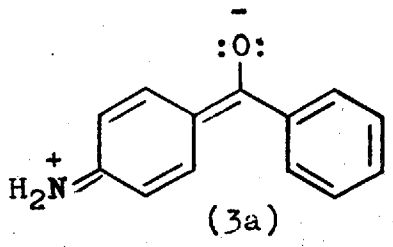
Only in the case of n,π^* states is the triplet excitation energy largely localised on the carbonyl group[22]. In figure 1, the three common types of T_1 states of aryl ketones are exemplified for benzophenone (1), 2-acetonaphthone (2), and 4-aminobenzophenone (3) in terms of major contributing structures.



(1a) (1b) (1c)

(2a) (2b)

Fig. 1.



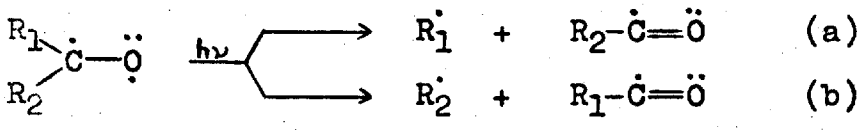
(3a)

Since alkyl ketones do not have the possibility of the π^* electron being delocalised into the ring (e.g. 1c), aryl ketones are somewhat less reactive for primary processes which involve attack by an electrophilic carbonyl oxygen in the n,π^* state. Also, ketones with lowest π,π^* states have some radical but little electrophilic character on oxygen and have a large contribution from structures such as 2b in which the π^* as well as the π electron and electronic excitation are delocalised into the ring. Further ketones with lowest CT. states are expected to have both new and different primary processes available (e.g. deprotonation as a strong acid) and low electrophilic (but possibly high nucleophilic) reactivity at carbonyl oxygen.

Primary Photochemical Processes of Ketones and Aldehydes

There are four general primary photochemical processes of the carbonyl group which are commonly encountered.

a) Cleavage of the bond α to the carbonyl function (Norrish Type I)[23, 24].



This reaction is frequently followed by elimination of carbon monoxide (in the vapour phase photolysis), but this reaction is almost entirely suppressed in solution at room temperature. This is probably due to the "cage" effect in which the newly-formed radicals are unable to separate because of the solvent cage which surrounds them. Consequently, recombination of radicals occurs faster than elimination of carbon monoxide. At elevated temperatures, in solution, the quantum yield of CO from acetone is still very small[25], but that of diethyl ketone is relatively large[26]. The difference is probably due to the greater stability of the acetyl versus the **propionyl** radical since the difference in quantum yields of CO also shows up in vapour-phase photolyses of these two compounds at 25°. The radicals present after the decarbonylation step may recombine, abstract hydrogen or undergo secondary fission to yield hydrocarbons and olefins. If R_1 and R_2 are different then both of the alternative processes of bond cleavage (a) and (b) can occur. However when R_2 is a reactive hydrogen atom (i.e. in aldehydes), the major mode of free radical decomposition in the first absorption band[23] is:

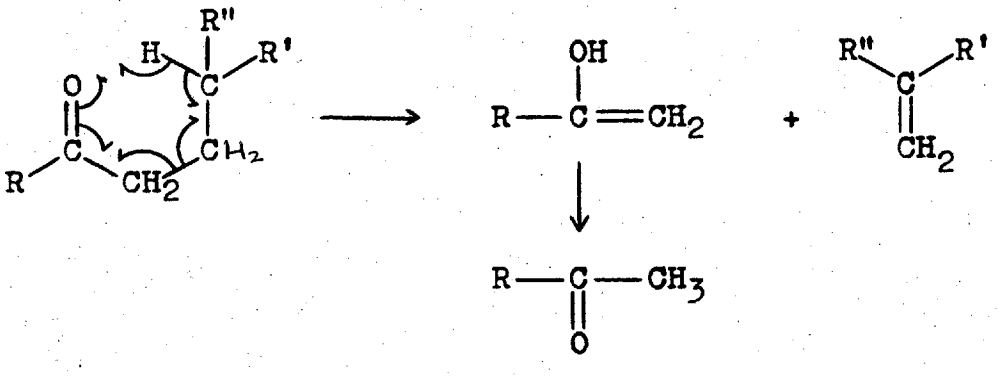
$$R.CHO \xrightarrow{h\nu} R^{\bullet} + {}^{\bullet}CHO$$

Photodissociation of acetaldehyde into $H^{\bullet} + {}^{\bullet}CH_3CO$ radicals has been only observed in flash photolysis[27], although it may be an important process at short wavelengths. It is however relevant to note that the aldehyde hydrogen is easily abstracted by radicals and hydrogen atoms producing $R\dot{C}O$ radicals in a secondary thermal reaction.

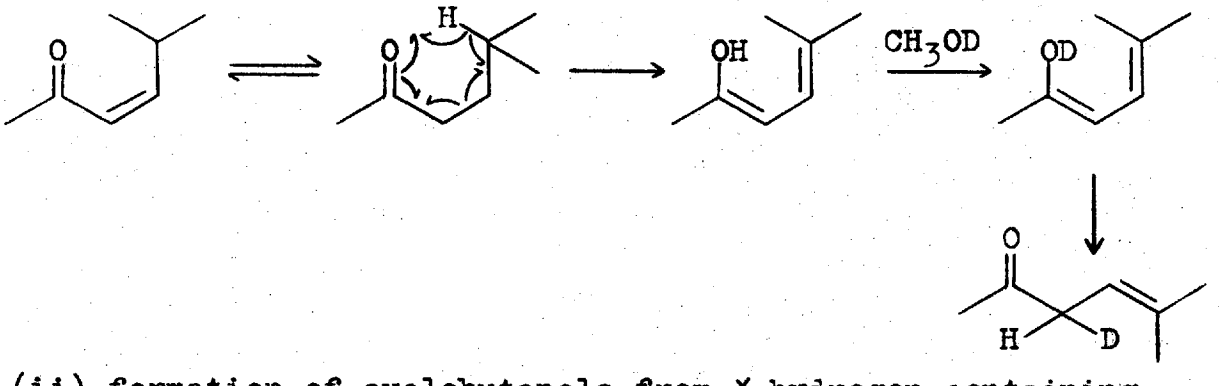
For ketones in which R_1 and R_2 are alkyl groups without a

γ-hydrogen atom, the free radical decomposition is the major process in the near ultra violet photolysis. This process becomes relatively less efficient when one of the alkyl groups contains a hydrogen atom on the γ-carbon and a type II process can occur.

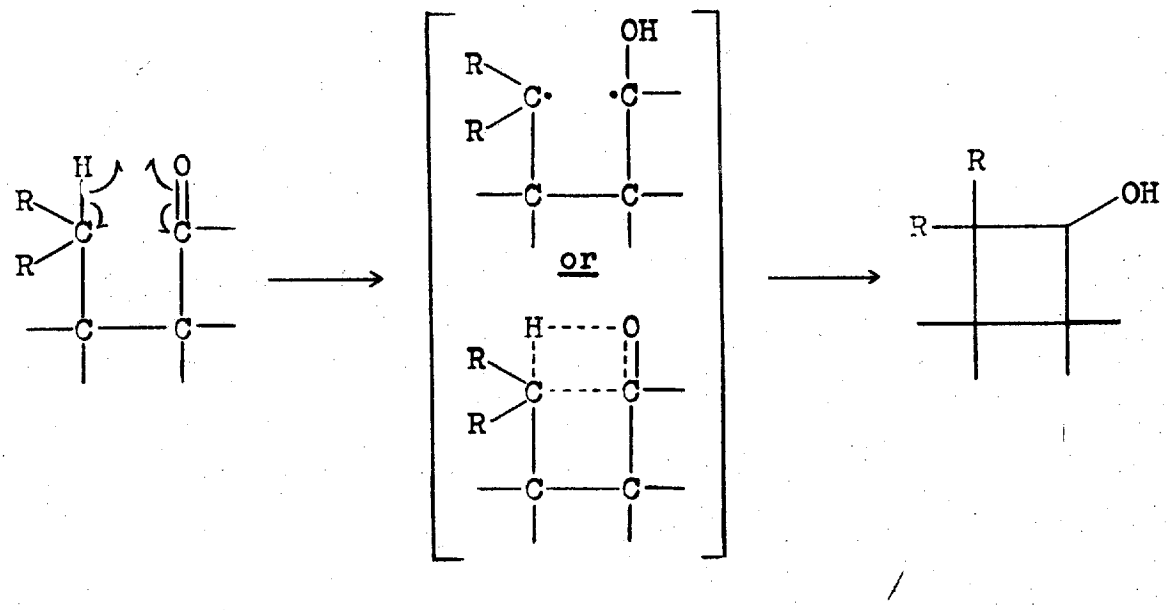
b) γ-hydrogen abstraction followed by elimination of an olefin (Norrish Type II)[28].



This reaction is a mode of intramolecular decomposition common to all aliphatic aldehydes and ketones having a γ-hydrogen atom on the alkyl chain which is transferred to the carbonyl group. In many cases studied, such transfer apparently occurs through a six membered transition state[29-33]. Variations of the type II process are (i) the bond migration of α,β-unsaturated ketones[34],



(ii) formation of cyclobutanols from γ-hydrogen-containing carbonyl derivatives[35, 36].



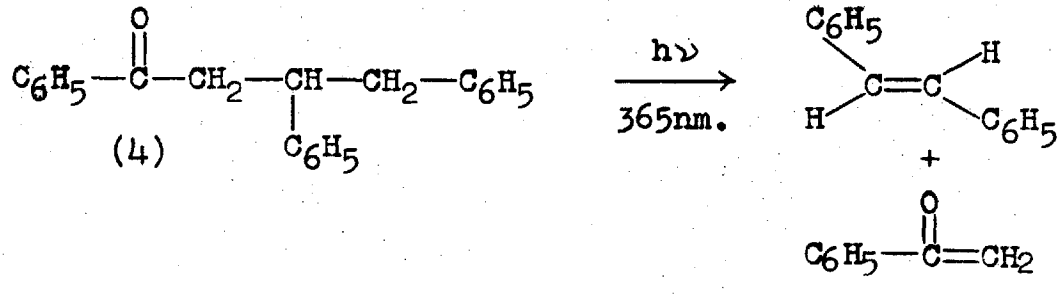
Either the intermediate is cyclic, or ring-closure occurs much faster than rotation about the single bond, which may be seen from the fact that the products derived from optically active ketones display partial retention of optical activity.

There seems to be some controversy in the literature as to the nature of the excited state involved in the type II process. Brunet and Noyes[37], from oxygen-quenching experiments, concluded that an excited triplet was not involved in the type II process. In addition, Michael and Noyes[38] observed that the addition of biacetyl quenches the type II split in the photolysis of methyl n-propyl ketone and suggested that both the energy-transfer process and the type II process occur via a singlet excited state of the ketone. On the other hand, Ausloos and Rebbert[39] report that at 313nm. type II process are quenched by the addition of biacetyl and that the light emitted by various ketone-biacetyl mixtures containing 1mm. of oxygen is identical with that emitted by pure ketone alone. Thus they conclude that the energy transfer process gives only triplet excited biacetyl and that consequently the type II process occurs via an excited triplet state. Their conclusion is further supported by the

study of the photolysis of ketone-aldehyde mixtures at 313nm. in which they show that the type II process of n-butyraldehyde is photosensitised by triplet acetone[40]. However, other workers[41-43] have shown that both singlet and triplet n,π* states undergo the type II elimination, since only part of the reaction can be quenched by conjugated dienes, which are very efficient triplet quenchers, but inefficient singlet quenchers. The percentage of singlet reaction depends on the strength of the γ-CH bond. Cyclobutanol formation from aliphatic ketones occurs mainly from the triplet state[41, 43], since significant decreases in the ratio of cyclisation to elimination products occur with increasing concentration of triplet quencher.

With aromatic ketones, where intersystem crossing quantum yields are generally unity, both reactions occur from the triplet state[44] as shown by the fact that pentadiene effectively quenches the photoelimination of γ-phenylbutyrophenone[45].

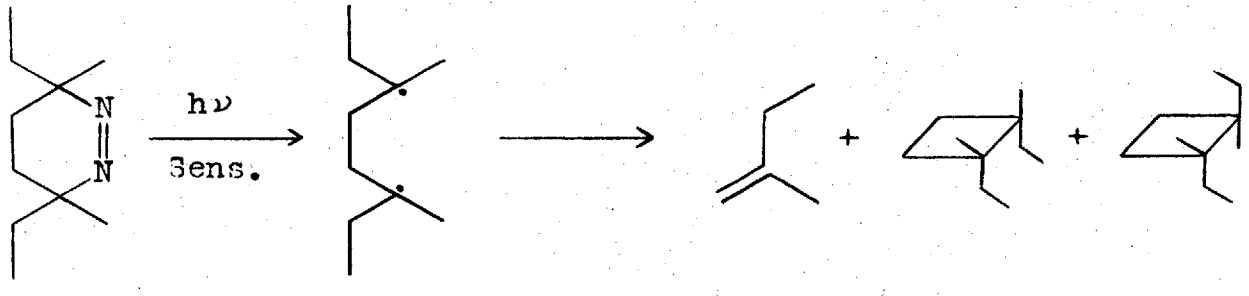
Since both cyclisation and elimination products are formed together, Yang[35], suggested a 1,4-biradical as the common intermediate, and there is now little doubt that triplet ketones do, in fact, undergo type II processes exclusively via 1,4-biradicals. There is evidence that the triplet state type II photoelimination proceeds via a biradical intermediate, even when energetically it could proceed concertedly. Irradiation of (4) at 365nm. yields stilbene which is 98-99% <u>trans</u>[46]:



The reaction to give stilbene and acetophenone enol is calculated to be at least 50k.cal./mole exothermic, so that the system must have sufficient energy for a concerted process. The concerted reaction cannot occur however since triplet stilbene should give rise to a 60:40 cis:trans mixture[47].

The actual lifetimes of even the longer-lived biradicals encountered in type II processes are not long enough to be trapped by tri-n-butyl tin hydride which would therefore put an upper limit of 10^{-7} sec. on the valerophenone-derived biradical.

Biradical lifetimes are particularly important when considering the stereospecificity of their reactions, since 1,4-biradicals are apparently not sufficiently long-lived to establish complete rotational equilibrium. Kinetic analysis of the results obtained by Bartlett and Porter[48] on the biradical obtained from meso or d,l (5) indicates that the singlet biradical reacts 30 times faster than the triplet biradical, with the latter reacting about half as fast as rotation about a 1,2-bond.



(5)

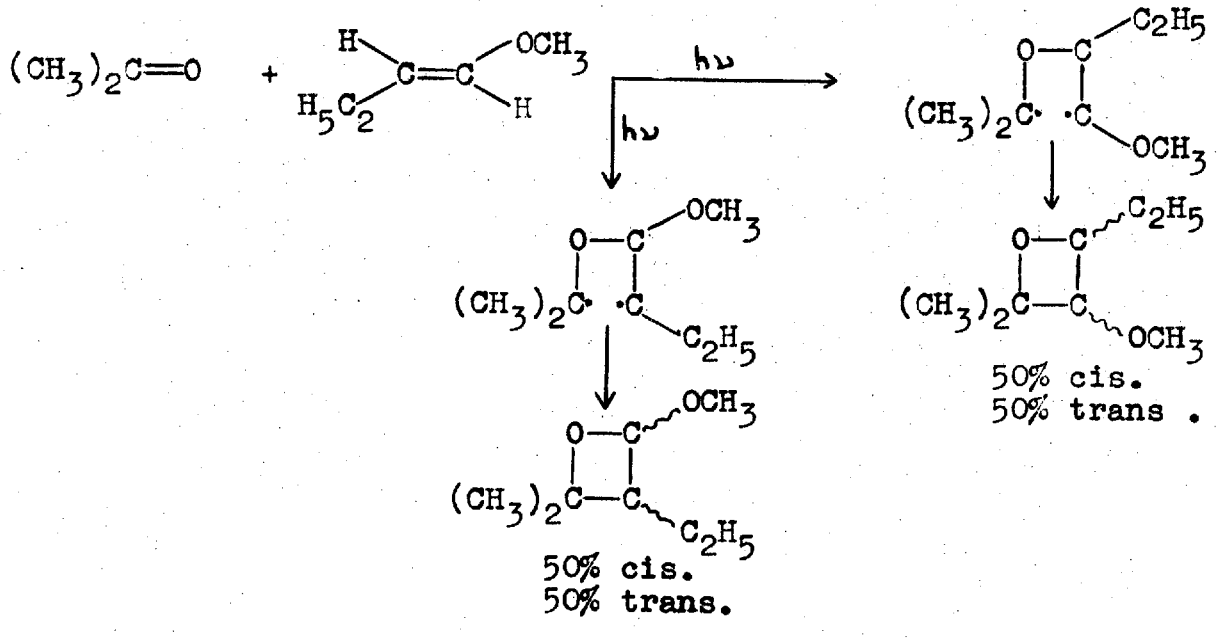
Hence, even though spin-spin interactions are expected to be small, the rate of spin inversion is still rate determining in reactions of the triplet generated biradical. Similar results exist for triplet biradicals involved in type II processes[49].

Ring and γ-substituents, whilst producing large changes in the percent disproportionation undergone by biradicals, do not affect the cyclisation: elimination ratio very much. α- and β-Substituents, on the other hand, do produce marked effects because of the steric factors which they introduce. Wagner[50] suggests that substituents could affect the ease with which the biradicals reach the necessary conformation for cleavage. Since efficient cleavage requires maximum p-orbital overlap of the developing double bond, the best conformation must be the one in which the p-orbitals of C_1 and C_4 are both parallel to the C_2-C_3 bond. Both α- and β-substituents alter the cyclisation: elimination ratio of acyclic ketones[51]. For example, α,α-dimethyl-valerophenone undergoes 80% cyclisation compared to 15% for unsubstituted valerophenone. In contrast, β,β-dimethyl-butyrophenone undergoes little, if any cyclisation. Models show that considerable 1,2-eclipsing interactions are present in the most likely conformation for cleavage which may explain the retarding effects of α-substituents. Likewise, development of 1,3-diaxial interactions during cyclisation may explain the retarding effect of β-substitution.

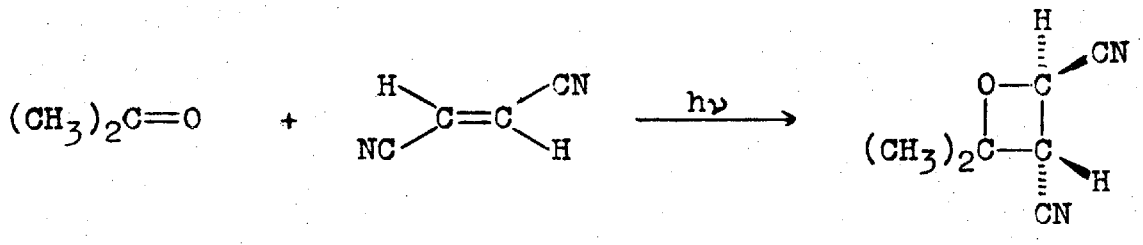
Electronegative groups at the α-carbon enhance the photoreactivity of carbonyl triplets. The results of Evans and Leermakers[52] show that α-ketodecanoic acid is 3-5 times more reactive than triplet 2-hexanone, and that triplet α-methoxybutyrophenone abstracts a γ-hydrogen from its propyl group six times more rapidly than triplet butyrophenone itself[53].

c) Addition to an Unsaturated Linkage.

Carbonyl compounds may form oxetanes on irradiation in the presence of olefins. The reaction was first reported by Paterno and Chieffi[54] and first studied mechanistically by Buchi[55] and is thus known as the Paterno-Buchi reaction[56]. The reaction is a general one for aliphatic and aromatic ketones and aldehydes but cyclic and unsaturated ketones apparently do not undergo a similar carbonyl addition. The orientation of the addition of alkyl aldehydes to olefin indicates that Markownikoff addition is preferred. No evidence is available to determine whether the addition step is a one step or a multistep process[57, 58]. At least two mechanisms appear to operate in the formation of oxetanes from alkyl ketones and ethylenes. For electron-rich ethylenes (polyalkyl olefins, enol ethers, etc.) attack by the n,π* ketone triplet apparently occurs and a biradical intermediate is produced which then collapses non stereospecifically to products[59]. Energy transfer to the ethylene usually competes with the cycloaddition process.



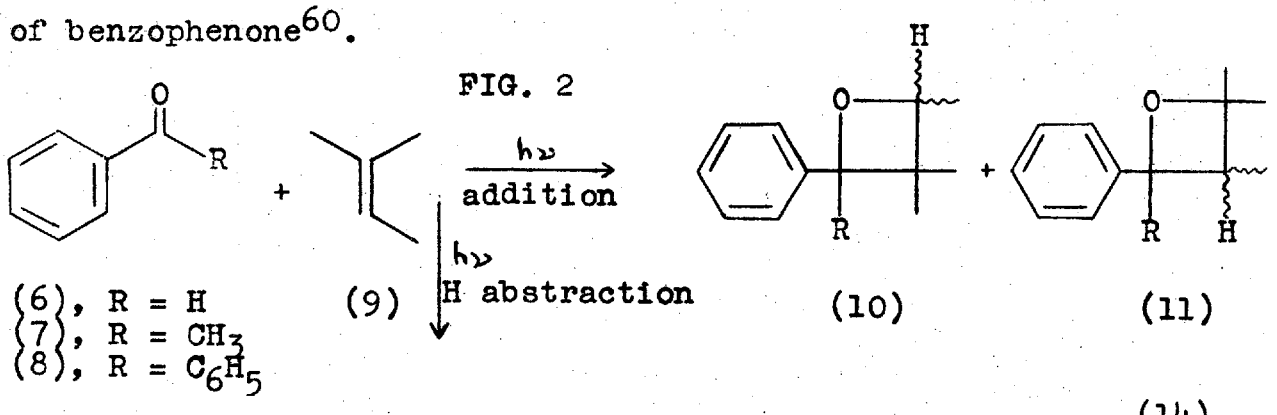
for electron deficient ethylenes (dicyanoethylenes, maleic anhydride, etc.) the n,π* singlet apparently reacts with the ethylene to yield the oxetane in a stereospecific process[53].



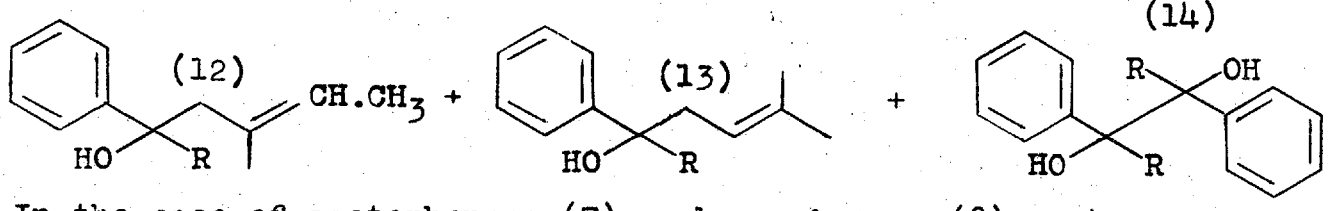
If the ethylene is not "sufficiently" electron poor, then only energy transfer to produce cis-trans isomerisation occurs.

The photocycloaddition of aryl aldehydes and ketones is qualitatively similar to alkyl aldehydes. The yield of oxetanes from the photocycloaddition of benzophenone and derivatives depends markedly on the structure of the olefin as well as the structure of benzophenone[60].

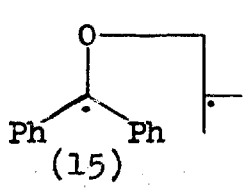
FIG. 2



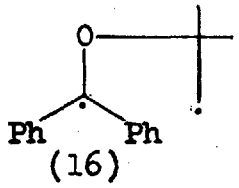
(6), R = H
(7), R = CH_3
(8), R = C_6H_5



In the case of acetophenone (7) or benzophenone (8), oxetane formation with (9) is more stereoselective[56] than with benzaldehyde (6), since more than 90% of the oxetanes belong to type (10) while, with (6), the ratio of (10):(11) is 1.6:1, with all four isomeric oxetanes being present. The stereoselective formation of (10) from (7) or (8) can be explained by considering the stability of the possible biradical intermediate.



(15)



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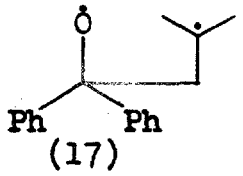

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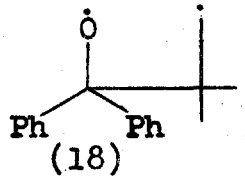
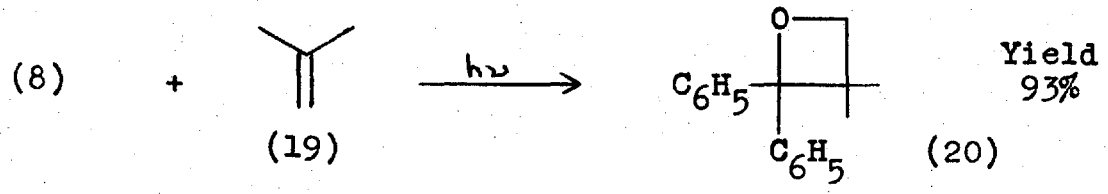


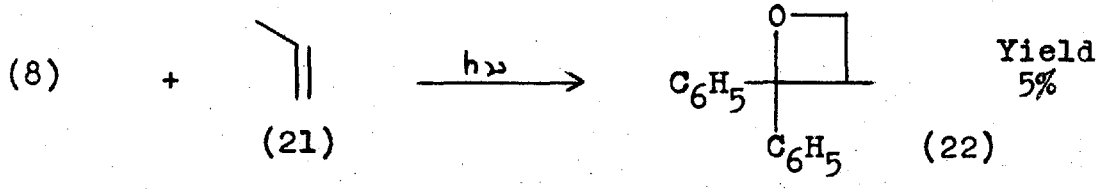
(18)

The most stable biradical should be (15) because of stabilisation of odd electron centres by the maximum number of phenyl and methyl groups. The next lowest energy biradical should be (16) while (17) and (18) should be of high energy since they involve alkoxy radicals.

The effect of structure of the olefin is illustrated by comparing the reaction of (8) with (19) to give (20) and of (8) with (21) to give (22)[60].



(19) (20)



(21) (22)

The results can be explained by assuming the triplet energy of the unreactive olefin is below that of the triplet of the carbonyl, and triplet-triplet energy transfer from the carbonyl group to the olefin takes place to the virtual exlusion of oxetane formation.[56].

Both 1- and 2-naphthaldehydes react with (9) to give the corresponding oxetane[56]. Although net quantum yield is low, good overall yields are possible because of the inertness of

these compounds to other photochemical reactions. Naphthyl aldehydes possess T_1 (π,π^*) states in general, and are therefore expected to be relativel inert to the normal photochemical reactions of the excited carbonyl function[61]. The efficient oxetane formation may be a reaction of S_1 (n,π^*) which is expected to be reactive but short lived, thus offering a possible explainations of the low quantum yield.

d) Intermolecular Hydrogen Abstraction or Photoreduction.

The ability of a photoexcited ketone or aldehyde to abstract a hydrogen atom from good hydrogen donors in the solution phase has been well known for many years[62].

$$R_2C{=}O \xrightarrow[\text{H donor}]{h\nu} R\dot{C}_2{-}OH$$

Hydrogen abstraction by benzophenone and its derivatives is one of the most extensively studied primary photochemcial reactions[63-68]. Benzophenone will abstract a hydrogen from nearly any molecule containing a C-H bond, including benzene[66], although the rate of abstractions varies widely dependant on the particular molecule. The O-H bond is more resistant to abstraction but N-H, Sn-H and S-H bonds are quite reactive. Factors which tend to weaken a C-H bond, or make it more nucleophilic, facilitate the reaction. The reactive species is again the n,π^* triplet state[66] and, although S_1 may also be reactive, its short lifetime precludes efficient hydrogen abstraction. The reaction of benzophenone with alcohols generally results in formation of benzpinacol.

$$(C_6H_5)_2.C{=}O \xrightarrow[R_2CHOH]{h\nu} (C_6H_5)_2.\dot{C}OH \xrightarrow{(C_6H_5)_2.COH}$$

$\longrightarrow (C_6H_5)_2.COH.COH.(C_6H_5)_2$

Hydrogen abstraction is often a competing process in other photochemical reactions. For example, in the previous section, compounds (12), (13) and (14) are derived from allylic hydrogen abstraction by excited benzaldehyde molecules followed by combination of the α-hydroxybenzyl radical and the allylic radical or dimerisation of the α-hydroxybenzyl radicals.

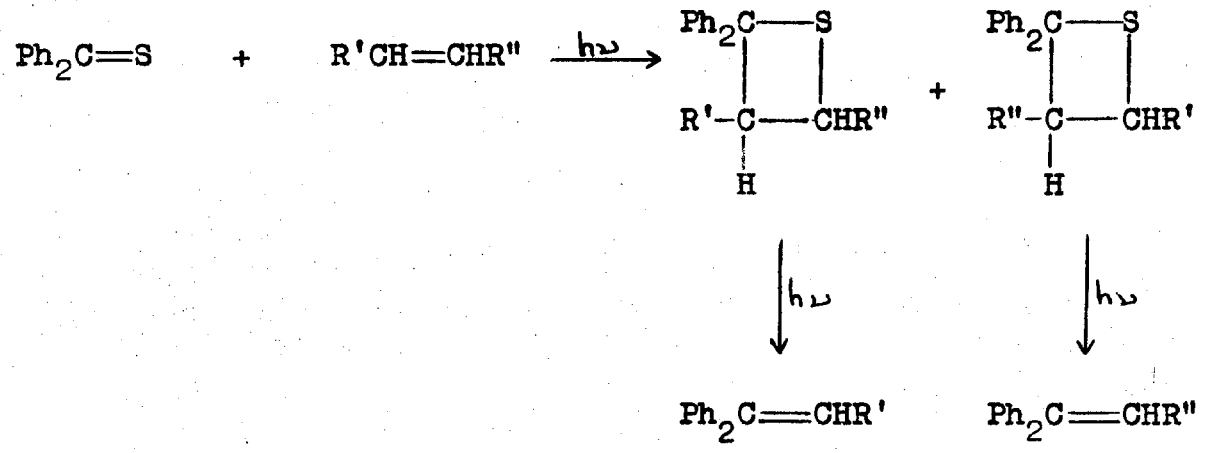
Compounds such as 1-naphthaldehyde and p-aminobenzophenone have lowest π,π* triplets and those such as o-hydronybenzophenone photoenolize and thus do not abstract hydrogen.

Thioketones

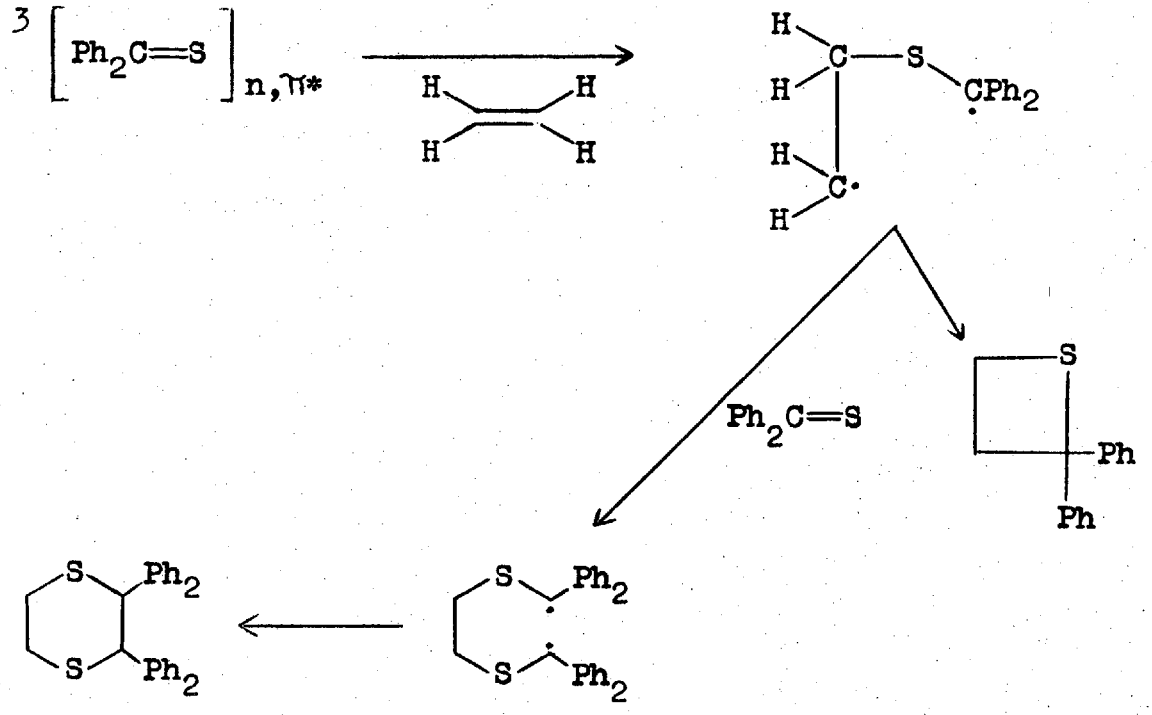
Reported photochemical reactions of thioketones are relatively few and the majority have been concerned with thiobenzophenone.

The difference in chemistry of carbonyl and thiocarbonyl compounds may be attributed to differences between 2p-2p and 3p-2p π-bonding and the importance of resonance forms such as $\overset{+}{C}-\overset{-}{S}$ and $\dot{C}-\dot{S}$ for the thiocarbonyl group. It appears that the triplet state is n,π* but the energy (E_3~40) is rather low due to an n,π* excitation of sulphur which involves a 3p rather than a 2p electron on oxygen.

Irradiation of thiobenzophenone in the presence of olefins leads to cycloaddition elimination to form 1,1-diphenylalkenes[69] in good yield and, in the case of terminal olefins, in roughly equal amounts.



Ohno et al.[70-73] have published several papers on the photocycloaddition of thiobenzophenone to styrenes to give either 1,4 dithianes or thietanes depending on the substitution pattern of the styrene.



The key factor in determining the path taken is believed to be the steric hindrance to the addition of the second molecule of thiobenzophenone. When thiobenzophenone is irradiated with electron deficient olefins, such as acrylonitrile, no photocycloaddition reaction occurs from the n,π* state[74].

However, when the π,π^* band is irradiated, thietanes are formed in good yield.

Oster et al.[75] have shown that irradiation of thiobenzophenone in ethanol in the presence of oxygen yields benzophenone whereas irradiation in a helium atmosphere, in the presence of a hydrogen donor solvent gave dibenzhydryl disulphide, benzhydryl mercaptan and a tetrasulphide.

$$Ph_2C{=}S \xrightarrow[\substack{EtOH\\Helium}]{h\nu} Ph_2CHSH + Ph_2CH\text{-}S\text{-}S\text{-}CHPh_2 + (Ph_2CH\text{-}S\text{-}S\text{-})_2CPh_2$$

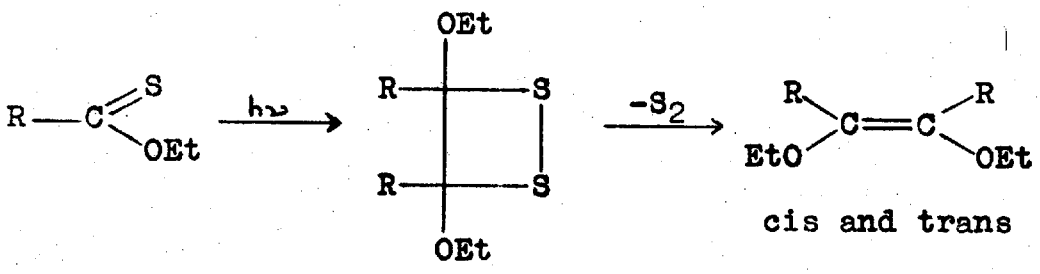
This is in contrast to benzophenone which under similar conditions is converted into benzpinacol. The intermediate radicals in the two cases must therefore differ.

$$Ph_2C{=}O \xrightarrow[H\ donor]{h\nu} Ph_2\dot{C}OH \xrightarrow{coupling} Ph_2COH.COHPh_2$$

$$Ph_2C{=}S \xrightarrow[H\ donor]{h\nu} Ph_2CHS\cdot \begin{cases} \xrightarrow{coupling} Ph_2CH.S.S.CHPh_2 \\ \xrightarrow{H\ donor} Ph_2CHSH \end{cases}$$

Reduction may involve hydrogen abstraction by the T_1 (n,π^*) state by analogy with benzophenone. The abstraction step may involve the thiocarbonyl carbon.

To date, published work on the photochemistry of thionoesters is due to Schmidt et al.[76, 77] who have photolysed alkyl thionoesters in the absence of solvent to yield olefins. The 1,2 dithiacyclobutane is suggested as an intermediate in the photolysis.



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DISCUSSION

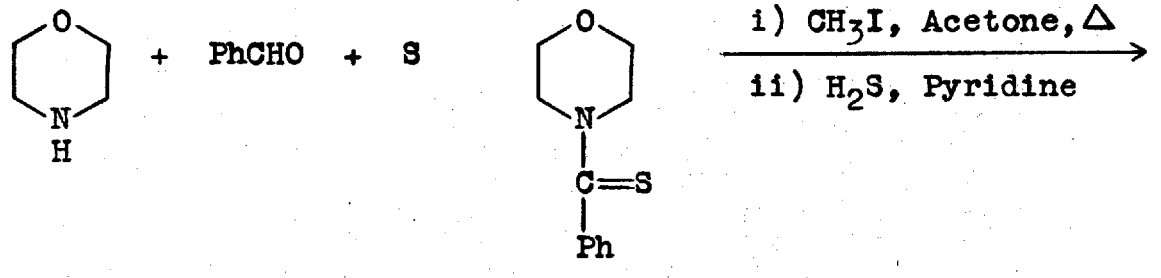
Preparation of thionoesters

Thionoesters may be prepared in a variety of ways. A brief outline, together with the limitations of each method, is described below.

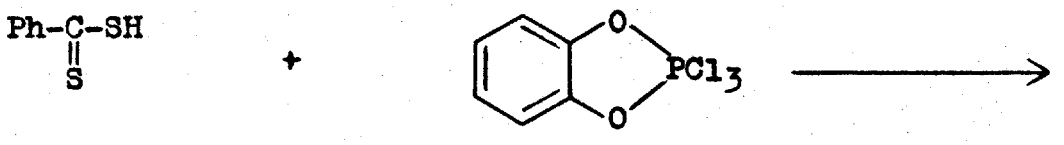
i) The action of thionoacyl chlorides on alcohols.

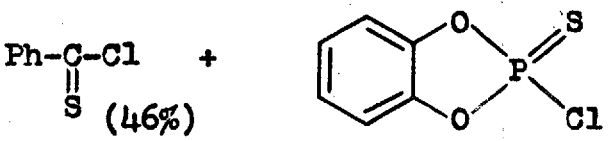
Several thionoacyl chlorides have been described in the literature. These have usually been prepared by treating the dithioacid with thionyl chloride[6] or pyrocatechyl phosphorus trichloride[7].

a) $\underset{\text{or } PhLi}{PhMgBr} + CS_2 \longrightarrow Ph\text{-}\underset{\underset{S}{\|}}{C}\text{-}SH \xrightarrow{SOCl_2} Ph\text{-}\underset{\underset{S}{\|}}{C}\text{-}Cl$ (65-80%)

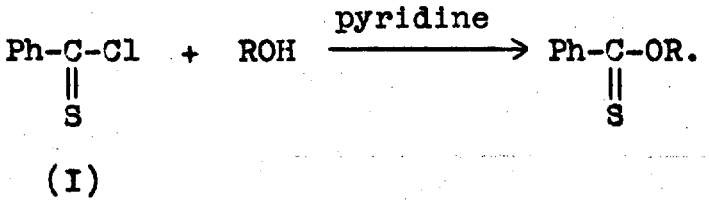
b) 

$Ph\text{-}\underset{\underset{S}{\|}}{C}\text{-}SCH_3 \xrightarrow{NaSH} Ph\text{-}C\text{-}SH \xrightarrow{SOCl_2} Ph\text{-}\underset{\underset{S}{\|}}{C}\text{-}Cl$ (55%)

c) 



There are many examples of the alcoholysis of aromatic thionoacyl chlorides to thionoesters[6, 8, 9]. The alcohol in pyridine or, as its sodium salt, in benzene is treated with thionoacyl chloride to yield the thionoester. Yields of ester are good, assuming that appropriate precautions are taken to exclude light.



(I)

The method is limited by the difficulty experienced in the preparation of thioacyl chlorides from dithioacids. The yields are often low and the compounds are difficult to obtain in a high degree of purity. Thiobenzoyl chloride (I) should be stored in the dark at low temperature. With two exceptions[2, 10], no aliphatic thionoacyl chlorides have been reported, a fact that must be due to the instability of such compounds under the preparative conditions[11].

ii) The sulphydrolysis of imino esters.

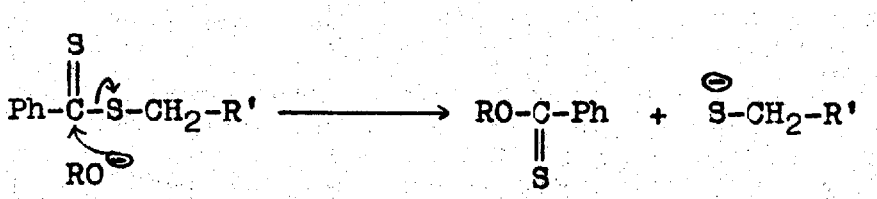
Imino esters are readily available by treating an alcohol and a nitrile with dry hydrogen chloride gas in a suitable inert solvent such as ether[12]. The imino esters on treatment with hydrogen sulphide give the corresponding thionoester[11 - 16].

$$ROH + R'CN \xrightarrow[\text{pyridine}]{\text{dry HCl,}} RO\text{-}C(=NH_2Cl)\text{-}R' \xrightarrow[\text{pyridine}]{H_2S,} RO\text{-}C(=S)\text{-}R'$$

This method has by far the widest scope of the published methods because of the ready availability of the starting materials. It is limited by the acid-sensitivity of the alcohol. Aliphatic thionoesters can also be made by this method. The yields are normally good, but water must be rigorously excluded to prevent hydrolysis of the imino ester.

iii) Alkoxide displacements on thioacylthioglycollic acids.

Thiobenzoylthioglycollic acid (IIa)[17] has been known in the literature for some time but its use has been confined almost exclusively to the preparation of thionobenzoates of compounds containing the amino function[18, 19]. It occurred to us that treatment of this compound with an alkoxide should give the corresponding thionobenzoate.



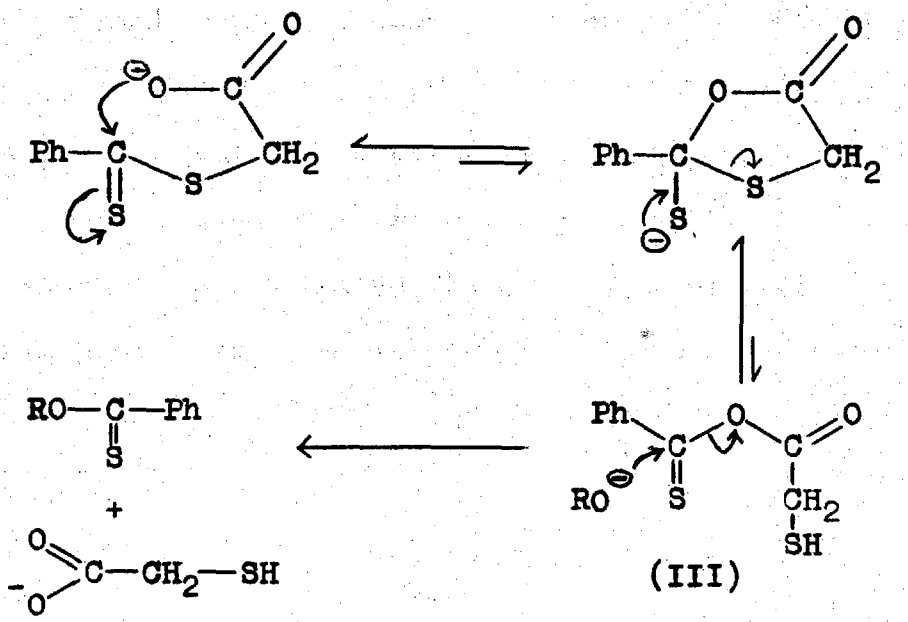
(II) a, R = COOH.

b, R = COOEt.

c, R = $CONH_2$.

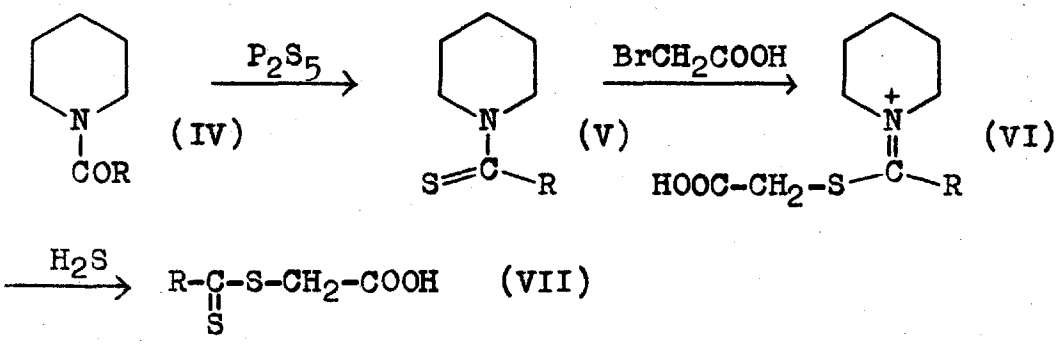
With (IIa), the displacement was found to be very rapid and with simple alcohols yields were in excess of 90%. Initially, sterols and some diols presented problems in that yields were only of the order of 50%, but, by

slightly modifying the procedure, viz., adding imidazole, yields were significantly improved to 70 - 80%. The reason for the improvement in yield was thought to be that sodium imidazole gave more efficient formation of the alkoxide than did sodium hydride. As previously mentioned, the displacement reaction on (IIa) was extremely rapid and this we felt surprising with such a system. The ethyl ester (IIb), and the amide (IIc) were expected to displace even more rapidly. However, experiments showed that (IIb) reacted more slowly, and (IIc) did not react at all. It was thought then perhaps that the sodium salt of (IIa) was undergoing an intramolecular rearrangement to give a small equilibrium concentration of the mixed anhydride(III).



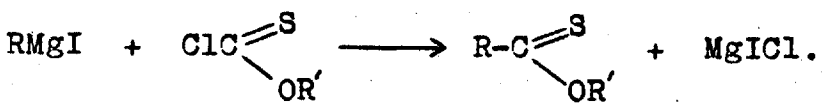
The anhydride (III) would be expected to undergo a rapid displacement with alkoxide to give the thionobenzoate and thioglycollic acid.

The acid (IIa) is readily available by condensing sodium dithiobenzoate with sodium monochloroacetate[19] and is obtained as a red crystalline solid which is indefinitely stable. When the required dithioacid is not readily available, another method can be used for the preparation of the thioacyl thioglycollic acids[20]. Treatment of the acyl piperidide (IV) with phosphorus pentasulphide gives the thioacyl piperidide (V) which with bromoacetic acid gives the imino ester (VI). Reaction of the latter with hydrogen sulphide gives the thioacylthioglycollic acid.



iv) Reaction of Grignard reagents on chlorothionoformates[13,21-23].

Chlorothionoformates are made by the reaction of alcohols with excess thiophosgene[24]. Reaction of these with Grignard reagents gives thionoesters in poor yield.



v) From ortho-esters.

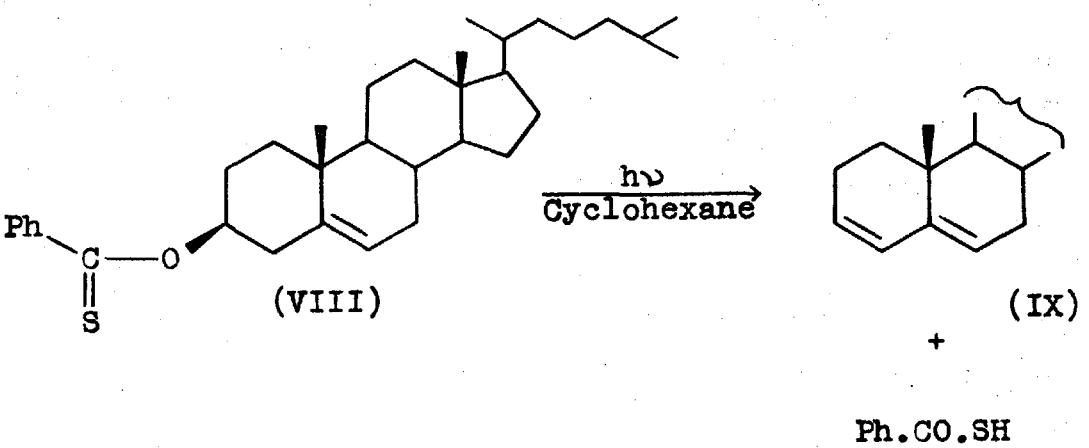
Preparation of thionoester from ortho esters may be achieved by treatment with boron trisulphide[25] or with H_2S in the presence of a Lewis acid catalyst[26].

$$R'\text{-}C\text{-}(OR)_3 \xrightarrow[ZnCl_2/H_2S]{B_2S_3 \text{ or}} R'\text{-}\underset{\underset{S}{\|}}{C}\text{-}OR.$$

In our hands, the most suitable methods were those of (i) - (iii) with the greater emphasis on method (ii)

The photolysis of steroidal thionobenzoates

Cholesteryl thionobenzoate (VIII), prepared by method (i) or (iii), was found, on irradiation in cyclohexane using pyrex-filtered light from a medium pressure mercury lamp, to rapidly eliminate thiolbenzoic acid to give cholesta-3,5-diene (IX) in very high yield. The thiolbenzoic acid, after oxidation with hydrogen peroxide, was isolated and identified as dibenzoyl disulphide.

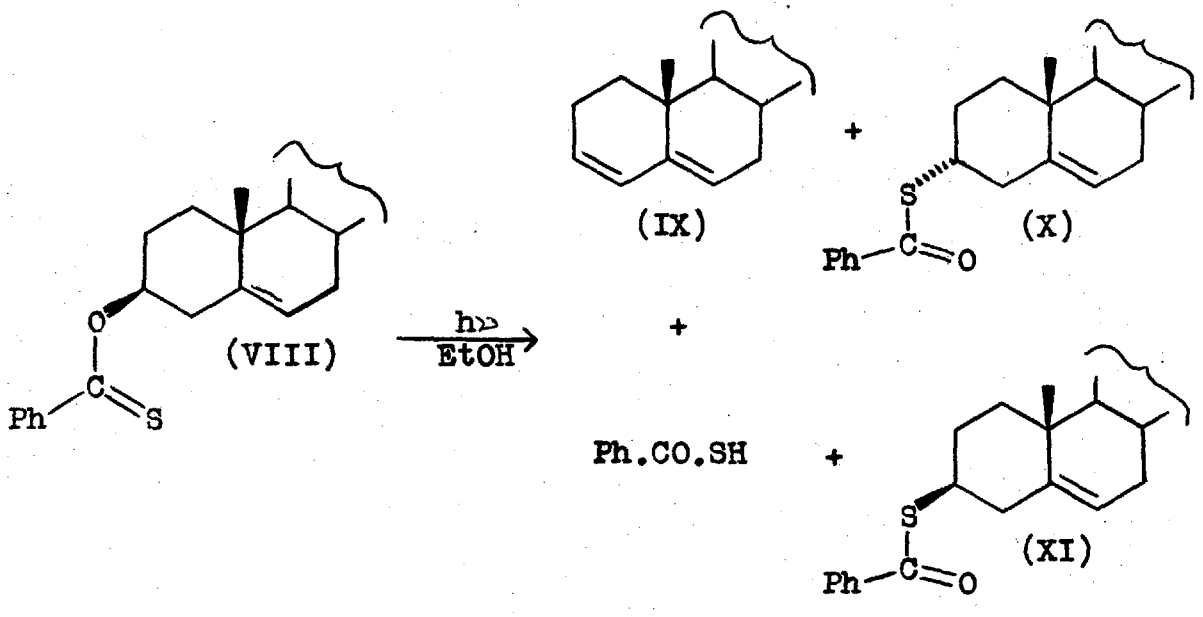


(VIII) (IX)

+

Ph.CO.SH

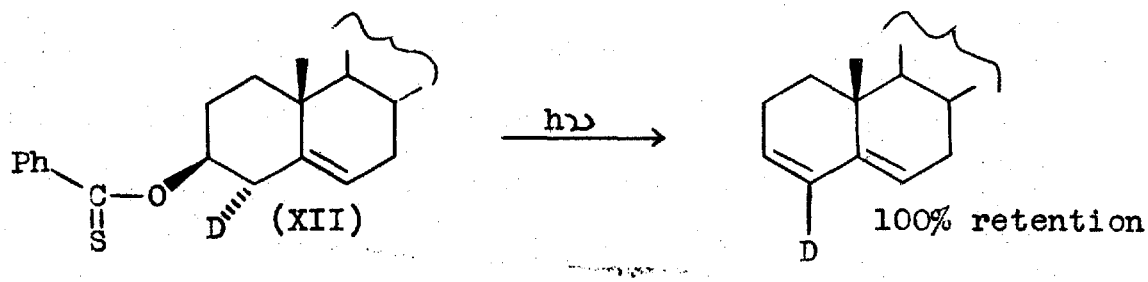
If irradiation was continued after elimination was complete, the thiolbenzoic acid added on to the newly-generated diene system. This could be prevented by addition of triethylamine to the system. When the photolysis was carried out in alcohol solvent, readdition took place much more quickly. From the reaction mixture, cholesteryl 3α- and 3β-thiolbenzoates (X) and (XI) could be isolated as well as the expected diene (IX) and thiolbenzoic acid.



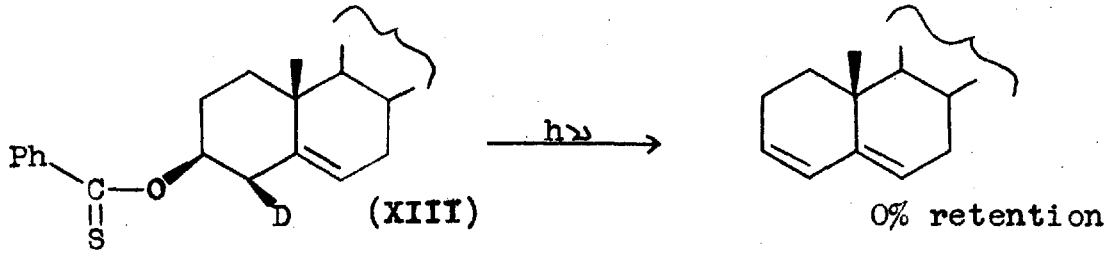
The structure of (XI) was confirmed by preparing an authentic sample by displacement of cholest-5-ene-3β-ol tosylate with potassium thiolbenzoate in acetone[27], and from its n.m.r. spectrum which showed a characteristic peak at τ6.50 $W_{\frac{1}{2}}$ = 22c/s. The structure of (X) also followed from its n.m.r. spectrum, which showed a peak at τ6.11 $W_{\frac{1}{2}}$ = 8c/s., and comparison of its physical constants with those reported in the literature[27]. It was shown that (X) and (XI) were

obtained from a secondary reaction of attack of the thiolacid on the diene by photolysing a mixture of thiolbenzoic acid and (IX) in ethanol. A mixture of all possible isomers was obtained. Mass spectral analysis of the mixture showed M^+ at 506, with no higher masses, thereby showing that they were all mono addition products. T.l.c. examination showed the same product distribution as was obtained from the photolysis of (VII) in ethanol.

Another worker[28] in this laboratory showed that the elimination of thiolacid from (VIII) occured in a stereospecific manner. The compounds 4α-deutero-cholesteryl thionobenzoate (XII) and 4β-deutero-cholesteryl thionobenzoate (XIII) were each photolysed in turn. The former compound showed complete retention of deuterium whereas the latter showed no retention of deuterium.

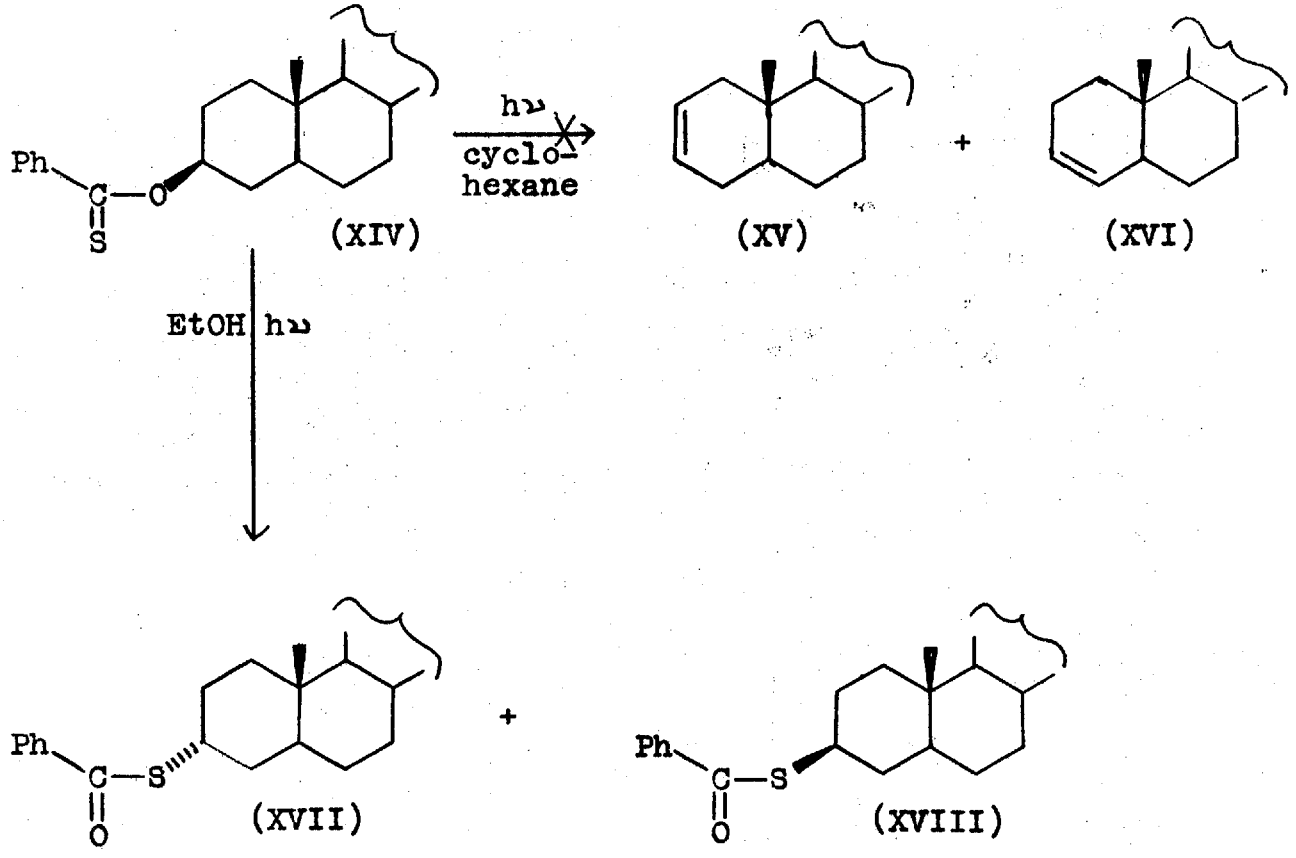


(XII)



(XIII)

Since cholest-5-ene-3β-ol thionobenzoate underwent such a facile elimination on photolysis, the saturated analogue, cholestan-3β-ol thionobenzoate (XIV) was prepared by methods (i) and (iii). By analogy with the photolysis of (VIII), irradiation of (XIV) was expected to yield perhaps a mixture of cholest-2-ene (XV) and cholest-3-ene (XVI).

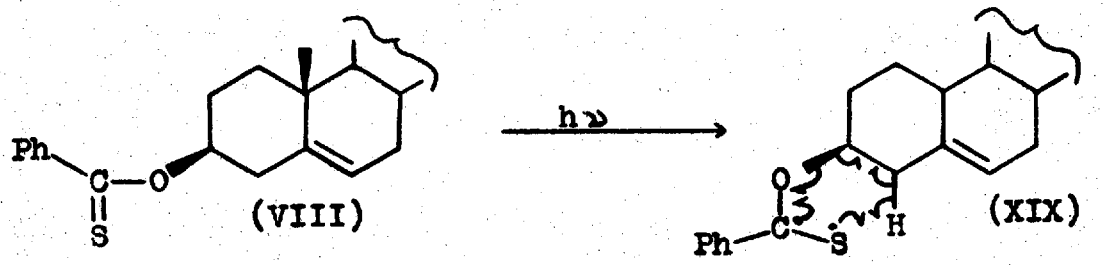


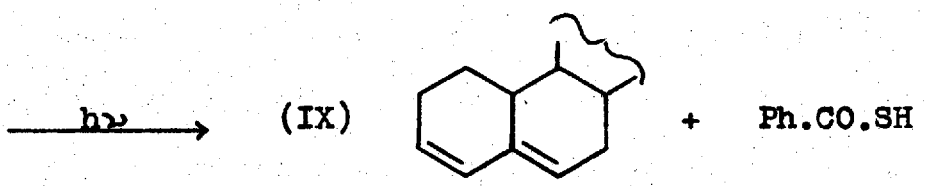
However, on irradiation of (XIV) in cyclohexane, the reaction proceeded about 70 times slower than (VIII) and gave rise to a complex mixture of products in which neither (XV) nor (XVI) could be detected. When the photolysis of (XIV) was carried out in the presence of triethylamine, no triethylamine thiolbenzoate could be isolated.

If the photolysis of (XIV) was carried out in ethanol, a mixture of (XVII) and (XVIII) could be isolated in low yield.

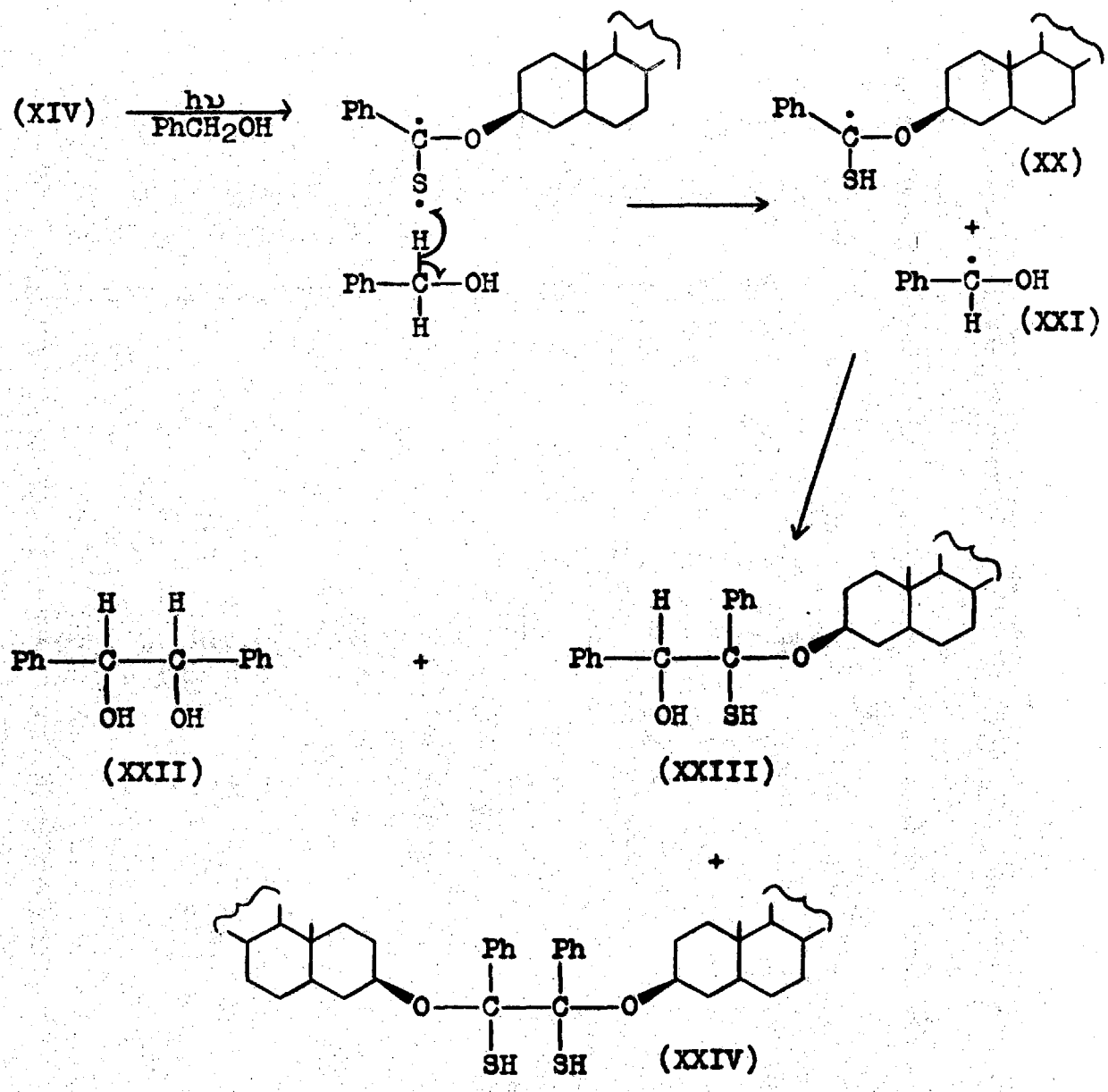
The two thiolbenzoates were identified by direct comparison with authentic samples prepared by displacement of the corresponding tosylates with potassium thiolbenzoate in acetone.

From these experiments, it appeared that it was necessary to have a double bond capable of conjugating with the newly forming double bond and it is this that gives the driving force for the elimination of the thiol acid. The stereospecificity of the reaction suggests that the reaction proceeds through a cyclic intermediate (XIX):





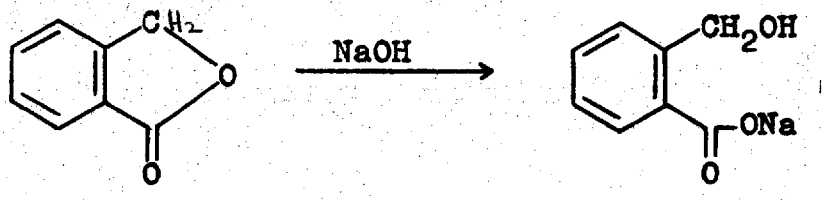
Although cholestan-3β-ol thionobenzoate (XIV) did not photolyse under normal conditions, it was found that, in benzyl alcohol, the disappearance of thionoester proceeded smoothly. One could thus predict that perhaps the first step in the reaction would be abstraction of a hydrogen atom from the benzyl alcohol by the excited thionobenzoate group to yield radicals (XX) and (XXI):



These could then combine with themselves or with each other to form compounds such as (XXII), (XXIII) or (XXIV), or they could further hydrogen abstract.

When the reaction was carried out, it was found that the heat necessary to remove the excess benzyl alcohol from the reaction mixture caused decomposition of the product. Examination of the t.l.c. showed there to be at least ten products. Thus, it was necessary to use a compound similar

to benzyl alcohol which could be easily removed from the reaction mixture. One possibility which sprung to mind was phthalide (XXV) which could be removed from the reaction mixture by treatment with base.



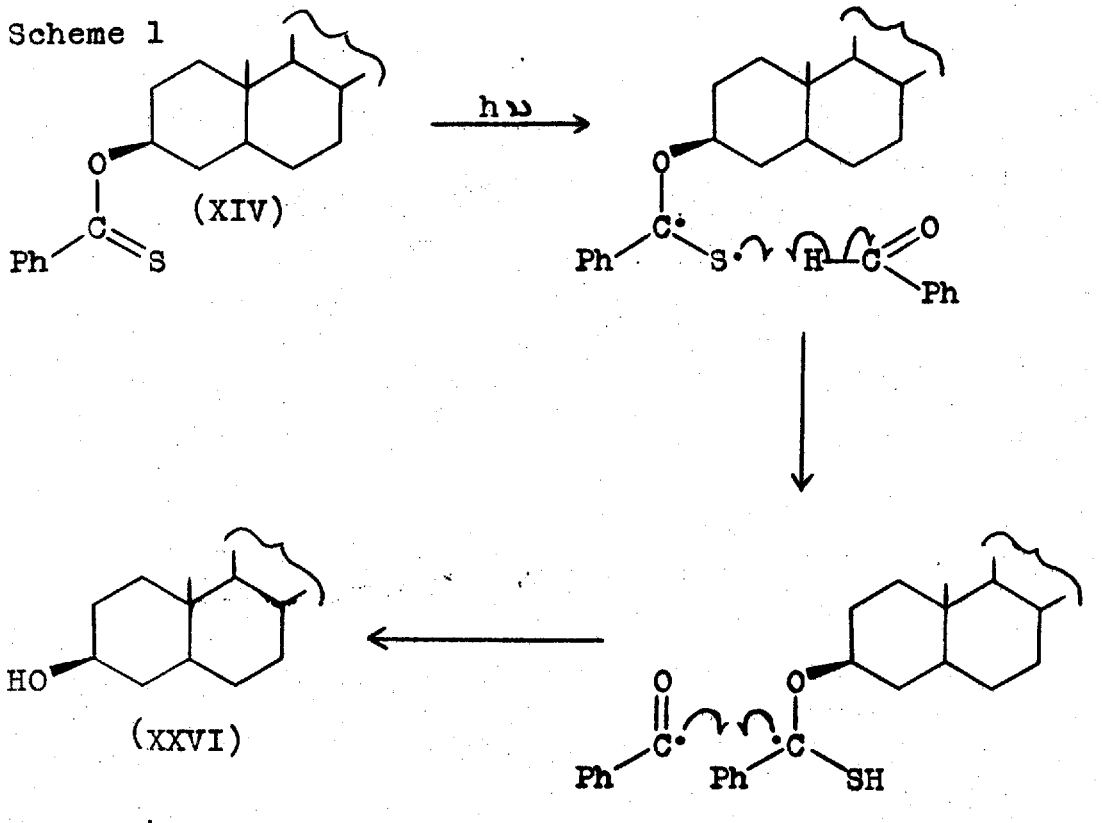
(XXV)

Since (XXV) was a solid, the reaction was carried out in a concentrated solution of (XXV) in dichloromethane. However, no reaction took place. It therefore became apparent that benzyl alcohol was not responsible for the photolytic decomposition of (XIV) but that the reaction was due to some impurity. One impurity is benzaldehyde. Consequently, a solution of (XIV) in dichloromethane containing a twenty-five molar excess of benzaldehyde was irradiated with light from a high pressure mercury lamp. Photolysis took place quite smoothly. Control experiments, in which there were mixtures of benzaldehyde and benzyl alcohol in varying ratios, showed that the rate of photolysis was dependant on the concentration of benzaldehyde. When the molar ratio of (XIV)/benzaldehyde was 1 : 2, the reaction stopped after 20% reaction.

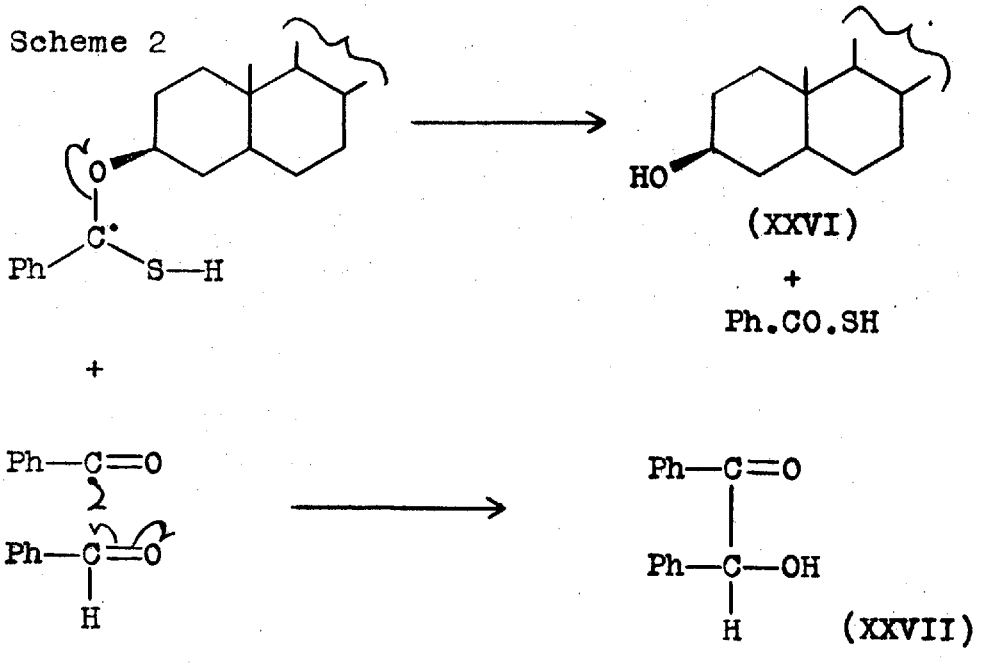
In the large scale reaction with benzaldehyde and dichloromethane, the reaction tended to be messy but one could isolate cholestanol (XXVI) and benzoin (XXVII) as major products. The mechanism for this reaction could be

rationalised in several ways.

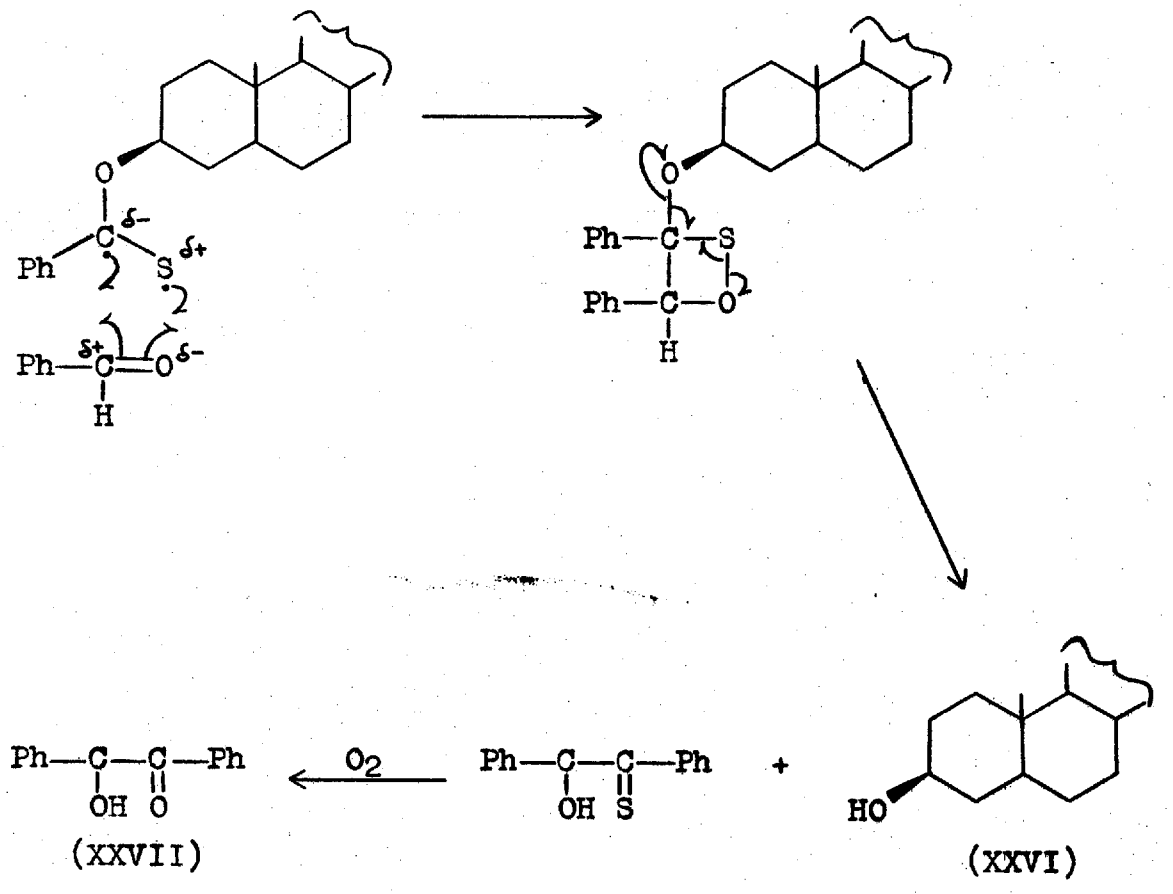
Scheme 1



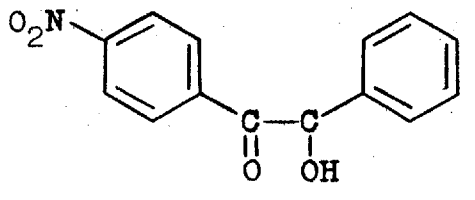
Scheme 2



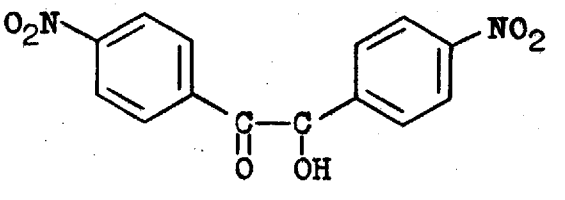
Scheme 3



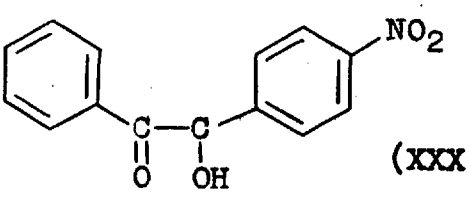
To indicate which mechanism was operating, the photolysis was carried out with p-nitrobenzaldehyde instead of benzaldehyde. If scheme 1 is correct, then one of the products should be (XXVIII). Similarly one of the products for scheme 2 or 3 should be (XXIX) or (XXX) respectively.



(XXVIII)

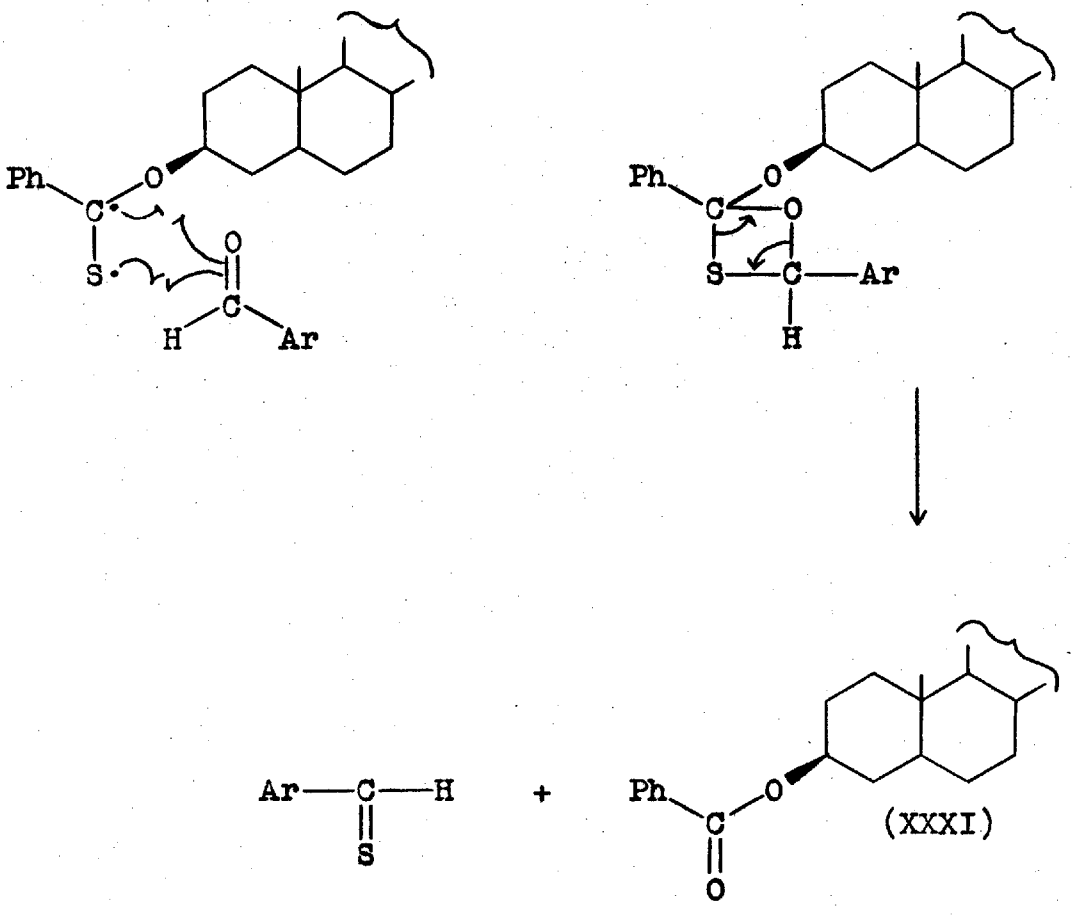


(XXIX)



(XXX)

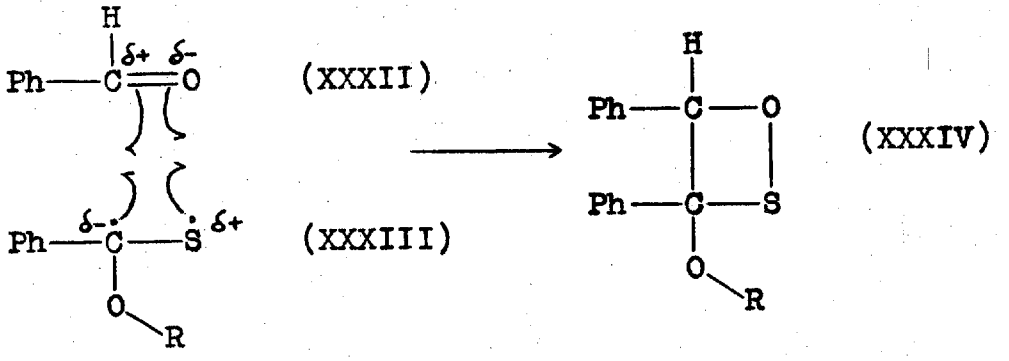
However, when the experiment was carried out, the photolysis was four times slower and the major compounds were found to be cholestan-3β-ol (XXVI) and cholestan-3β-ol benzoate (XXXI). There were at least ten minor components, none of which were characterised. The formation of (XXXI) points to a cyclic mechanism:



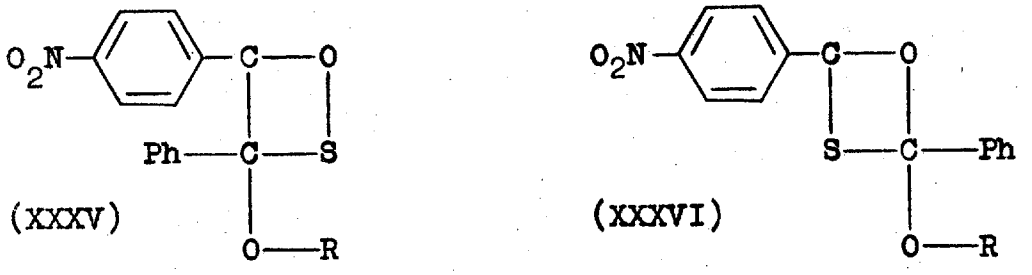
although it does not necessitate that the formation of (XVI) and (XVII) results from the cyclic mechanism.

In the case of benzaldehyde, the carbonyl group is quite polar and can be written as having a partial negative charge on the oxygen and a partial positive charge on the carbon as shown in (XXXII). The excited thionobenzoate on

the other hand will be polarised in the reverse way as in (XXXIII). Consequently there is only one course of addition to form (XXXIV)



However, in the case of p-nitrobenzaldehyde, the electron withdrawing nature of the nitro group makes the carbonyl group less polar than benzaldehyde. In this instance, there is no obvious manner of addition by the excited thionobenzoate and so two possible intermediates (XXXV) and (XXXVI) can be formed.



As mentioned before, the Δ^5 double bond is necessary for the elimination of thiobenzoic acid from cholesteryl thionobenzoate. In general, therefore, compounds of the type:

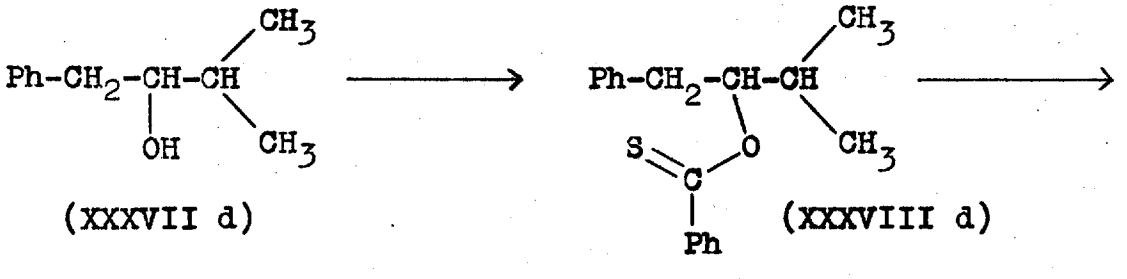
$$Ph\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CS\text{-}Ph$$

should behave in a similar manner to cholesteryl thionobenzoate

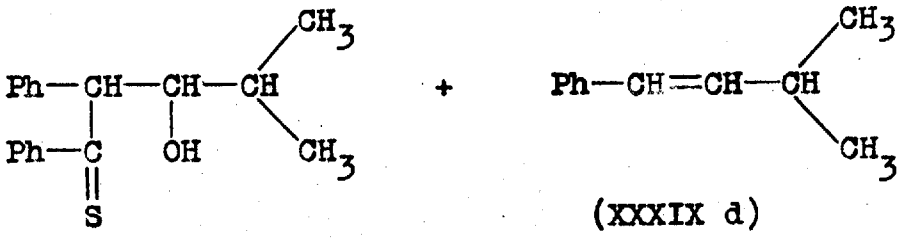
since the incipient double bond would be conjugated with the phenyl residue. With this in mind, a series of substituted 2-phenylethyl thionobenzoates were made. One worker[28] prepared a series of p-substituted 2-phenylethyl thionobenzoates and a series of 2-phenylethyl p-substituted thionobenzoates. It was found that, in general, thiobenzoic acid was eliminated to give styrene in good yield. Readdition of the thiol acid to the styrene was shown to be a thermal process which could be prevented by the use of triethylamine, p-nitrobenzoyl peroxide or by carrying out the reaction at low temperature.

So far, the phenylethyl thionobenzoates which had been irradiated had only the phenyl substituent on the ethyl residue. To gain an insight into the effects of multiple substitution on the reaction rate and/or products, a further series of compounds were made.

3-methyl-1-phenyl-butan-2-ol (XXXVII d) was prepared by the action of benzyl magnesium chloride on isobutyraldehyde[29] or by reduction of benzyl iso-propyl ketone with sodium borohydride in methanol. It was converted to its thionobenzoate (XXXVIII d) by method (iii) in good yield.



(XXXVII d) (XXXVIII d)



(XL d)

+

(XXXIX d)

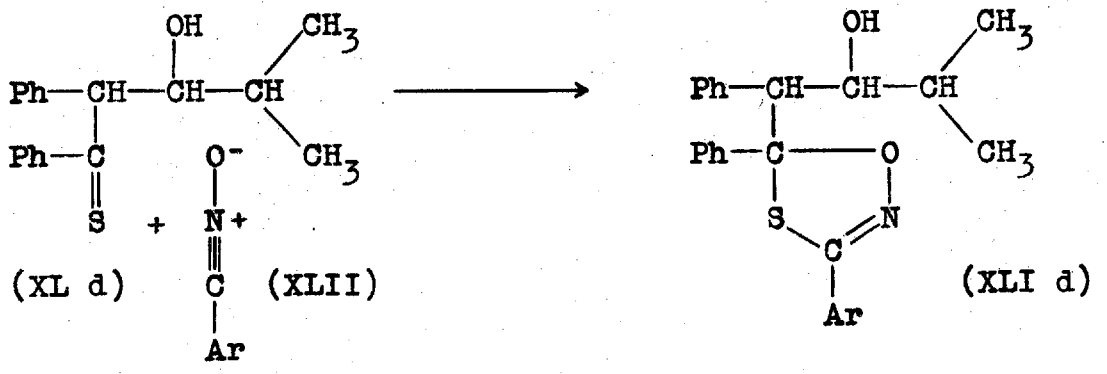
+

Ph-CO-SH

The thionobenzoate (XXXVIII d), on irradiation in dichloromethane, gave a purple solution. Examination of the solution showed that the expected styrene (XXXIX) was formed in 41% yield. The purple material was deduced to be the thioketone (XL d) from the u.v. spectrum which showed $\lambda_{max}^{cyclohexane}$ at 553 and 316 nm. (ϵ=94 and 12,650 respectively) and the i.r. spectrum which showed bands at 1210 cm^{-1} (attributed to the C=S bond) and 3400 cm^{-1} (attributed to the OH group). The n.m.r. spectrum showed the methyl groups of the iso-propyl group as a sharp doublet at τ9.04 and a hydroxyl group at τ3.51 as a broad singlet exchangeable with D_2O. The phenyl group attached to the thiocarbonyl moiety showed two low-field doublets at τ2.06 for the two ortho protons. There was also a doublet at τ4.83 and a double doublet at τ5.45 assigned to the protons of the ethyl residue. Mass spectrum showed no molecular ion at 284 but a strong M-18 peak at 266. Other fragment losses in the mass spectrum were readily explained on the basis of (XL d).

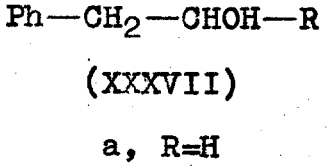
The thioketone (XL d) tended to be rather unstable on standing. However, it was readily characterised by forming an oxathiazole (XLI d) by reaction with p-nitrophenyl

nitrile oxide (XLII).



The reagent was liberated <u>in situ</u> by treatment of the hydroxamic acid chloride (XLIII) with triethylamine[32]. The hydroxamic acid chloride was prepared by the action of chlorine on a cold solution of p-nitrobenzaldoxime in anhydrous ethyl acetate.

It seemed rather strange that replacing an ∝-H in 2-phenyl ethanol by an iso-propyl group should make such a tremendous difference in the ratio of styrene to thioketone. To see if there were any gradual change in the ratio, a series of alcohols (XXXVII a-f) were prepared and converted to their thionobenzoates (XXXVIII a-f).



(XXXVII)

a, R=H

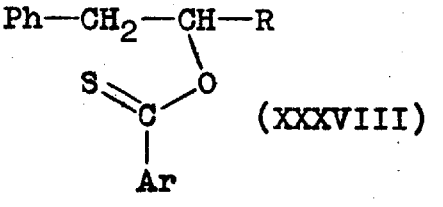
b, R=Me

c, R=Et

d, R=i-Pr

e, R=t-Bu

f, R=Ph

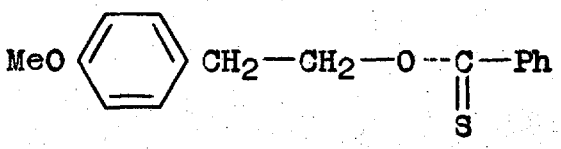


Alcohols (XXXVII b-d,f) were prepared by reduction of the corresponding ketone with sodium borohydride[33]. Alcohol (XXXVII e) was prepared by reaction of tert-butylmagnesium bromide with phenylacetaldehyde[34]. They were converted to their thionobenzoates by method (iii) in good yield except for the tert-butyl compound.

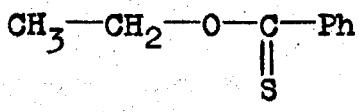
Each compound was irradiated in turn with light from a medium pressure mercury lamp. (XXXVIII a) was found to yield only the styrene (XXXIX a) in 71% yield. Compounds (XXXVIII b-e) gave the ratio of thioketone to styrene as 15/85, 28/72, 41.5/58.5 and 58/42 respectively. (XL b) was too unstable to have a good analysis or have an oxathiazole derivative made from it. (XL c,d) were fairly stable crystalline solids and (XL e) was an oil and, although it was analysed correctly and was characterised as the oxathiazole derivative, it tended to decompose[35], even at 0^{o}. Compound (XXXVIII f) produced neither thioketone nor styrene but gave benzaldehyde (XXXIX f) (65%) and desoxybenzoin (XL f) (10%).

At this stage we were able to secure the services of Professor G. Porter and Dr. J. Wirz, who performed some flash photolysis experiments for us. No transient absorptions were observed by conventional spectroscopic flash photolysis of 10^{-6} - 10^{-4}M solutions of thionobenzoates in degassed cyclohexane. Spectra recorded 5μs after the peak of the photolytic flash were identical to those obtained from mixtures of starting material and photoproducts.

Therefore, the products of photoelimination appear within a period of less than a few μs after excitation. When a frequency-doubled pulse of a ruby laser was used as an excitation source[37] (output at 347 nm. ca. 50mJ, half-peak duration 20ns.), all thionobenzoates gave rise to a transient absorption below 520 nm. decaying by first-order kinetics. In dilute solutions, lifetimes ranged from about 50ns for the most reactive compounds such as (XLIV) to ca. 1μs for the unreactive derivative e.g. (XLV), $\phi \leqslant 0.02$.



(XLIV)



(XLV)

The transients were found to be quenched by the parent thionobenzoates at rates approaching diffusion-controlled. Thus in low viscosity solvents, the self quenching process becomes important at concentrations of starting material higher than 10^{-4}M. Oxygen, piperylene, and tetracene (in benzene) also quenched the transients at near diffusion-controlled rates. The build-up of the well-known[38] absorption of the tetracene triplet was shown to match the decay of the transients from thionoesters, clearly establishing energy transfer as the quenching mechanism. The absence of fluorescence from thionobenzoates implied an upper limit of 1ns. for the lifetime of the excited singlet state. The above observations leave little doubt that the transients are due to absorption by the lowest triplet state of each of the parent compounds. The lowest triplet state of

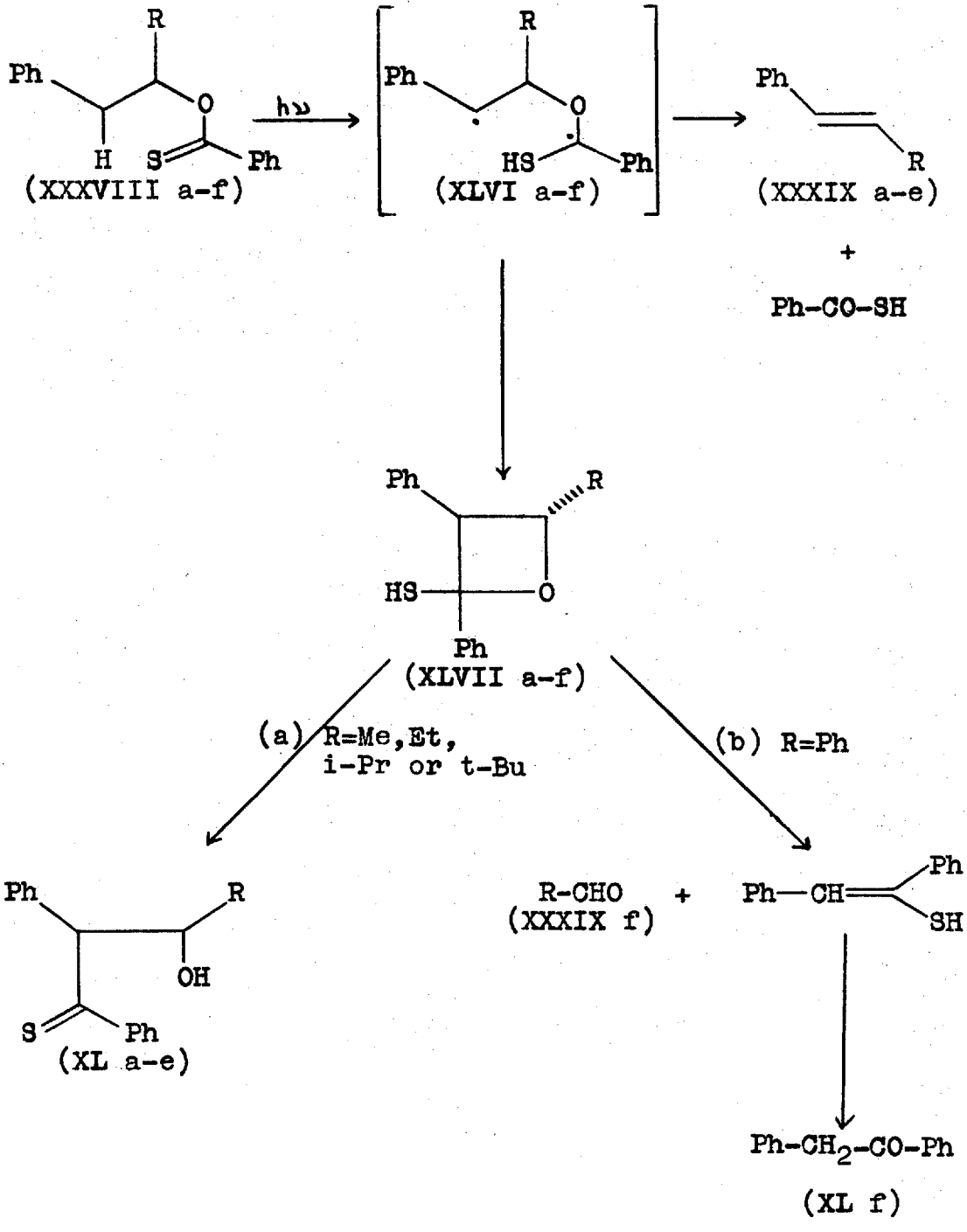
thionobenzoate esters is expected to be essentially of n,π^* configuration because of (a) a blue shift of the phosphorescence spectrum in polar media, (b) the short lifetime even in the absence of photoreaction and (c) an energy gap of about 8000 cm^{-1}. between the onset of the n,π^* and π,π^* absorption bands.

The ratio of triplet lifetimes with and without quencher in solution, τ/τ^q, agreed, within the limits of error, with the ratio of photolysis rates, ϕ^o/ϕ^q, for q equal to oxygen, piperylene and thionobenzoate (self quenching). It is concluded, therefore, that the triplet state as observed by its transient absorption is identical with the quenchable photoreactive state and a reaction mechanism analogous to the one currently accepted for Norrish Type II is proposed. The flash photolysis experiments did not in general provide any evidence for the existence of a biradical intermediate. However, the results of the photolysis of compounds such as (XXXVIII a-f) provide evidence for the existence of a biradical intermediate. (Scheme 4)

On irradiation, the first stage of the reaction is abstraction of a hydrogen atom from the β-carbon by the excited thionobenzoate group. The biradical (XLVI) which is formed can follow one of two courses. For styrene formation, the phenyl group, the R group and the α and β-carbon atoms must lie in the same plane so as to provide maximum overlap between the newly forming double bond and

the phenyl group. However, when R is bulky, there is a degree of hindrance so that the phenyl group, R and the α and β-carbon atoms cannot become planar. Thus the most likely reaction path will then be cyclisation to form the oxetane (XLVII). This can then decompose by either path (a) or (b) as in scheme 4.

Scheme 4

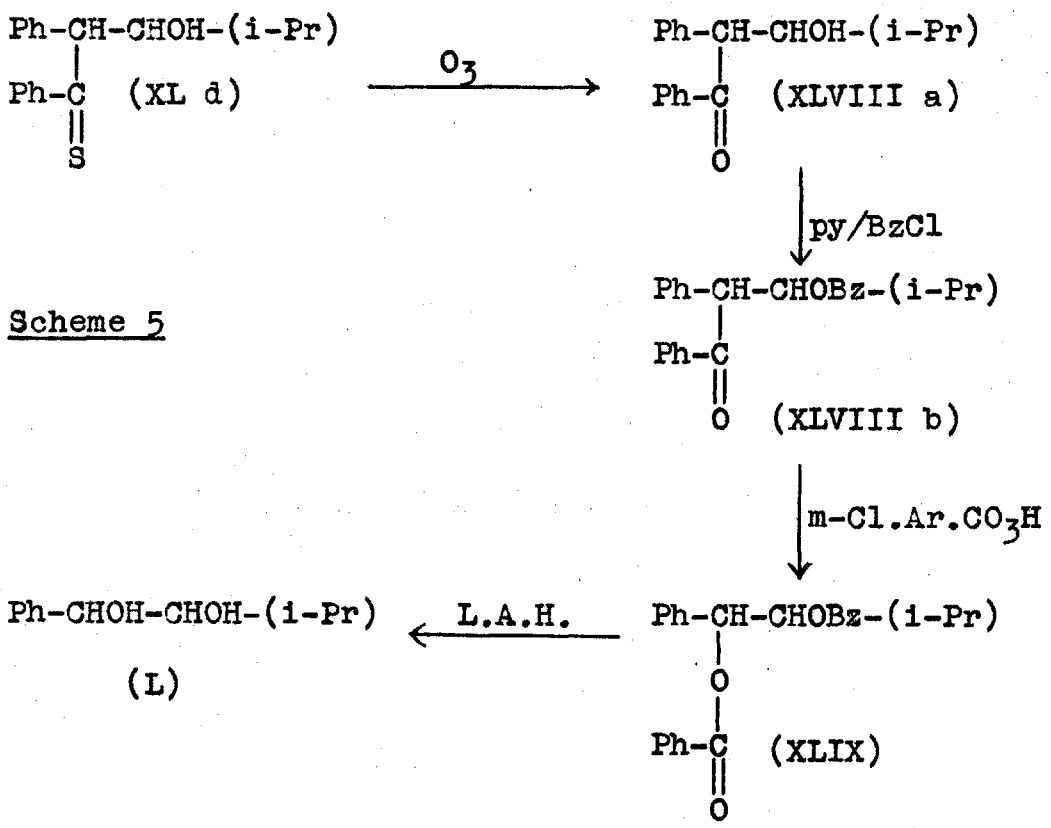


Although the oxetane intermediates could not be directly observed by their u.v. absorption in the reaction mixture, their lifetimes could however be determined from the first-order rates of formation of the thioketones (XL) by monitoring the absorption at 550 nm. Appearance half-lives for the thioketone (XL e) at room temperature were determined as 30 min., 8 min., 1 min., and 0.5s., in liquid paraffin, cyclohexane, ethanol and 10^{-3}M triethylamine in ethanol respectively. The ratio of styrene to thioketone formation was not significantly affected by base catalysis.

To gain an insight into the stereoselectivity of the reaction, a series of trans-styrenes (XXXIX b-e) were synthesised. The most obvious method was the treatment of the alcohols (XXXVII b-f) with phosphorus oxychloride in pyridine, since the alcohols had been used to prepare the thionoesters and the elimination with this reagent is known to proceed with the minimum amount of rearrangement[39]. The styrenes were distilled on a spinning band column and checked for purity on an analytical g.l.c. The authentic styrenes had identical retention times to the styrenes obtained from the photolyses. The n.m.r. spectra[40] were also identical especially at τ3.72 where there was an AB part of an ABX system with a coupling constant of 16 c/s. The i.r. spectra were also identical. The cis-styrenes also were prepared. Cis-(XXXIX b,c) were prepared by the hydrogenation of the corresponding acetylene using 5% palladium on barium sulphate as catalyst[41]. These were purified in the same way as the trans-isomers but, on the

g.l.c., the retention times were different to those of the trans-isomers. Further, the styrene from the photolysis showed no peak corresponding to the cis-isomers. Also, the n.m.r. showed a completely different AB pattern for the olefinic protons and the infra-red spectra were different. Consequently, no cis-(XXXIX d,e) were prepared since they are less likely to be formed from stereochemical considerations.

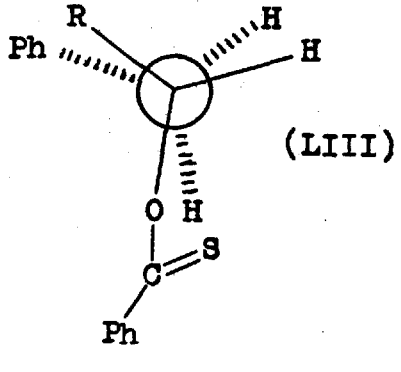
To investigate the stereochemistry of the thioketone, it was decided to degrade (XL d) since it appeared to be the most stable and was formed in good yield. The steps in the degradation are shown in scheme 5.



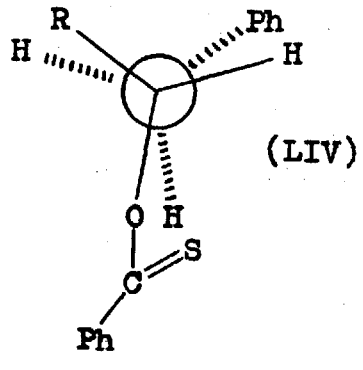
Scheme 5

The first step was oxidation of thioketone (XL d) to ketone (XLVIII). This was followed by treatment with m-chloro perbenzoic acid to give a Baeyer-Villiger rearrangement to a benzoate (XLIX). Both of these steps are known to proceed with retention of configuration. (XLIX) was converted to diol (L) which was then compared to threo and erythro-3-methyl-1-phenyl-butan-1,2-diol (LI) and (LII) respectively. (LI) and (LII) were both prepared from the trans-styrene (XXXIX d) by treatment with silver acetate and iodine[42]. The ester was then reduced with l.a.h. to give the threo-diol (LI), or treated with sodium hydroxide to give an epoxide, which was then hydrolysed with formic acid to give the erythro-diol (LII). N.m.r. of (LI) and (LII) showed that the coupling constants of the hydrogen atoms on C-1 and C-2 were 7 c/s. and $5\frac{1}{2}$ c/s. for the threo and erythro isomers respectively[41]. N.m.r. of the product obtained from degradation of the thioketone (LX d) showed that the coupling constant was 7 c/s. and was therefore the threo isomer. M.p. and i.r. confirmed this.

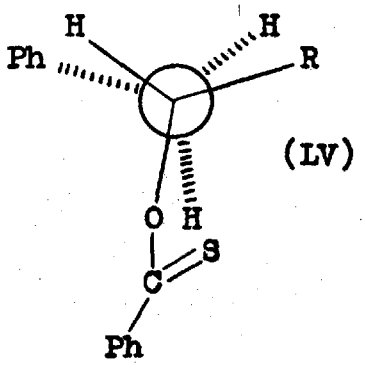
There are four conformations (LIII) - (LVI) that are possible during the hydrogen abstraction stage. Of these, (LIV) and (LV) have the least stereochemical interference and so are the most likely to be formed.



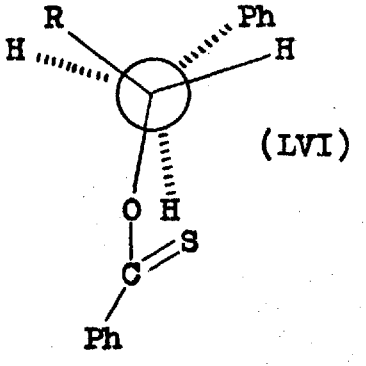
(LIII)



(LIV)



(LV)

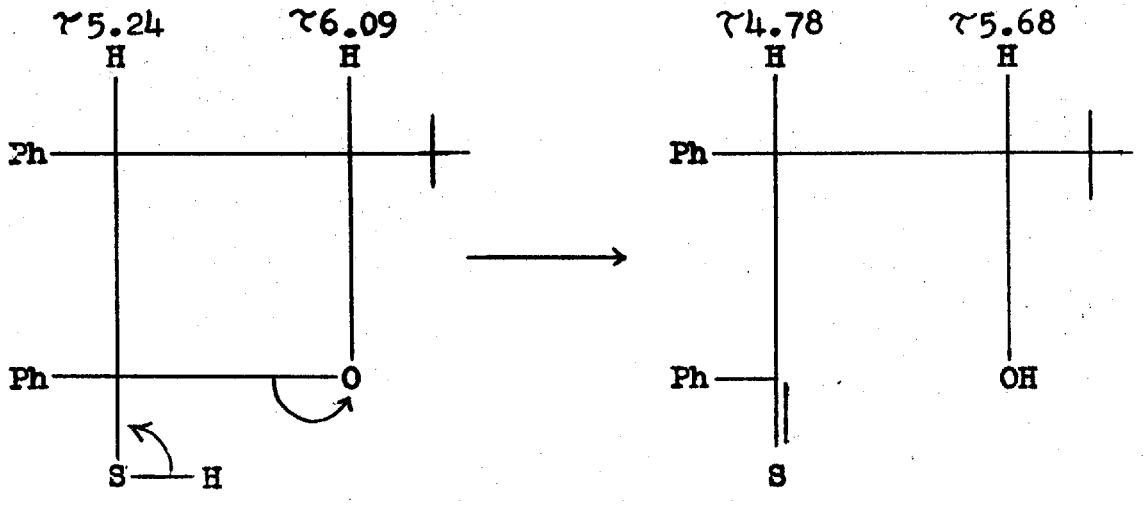


(LVI)

Either of these can cyclise then ring open as shown in scheme 4 to yield the thioketone having the threo configuration. By similar considerations, it can be shown that the most likely styrene to be formed will have the trans configuration.

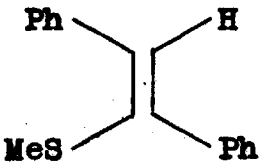
In the preparation of large quantities of thioketone (XL d) for the degradation described above, it was decided to use a high pressure mercury lamp in system B (see experimental section). This was primarily because this set-up was more suitable for larger quantities of material than system 'A' using a medium pressure lamp. When using the high pressure lamp, it was found there was a delay of several minutes before there was any appearance of the thioketone. This suggested that the intermediate oxetane was more stable than had been originally supposed, so several 'trapping' experiments were performed to try and isolate a stable derivative. First of all, the photolysis was carried out at -78°. At this temperature it was found that, after irradiation, the solution remained colourless for several hours. It was essential, however, to let the dichloromethane solvent dry for several days over grade I alumina, otherwise the solution became purple more rapidly.

To see if the intermediate could be observed in the n.m.r. spectrometer, a concentrated (15mg./ml.) solution of (XL e) in d_8-toluene was photolysed at -78°. When the solution became colourless, a spectrum was run at -78°. This showed two broad doublets at τ5.24 and τ6.09 (J=4½ c/s.). On allowing the solution to warm up, to let the thioketone form, then re-running the spectrum at -78°, the doublets had disappeared and two new doublets had formed at τ4.78 and τ5.68 (J=4 c/s.) as well as a broad singlet at τ7.03. These results can be explained in terms of an intermediate (XLVII e) going to thioketone (XL e).

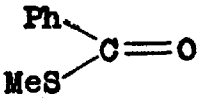


(XLVII e) (XL e)

Diazomethane was one reagent used to attempt to trap intermediate (XLVII d). A solution of diazomethane in ether at -78° was added to the solution containing the intermediate at -78°. On allowing the reaction mixture to warm up to room temperature, two products had formed. The first compound was deduced to be 1,2-diphenylvinyl methyl sulphide (LVII) from the n.m.r. spectrum which showed a singlet at τ2.67 (5H) a multiplet at τ2.96 (5H),



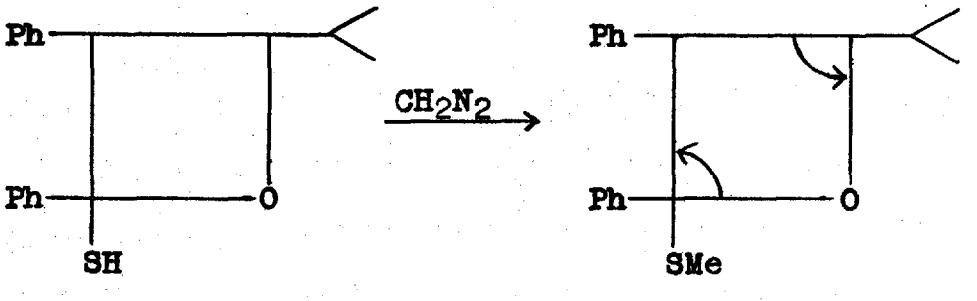
(LVII)

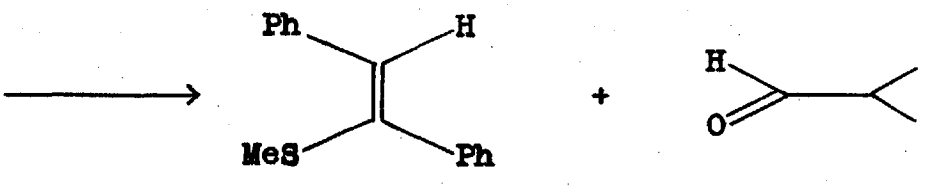


(LVIII)

a singlet at τ3.46 (1H) and a singlet at τ7.77 (3H). The mass spectrum showed a molecular ion at 226 with a fragmentation pattern which fitted a structure such as (LVII)[43]. The other compound was deduced to be methyl thiolbenzoate (LVIII) from the following data: the n.m.r. spectrum showed a multiplet at τ2.01 (2H), a multiplet at τ2.45 (3H) and a singlet at τ7.53(3H). The mass spectrum showed a molecular ion at 152 with a fragmentation pattern which fitted structure (LVIII). Both of these compounds may be formed in the manner shown in scheme 6.

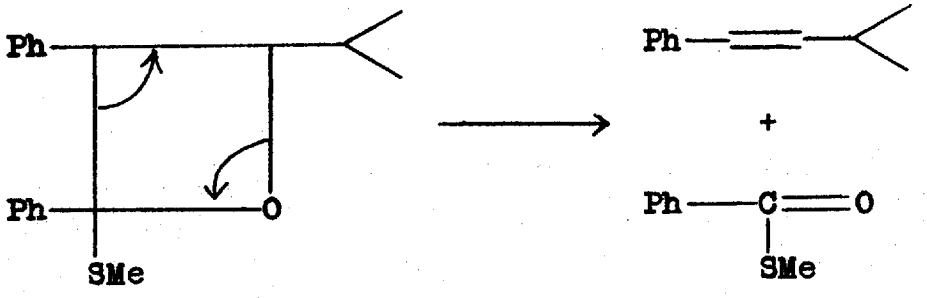
Scheme 6





(LVII)

or



(LVIII)

To prevent the ring opening on warming up, it was decided to oxidise the thiol to a sulphonic acid, then methylate this with diazo-methane. A series of oxidising agents were tried. These included m-chloroperbenzoic acid, benzoyl peroxide, p-nitrobenzoyl peroxide and ozone. However, with all of these, the major reaction product was the ketone (XLVIII a).

Another approach was to desulphurise the intermediate with Raney nickel. This, however, had no effect on the intermediate which rearranged to give the thioketone (XL d).

The use of iodine would be expected to give the disulphide. However, this reagent gave rise to a complex mixture of products.

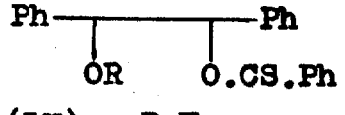
When intermediates (XLVII a-e) were allowed to warm up to room temperature, the yields of thioketone were higher than the room temperature experiments, while the yield of thioketone and styrene was nearer to 100% in this case showing that, in the room temperature experiment, the

thioketone must have been either decomposed by the triethylamine present in the reaction mixture or photolysed. (If the thioketone was allowed to stand at room temperature in the presence of an excess of triethylamine, it was rapidly decolourised). In the case of 2-phenyl-ethyl thionobenzoate there was a small amount of thioketone detected in the spectrophotometer. This reached a 'steady-state' after 30% photolysis. The results are shown in the table below with the room temperature results in brackets.

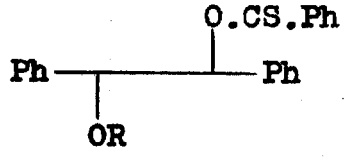
(XXXVIII)	Yield of thioketone (XL)%	Yield of styrene (XXXIX)%	Ratio (XL)/XXXIX
a, R=H	10* (0)	81 (71)	1.0/8.1 (∞)
b, R=Me	32* (10)*	61 (55)	1.0/1.9 (1.0/5.5)
c, R=Et	45 (20)	52 (51)	1.0/1.15 (1.0/2.55)
d, R=i-Pr	55 (29)	42 (41)	1.0/0.76 (1.0/1.4)
e, R=t-Bu	75 (37)	25 (27)	1.0/0.33 (1.0/7.3)

* Yield as estimated from u.v. spectrum

The next series of compounds to be investigated were the esters of meso and d,l-hydrobenzoin (LX a-c) and (LXI a-c) respectively.



(LX)a, R=H
b, R=O.CO.Ph
c, R=O.CS.Ph

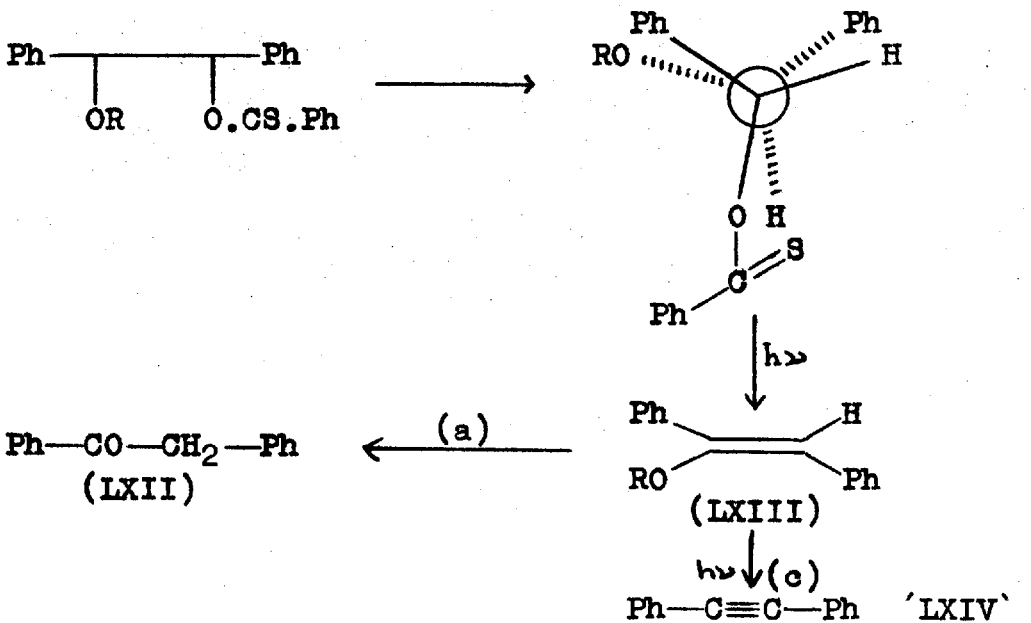


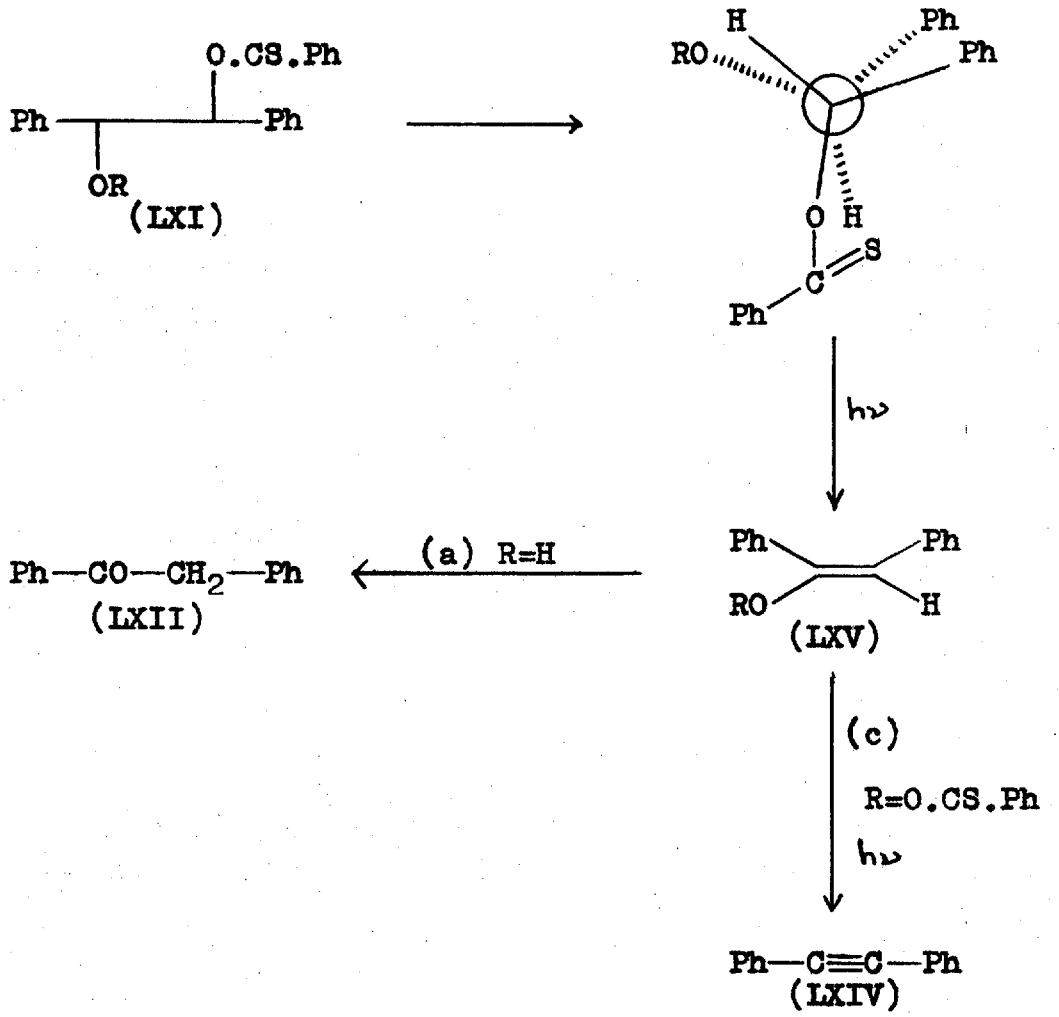
(LXI)a, R=H
b, R=O.CO.Ph
c, R=O.CS.Ph

Refluxing meso or d,l-hydrobenzoin with sodium hydride in t.h.f., then adding thiobenzoylthioglycollic acid, gave (LX a) or (LXI a) as major products. Benzoylation of these in the usual way gave (LX b) and (LXI b) respectively. (LX c) was prepared by method (iii) from meso-hydrobenzoin using imidazole. However, (LXI c) was not formed at all using this route. The best methods for the synthesis of this ester were from (LX b) using method (iii), or from d,l-hydrobenzoin using method (i). In either case, the best yields obtained were of the order of 7%.

The main reason for irradiating these esters was to compare the effects of the stereochemistry on the rate of photolysis and on the products formed. The meso-series (LX a-c) were expected to give rise to a trans-enol which, in the case of (a), would tautomerise to form desoxybenzoin or, in the case of (c), may further photoeliminate to form diphenyl acetylene as in scheme 7.

Scheme 7





In the case of the d,l-series, the first product was expected to be a cis-enol which, in the case of (a), would tautomerise to give desoxybenzoin or, in the case of (c) further photoeliminate to give diphenylacetylene.

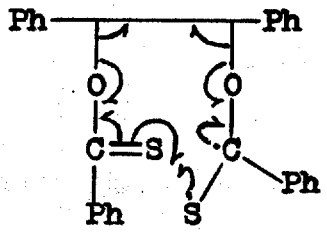
(LX a) was irradiated in either cyclohexane or dichloromethane, in the presence of triethylamine, to give desoxybenzoin in 65% yield. The reaction was slightly more clean and a little faster in cyclohexane. Without triethylamine there was no readdition product formed. However, a small amount of dibenzoyldisulphide was observed.

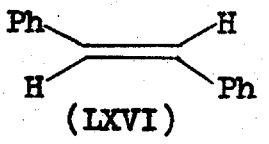
(LXI a) gave essentially the same results as (LX a).

When (LX c) was irradiated in dichloromethane with light from a high pressure mercury lamp, the photolysis proceeded at an almost negligable rate. On addition of triethylamine to the reaction mixture, the reaction proceeded more quickly but, even so, the rate of photolysis was about thirty times slower than phenylethyl thionobenzoate. There were four major products formed in the reaction. The first one was deduced to be trans-stilbene (LXVI) from its n.m.r. spectrum which showed two singlets at τ2.75 (10H) and τ3.39 (2H)[44]. The mass spectrum showed a mass ion at 180 and the u.v. showed a characteristic peak at 295 nm. (ε=27,000)[45]. It was formed in 51% yield. The next compound was deduced to be cis-stilbene (LXVII) from the n.m.r. which had a multiplet at τ2.58 (10H) and a singlet at τ2.79 (2H)[44]. Mass spectrum showed a molecular ion at 180 and the u.v. spectrum had λ_{max} at 280 nm. (ε=13,500)[45]. These and other physical data were identical to authentic samples. The identity of the third (LXVIII) and fourth (LXIX) compound proved a little more elusive. At first, (LXIX) was formed first then, as the reaction proceeded, (LXVIII) was formed, apparently at the expense of (LXIX). After a while, however, the concentration of (LXVIII) and (LXIX) reached a steady concentration relative to each other. In the n.m.r. spectrum, (LXVIII) had five aromatic protons in the ratio 2:3 and a singlet at τ4.87 corresponding to 2 protons. The i.r. spectrum showed a strong absorption at 1675 $cm.^{-1}$ which implied a

thiolbenzoate. These results suggested that Ph.CO.S- and an isolated $-CH_2-$ were present in the molecule. Mass spectrum had a molecular ion at 186. This was 35 units higher than the two groups mentioned above. Thus (LXVIII) was deduced to be chloromethylthiol benzoate which was confirmed by synthesis of an authentic sample[46]. The mechanism for the reaction was thought to be as in scheme 8.

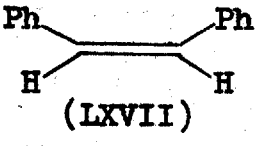
Scheme 8





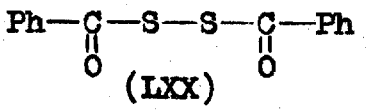
(LXVI)

+

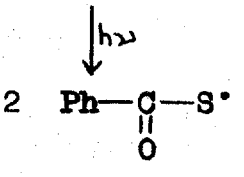


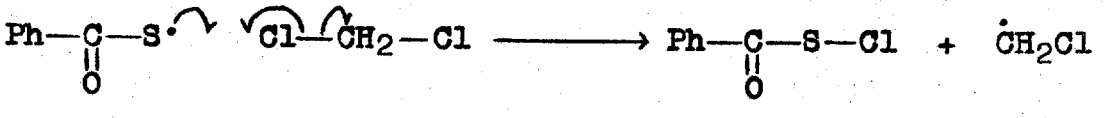
(LXVII)

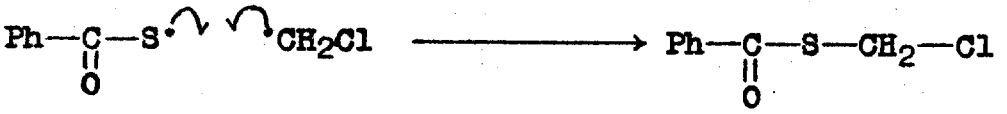
+



(LXX)



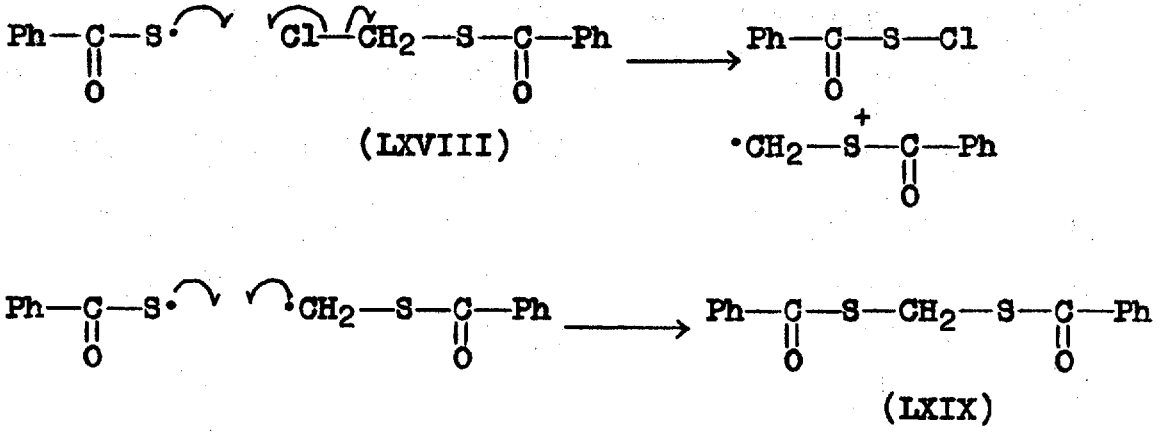




(LXVIII)

The first step of the reaction would be for the photo-excited thionbenzoate to undergo a cyclic elimination to form trans stilbene and dibenzoyl disulphide. Under the reaction conditions, the dibenzoyl disulphide can further fragment to form thiobenzoyl radicals. One of these can abstract hydrogen from the solvent and the other can combine with the chloromethyl radical to form (LXVIII) as in scheme 8. From this it was deduced that (LXIX) was dibenzoyl disulphide. The r.f's. on t.l.c. were identical, the melting points and i.r. spectra were similar but there were some important differences. In the first instance, dibenzoyl disulphide crystallised from ethanol as plates while (LXIX) crystallised as needles. More important was the fact that (LXIX) showed a singlet at τ5.30, corresponding to two protons, as well as ten aromatic protons split in the ratio 2:3. Further, the mass spectrum of the compound showed a molecular ion which was 14 units higher than that of dibenzoyl disulphide. From this, it was deduced that (LXIX) was methanedithiol dibenzoate[47]. Its formation can be explained as in scheme 9.

Scheme 9



The reaction is somewhat more complex than this however, since irradiation of dibenzoyl disulphide (LXX) under the same reaction conditions gives only (LXVIII) in 38% yield.

When cyclohexane was used as solvent, the major products were the stilbenes (LXVI) and LXVII). There were several minor products and a lot of polar material. No doubt the Ph.CO.S$^{\bullet}$ radical had reacted with the triethylamine.

Irradiation of (LXI c) was expected to give the same products as (LX c) with cis-stilbene predominating over trans-stilbene. However, when the compound was irradiated with cyclohexane as solvent, the major compound was found to be diphenyl acetylene. This was characterised by mass spectrum, infra-red and u.v. then compared with an authentic sample. Its formation can be explained by considering the conformation of (XLI c) in the elimination position as shown in scheme 7. Here, both thionoester groups are adjacent to a hydrogen atom so that, if elimination is faster than rotation about the C-C bond, the acetylene (LXIV) will be formed. If the reaction goes through an intermediate enol thionobenzoate (LXV) then the hydrogen atom will be on the correct side of the double-bond for abstraction. This is not the case with the meso esters since the intermediate enol thionobenzoate would be trans.

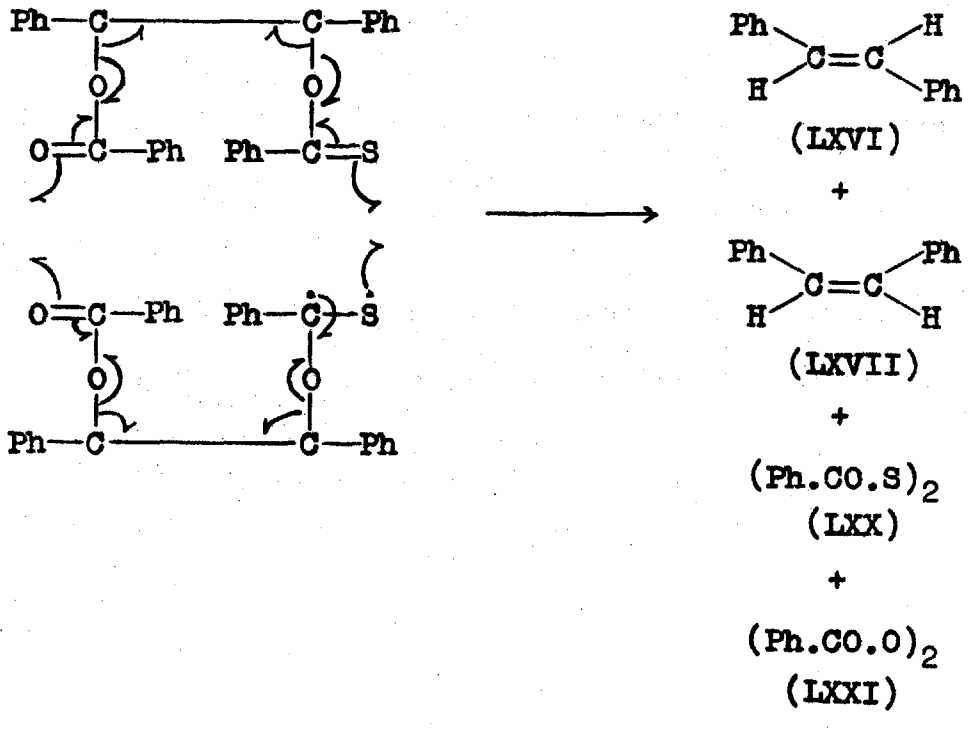
Irradiation of (LX b) using the same conditions as above produced no reaction. However, on increasing the concentration from 2×10^{-3}M to 6×10^{-3}M, the reaction proceeded as

before with (LXVI) - (LXIX) as major products when the solvent was dichloromethane, and (LXVI) and (LXVII) as major products when the solvent was cyclohexane.

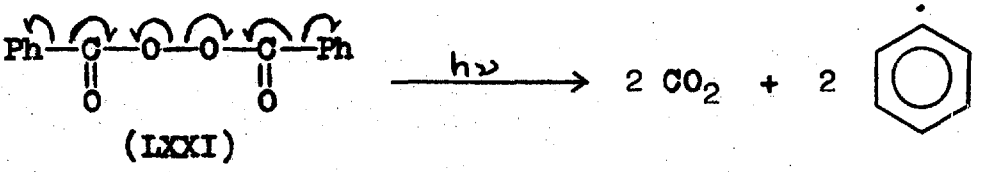
Irradiation of (LXI b) gave the same ratio of compounds with trans-stilbene predominating in both cases. This suggests that the mechanism is not concerted, as shown in scheme 10, but proceeds step-wise so that there is time for rotation about the C-C bond before the biradical collapses to the stilbene. On stereochemical grounds the trans-isomer will predominate.

The concentration dependance of this reaction implies that the reaction proceeds in an intermolecular fashion as shown in scheme 10.

Scheme 10



(LXX) $\xrightarrow[CH_2Cl_2]{h\nu}$ (LXVIII) + (LXVIII) + (LXIX) as in schemes 8&9



(LXXI)

Dibenzoyl peroxide (LXXI), which is also formed in the reaction, can also photolyse to give CO_2 and phenyl radicals[48].

EXPERIMENTAL

Unless otherwise stated, the following data apply to experiments described in this section:

Melting points were taken on a Kofler block and are uncorrected.

I.r. and u.v. spectra were recorded on a Unicam SP 200 and SP 800 respectively.

Mass spectra were taken with an A.E.I. MS9 double focussing spectrometer.

N.m.r. spectra were recorded with a Varian A-60 instrument and refer to deuterochloroform solutions with tetramethyl silane as internal standard. The following abbreviations refer to the n.m.r. data. s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet

Rotations were measured on a Perkin Elmer 141 polarameter and are for chloroform solutions.

Analytical g.l.c's. were performed on a Perkin-Elmer F-11 instrument with a 2 metre x $\frac{1}{8}$" o.d. silicone gum rubber E 301 on chromosorb G-AW-DMCS $2\frac{1}{2}$:$97\frac{1}{2}$, 80-100 mesh (496-0732)

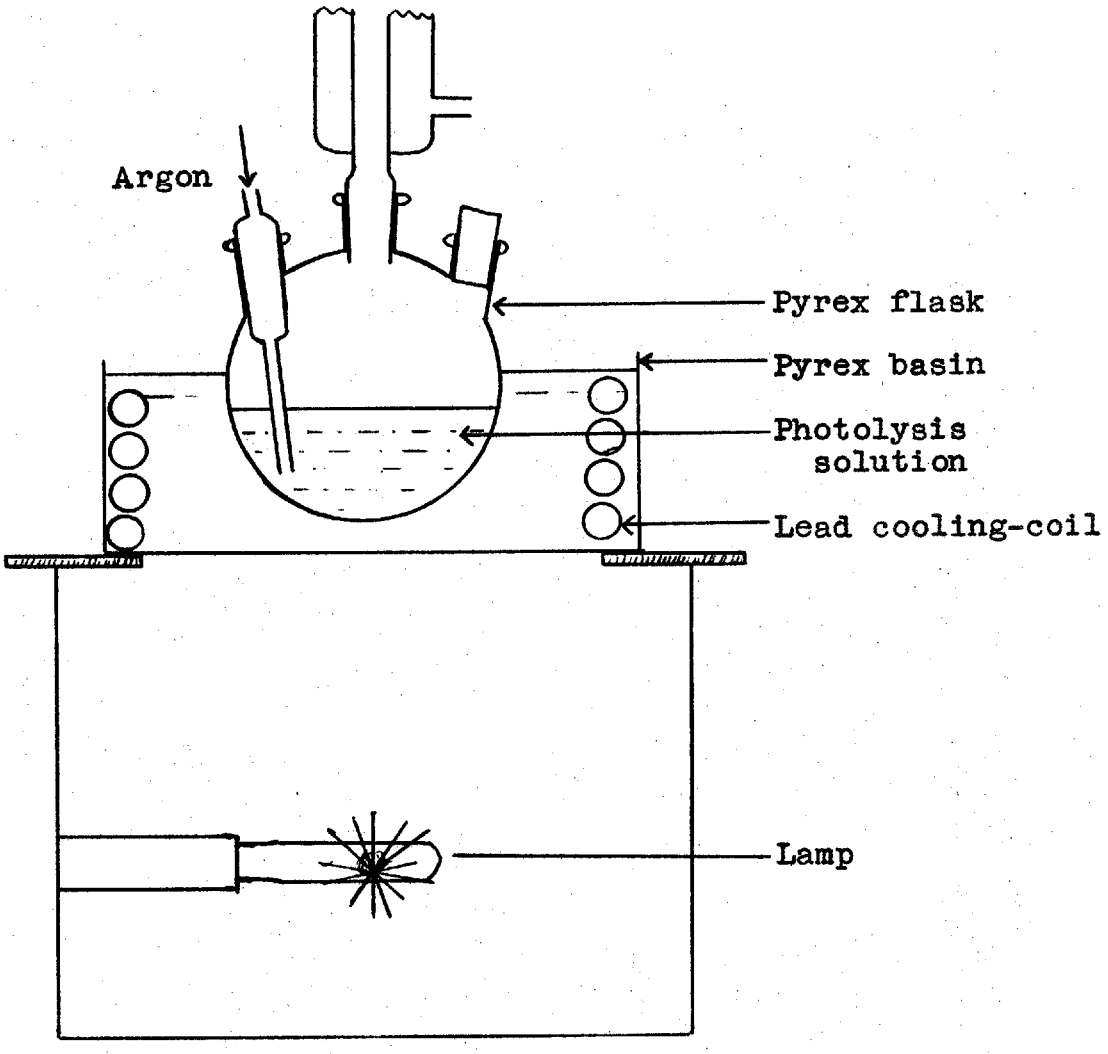
All solvents were dried by standard techniques.

Experiments marked thus * were carried out in conjunction with Dr. P.J. West.

The lamps used for the photolyses were: Philips MBU/U 125 W medium pressure blacklight lamp with the dark outer glass cover removed, and HPK 125 W BA 15 D TYP 5720 3B/00 high pressure mercury lamp.

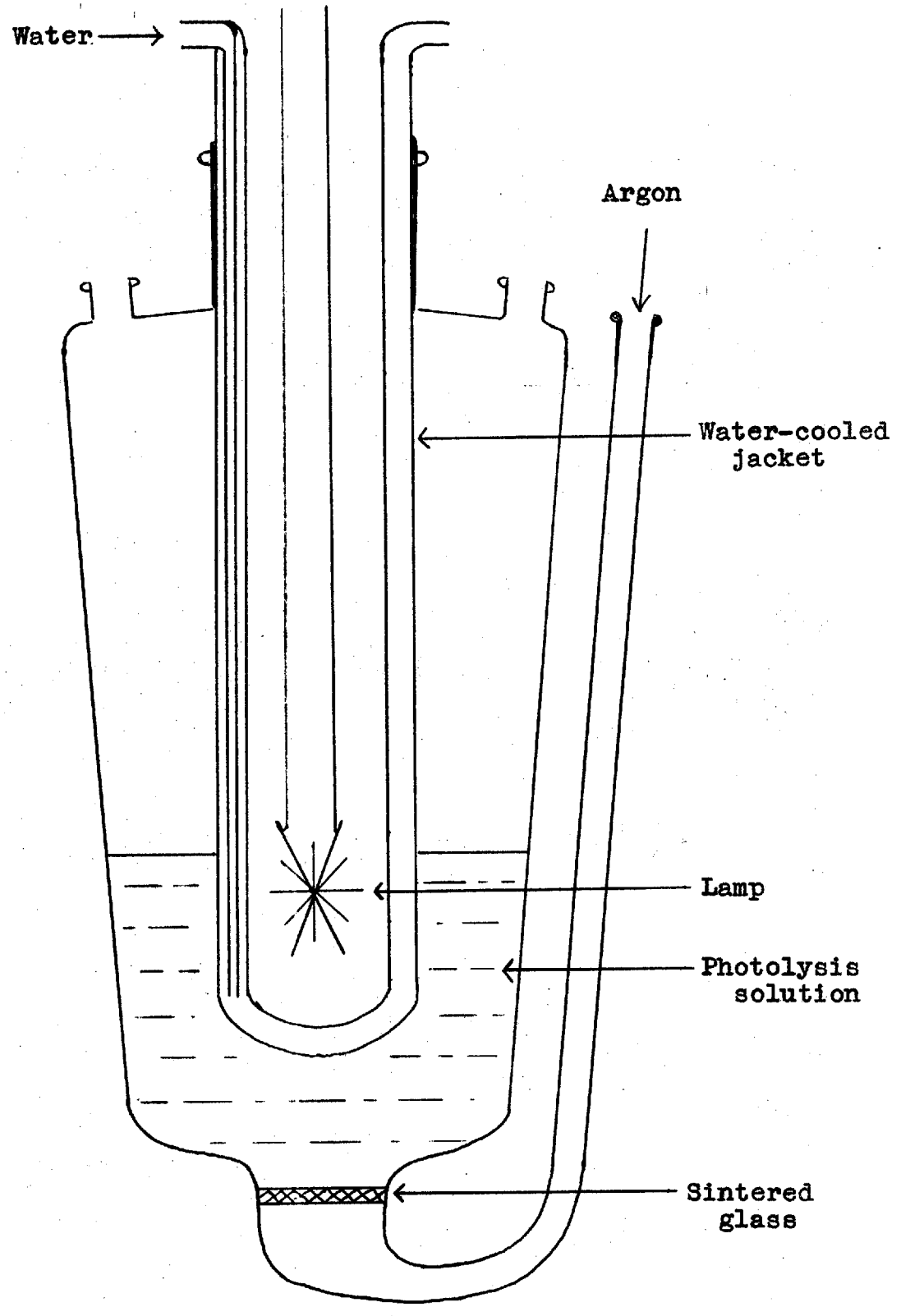
Two basic systems were used for the photolyses:

System A



The ester in degassed solvent was contained in a 3-necked pyrex flask cooled externally in a pyrex water bath (fitted with cooling coil) and equipped with an inlet for dry, oxygen-free argon and a condenser fitted with a drying tube. Aluminium foil lined the box containing the lamp and was placed over the top of the basin and flask to act as reflector.

System B


Water
Argon
Water-cooled jacket
Lamp
Photolysis solution
Sintered glass

The ester, in degassed solvent, was irradiated in a container which had a sintered disc at its base through which argon could be passed. The container was fitted with 2-necks. One for a condenser and a drying tube and the other for removing aliquots. The lamp was fixed to the end of a probe in a pyrex water-cooled thimble which dipped into the solution. The whole system was wrapped in aluminium foil to act as a reflector.

Thiobenzoyl chloride (I)

Phenyl magnesium bromide was prepared in the usual way from magnesium turnings (24g., 1 mole) and bromobenzene (157g., 1 mole) in anhydrous ether (500 ml.) under argon. The solution was cooled to -20° then carbon disulphide (228g., 3 moles) was added dropwise, with stirring. When addition was complete, the reaction mixture was allowed to warm up to room temperature overnight.

The red, semi-solid mass was poured on to crushed ice, acidified with concentrated hydrochloric acid and extracted with ether. The ethereal solution was washed with water then twice with 4N sodium hydroxide solution. The basic washings were washed with ether then re-acidified. The thiobenzoic acid was extracted into ether then washed with water till neutral. After drying (Na_2SO_4), the ether was evaporated to a volume of 500 ml. Thionyl chloride (238g., 2 moles) was added dropwise under argon.

The reaction mixture was allowed to drip slowly into a 100 ml. flask under vacuum (1mm.) to distill excess thionyl chloride and ether. When these had been removed, the flask was heated at 50-65°/0.1 mm. till no more yellow compound distilled. At this stage, the flask was plunged into a Wood's metal bath at 160° to distill the thiobenzoyl chloride (I)[6].

B.p. 80°/0.1 mm. Yield 51g. (32%).

Thiobenzoylthioglycollic acid (IIa).

Phenyl magnesium bromide was prepared in the usual way from bromobenzene (157g., 1 mole) and magnesium turnings (24g., 1 mole) in anhydrous ether under argon. When the reaction was complete, the solution was cooled to -20° then treated dropwise with carbon disulphide (228g., 3 moles) with stirring. The reaction mixture was allowed to warm up slowly overnight. The red, semi-solid mass was poured on to crushed ice and extracted with ether till the washings were colourless. The ethereal solution was washed with a little saturated sodium bicarbonate solution and the aqueous solutions combined.

Chloroacetic acid (94.5g., 1 mole) was neutralised with sodium bicarbonate then added to the aqueous solution above. The reaction mixture was allowed to stand at 0° for 3 days then acidified with ice-cold concentrated hydrochloric acid. The red precipitate which formed was filtered off and the aqueous solution was extracted with chloroform. The filtrate was dissolved in the

chloroform extract, dried (Na_2SO_4) and evaporated to a volume of 300 ml. Hot petroleum ether (150 ml. 60-80°) was added to the chloroform solution and allowed to cool. The crystals which formed were filtered off to give thiobenzoylthioglycollic acid (IIa)[17] as bright red needles.

(56g., 26%); Mp. 127-128°

Cholest-5-ene-3β-ol thionobenzoate (VIII). (Method i).

Thionbenzoyl chloride (5 ml.) was added to cholesterol 7.8g., 0.02 mole) in pyridine (50 ml.) at 0°. The mixture was left overnight at room temperature then poured into an excess of 2N hydrochloric acid. The aqueous mixture was extracted with ether and the ether solution was washed with water, dried (sodium sulphate) and evaporated. The residue was dissolved in a little benzene and chromatographed on acid washed silica gel (500g.). Elution with light petroleum (40-60°) gave cholest-5-ene-3β-ol thionobenzoate (VIII) (8.60g., 85%) as yellow needles.

M.p. 164-166° (60-80° light petroleum);

$[\alpha]_D$, -5° (C 1.0);

ν_{max}^{nujol}, 1227 cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 256, 228 and 420nm. ($\epsilon$=7,100, 8,000 and 140 respectively);

N.m.r. (τ), 1.90 (m, 2H), 2.67 (m, 3H), 4.60 (m, 2H), 7.30-9.25 (m, 43H).

The above sequence is illustrative of the procedure used when employing thiobenzoyl chloride as a thionobenzoylating reagent. In future preparations, the phase 'work-up as usual' will denote the isolation of a thionobenzoate by an exactly similar procedure to that described above.

Cholest-5-ene-3β-ol thionobenzoate (VIII). Method (iii).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmole) was added to a solution of thiobenzoylthioglycollic acid (2.12g., 10mmole) in anhydrous t.h.f. (100ml.). When effervescence ceased, imidazole (1.36g., 20mmole) was added then the solution was refluxed for 5 mins. Cholesterol (3.86g., 10mmoles) in anhydrous t.h.f. (50ml.) was added and the solution refluxed for a further 10 mins. The reaction mixture was cooled and diluted cautiously with water then extracted with ether. The ethereal solution was washed in turn with water, 2N HCl, satd. sodium bicarbonate, water, then dried (sodium sulphate) and evaporated to give an orange solid. This was dissolved in benzene and chromatographed as above to yield cholest-5-ene-3β-ol thionobenzoate (VIII) (4.5g., 89%) identical to an authentic sample.

The above sequence is illustrative of the procedure used when employing thiobenzoylthioglycollic acid, sodium hydride and imidazole as a thionobenzoylating reagent. In future preparations, the phase 'work-up as usual' will denote the isolation of a thionobenzoate by an

exactly similar procedure to that described above.

Photolysis of cholest-5-ene-3β-ol thionobenzoate (VIII) in cyclohexane.

The thionobenzoate (506mg., 1mmole) in degassed 'Spectrosol' cyclohexane (250ml.) was irradiated with light from a medium pressure mercury lamp using system 'A'. The reaction was followed by observing the disappearance of the thionobenzoate u.v. peaks at 252 and 288nm. After 20 mins., these peaks had completely disappeared and peaks at 228 and 235nm. had appeared. The reaction mixture was extracted with 4N sodium hydroxide. The aqueous solution was treated with 20 volume hydrogen peroxide (5ml.) and allowed to stand for 10 mins. The mixture was extracted with ether then the ether extract was dried (Na_2SO_4) and evaporated to give dibenzoyl disulphide (110mg) as colourless plates, mp. 129-130° (from ethanol).

The cyclohexane solution was washed with water, dried (Na_2SO_4) and evaporated. The residue was chromatographed on grade III alumina (100g.). Elution with light petroleum (40-60°) gave cholesta-3,5-diene (IX) (330mg., 90%) as fine needles mp. 78-80° (from methanol-acetone) identified by direct comparison with an authentic sample.

Photolysis of cholest-5-ene-3β-ol thionobenzoate (VIII) in ethanol.

The thionobenzoate (VIII) (253mg., 0.5mmole) in absolute

ethanol (100ml.) was irradiated as above. When the photolysis was complete, the ethanol was removed *in vacuo* and the residue chromatographed on a 60 x 20 x 0.1cm. silica gel GF_{254} chromatography plate. Elution with petroleum ether, 40-60°/dichloromethane 4:1 gave two major components. The first was cholest-5-ene-3α-thiol benzoate (X) (42.5mg., 17%) mp. 156-157° (from acetone) and the second was cholest-5-ene-3β-thiol benzoate (XI) (32.5mg., 13%) mp. 147-148° (from acetone).

λ_{max}^{EtOH} in each case was 239 and 270nm. (ϵ=11,500 and 8,300 respectively)

The cholest-5-ene-3β-ol thiolbenzoate was identified by comparison with an authentic sample. The cholest-5-ene-3α-ol thiolbenzoate was reduced with lithium aluminium hydride in ether to give the thiol mp. 100-101° (acetone) whose physical constants were identical to those in the literature[27].

Cholest-5-ene-3β-thiol benzoate (XI).

Cholesteryl tosylate (1.0g.) in acetone (20ml.) was refluxed with potassium thiolbenzoate (1.0g.) for 6 hours. The mixture was poured into water and extracted with ether. The ether extract was washed with water, dried and evaporated. The residue was chromatographed on grade III alumina (100g.). Elution with petroleum ether 40-60°/dichloromethane 1:1 gave cholest-5-ene-3β-thiol benzoate (XI) (0.60g.) as fine colourless needles.

M.p. 159-160° (from acetone);

ν_{max}^{nujol}, 1680 cm^{-1};

λ_{max}^{EtOH}, 239 and 270nm. (ε=11,500 and 8,300 respectively);

N.m.r. (τ), 2.0 (m, 2H), 2.48 (m, 3H), 4.54 (m, 1H), 7.50-9.31 (m, 43H).

This was identical to an authentic sample.

Photolysis of cholest-2-ene with thiolbenzoic acid.

Δ^2-cholestene (185mg., 0.5mmole) and thiolbenzoic acid (0.276mg., 2mmole) were irradiated together overnight in ethanol (50ml.) using a medium pressure mercury lamp. The mixture was poured into water and extracted with ether. The ether extract was washed with 1N sodium hydroxide and water then dried (Na_2SO_4) and evaporated. The residue was chromatographed on a 60 x 20 x 0.1cm. silica gel chromatography plate. Elution with petroleum ether, 40-60°/dichloromethane gave four compound all of which showed $\nu_{C=O}$ in the i.r. at 1680cm.$^{-1}$ indicative of a thiolbenzoate. Mass spectrum showed a molecular ion at 510 which corresponds to mono-thiolbenzoates of cholestane. The four compounds must have been therefore 2α, 2β, 3α and 3β-cholestanthiol benzoates.

Photolysis of cholesta-3,5-diene (IX) with thiolbenzoic acid.

Cholesta-3,5-diene (IX) (368mg., 1mmole) and thiobenzoic acid (1.1g., 8mmoles) were irradiated together in

ethanol (100ml.) overnight. The mixture was poured into water and extracted with ether. The ether extract was washed with 1N sodium hydroxide and water then dried (Na_2SO_4), and evaporated. I.r. spectrum of the residue showed $\nu_{C=O}$ at 1680cm.$^{-1}$ and the mass spectrum showed M^+ at 508. This indicated a mixture of monothiolbenzoates which was not characterised further.

Cholestan-3β-ol-thionobenzoate (XIV).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles) was added to a solution of thiobenzoylthioglycollic acid (2.12g., 10mmoles) in anhydrous t.h.f. (100ml.). When effervescence ceased, imidazole (1.36g., 20mmoles) was added then the solution was refluxed for 5 mins. Cholestan-3β-ol (3.88g., 10mmoles) in anhydrous t.h.f. (50ml.) was added and the solution was refluxed for a further 10 mins. Work-up as usual gave cholestan-3β-ol thionobenzoate (XIV) (432mg., 85%) as yellow needles.

M.p. 141-142° (from petroleum ether 60-80°);

$[\alpha]_D$, +3° (C 1.0);

ν_{max}^{nujol}, 1225 and 1235cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 251 and 289nm. ($\epsilon$=7,000 and 7,600 respectively);

N.m.r. (τ), 1.82 (m, 2H), 2.58 (m, 3H), 4.40 (m, 1H), 7.65-9.33 (m, 46H).

This was identical to an authentic sample.

Photolysis of cholestan-3β-ol thionobenzoate (XIV) in ethanol.

The thionobenzoate (XIV) (508mg., 1mmole) in ethanol (250ml.) was irradiated in the usual way with a medium pressure mercury lamp using system 'A'. The reaction was followed by u.v. When the thionoester peak disappeared, the solvent was removed in vacuo and the residue chromatographed on two 60 x 20 x 0.1cm. silica gel GF_{254} plates. Elution with petroleum ether, 40-60°/ dichloromethane 4:1 gave two major products. The first was cholestan-3α-thiol benzoate (105mg., 21%) m.p. 149-151° (from acetone) and the second was cholestan-3β-thiol benzoate (86mg., 17%) m.p. 140-141° (from acetone) identified by comparison with authentic samples.

Photolysis cholestan-3β-ol thionobenzoate (XIV) in the presence of benzaldehyde.

A solution of the thionobenzoate (XIV) (127mg., 0.25mmole) in dichloromethane (50ml.) containing benzaldehyde (1.33g., 12.5mmole) was irradiated in the usual way using a high pressure mercury lamp in system'A'. The reaction was followed by u.v. When the thionoester peak disappeared (21 mins), the solution was shaken with a saturated aqueous ethanolic solution of sodium bisulphite then with water. After drying and evaporation of solvent in vacuo the product was chromatographed on a 60 x 20 x 0.1cm. silica gel GF_{254} plate. Elution with dichloromethane gave benzoin (XXVII) (48.5mg., 93%) as white prisms.

M.p. 136-137° (from methylated spirit);

ν_{max}^{nujol}, 1680, 3400cm.$^{-1}$;

N.m.r. (τ), 2.06 (dd, 2H), 2.64 (m, 8H), 4.01 (s, 2H), 5.56 (broad s, 1H, exchangeable with D_2O.);

and cholestanol (XXVI) (92mg., 95%) as white leaflets.

M.p. 140-141° (from EtOH);

$[\alpha]_D^{25}$, + 27.6°;

ν_{max}^{nujol}, 3400cm.$^{-1}$

These constants were identical to authentic samples.

Photolysis of cholestan-3β-ol thionobenzoate (XIV) in the presence of p-nitrobenzaldehyde.

A solution of the thionobenzoate (XIV) (127mg., 0.25 mmole) was photolysed under identical conditions to those above. The reaction was followed by t.l.c. When the thionoester disappeared (1hr 20mins), the reaction was worked up in the same way to give cholestan-3β-ol benzoate (XXXI) (53mg., 43%) as white plates.

M.p. 136-137° (from ethyl acetate);

$[\alpha]_D^{25}$, + 21.2°;

ν_{max}^{nujol}, 1720cm.$^{-1}$;

N.m.r. (τ), 1.92 (m, 2H), 2.50 (m, 3H), 5.0 (m, 1H), 7.7-9.33 (m, 46H);

and cholestan-3β-ol (XXVI) (47mg., 48%), identical to authentic samlpes.

1-Phenyl-propan-2-ol (XXXVII b).

Sodium borohydride (7.6g., 0.2 mole) was added portion-wise to a cooled (water-bath) solution of 1-phenyl-propan-2-one (13.4g., 0.1 mole)[33] in methanol (100ml.) containing sodium hydroxide (c.a. 1g.). The reaction mixture was refluxed for 10 mins. then allowed to stand overnight. The solvent was evaporated to small volume and the excess sodium borohydride was destroyed with ice and 2N hydrochloric acid. The product was extracted with ether, and the ethereal solution was washed with saturated sodium bicarbonate solution then water. Drying (anh. sodium sulphate) followed by evaporation of the solvent left the product as a colourless oil. This was distilled in vacuo to give 1-phenyl-propan-2-ol (XXXVII b) (11.9g., 84%) as a colourless oil.

B.p. 82-83°/3mm. (Literature[49], 95°/7mm.);

ν_{max}^{film}, 3430cm.$^{-1}$;

N.m.r. (τ), 2.74 (s, 5H), 6.04 (m, 1H), 7.30 (d, 2H, J=6 c/s.); 8.07 (s, 1H) exchangeable with D_2O), 8.81 (d, 3H, J=6 c/s.).

1-Phenyl-butan-2-ol (XXXVII c).

Reduction of 1-phenyl-butan-2-one (14.8g., 0.1 mole) with sodium borohydride in an analogous way to above gave 1-phenyl-butan-2-ol (XXXVII c) (13.4g., 89%) as a colourless oil.

B.p. 75-6°/2½mm. (Literature[50], 76-78°/3mm.);

ν_{max}^{film}, 3430cm.$^{-1}$;

N.m.r. (τ), 2.73 (s, 5H), 6.04 (m, 1H), 7.29 (ABXm, 2H),
8.11 (s, 1H, exchangeable with D_2O),
8.54 (q, 2H, J=6 c/s), 9.04 (t, 3H, J=6 c/s).

3-methyl-1-phenyl-butan-2-ol (XXXVII d).

Reduction of 3-methyl-1-phenyl-butane-2-one (4.05g., 0.025 mole) with sodium borohydride in an analogous way to above gave 3-methyl-1-phenyl-butan-2-ol (XXXVII d) (3.15g., 77%).

B.p. 80-85°/4mm. (Literature[29], 118-122/15mm.);

ν_{max}^{film}, 3430cm.$^{-1}$;

N.m.r. (τ), 2.73 (s, 5H), 6.41 (m, 1H), 7.25 (m, 2H),
8.37 (s, 1H, exchangeable with D_2O),
8.40 (m, 1H), 9.01 (d, 6H, J=6½ c/s.).

3,3-Dimethyl-1-phenyl-butan-2-ol (XXXVII e)[34]

Magnesium turnings (14.4g., 0.6 mole) were covered with anhydrous ether (c.a. 20ml.) under nitrogen. Tertiary-butyl chloride (½ml.) was added and the reaction was started by grinding with a glas rod. When the ether was refluxing briskly, tertiary-butyl chloride (55.5g., 0.6 mole) in anhydrous ether (75ml.) was added dropwise with stirring over 6hrs. The reaction was stirred for an additional 10mins., then cooled to 0°.

Phenylacetaldehyde (36g., 0.3 mole) in an equal volume of ether was added over 2hrs., with stirring and keeping the temperature below 5°. The reaction mixture was decomposed by ice, cautiously, then by 3N sulphuric acid. The aqueous layer was extracted with ether, then the combined ether extracts were washed in turn with satd. sodium bicarbonate solution then water. The solution was dried (sodium sulphate) and evaporated in vacuo. Distillation of the resulting oil gave 3,3-dimethyl-1-phenyl-butan-2-ol (XXXVII e) (67g., 63%).

B.p. 66-73°/1mm. (Literature[34], 78.5/2mm);

ν_{max}^{film}, 3450cm.$^{-1}$;

N.m.r. (τ), 2.74 (s, 5H), 6.59 (dd, 1H, J_{ax}=2.25 c/s., J_{bx}=10.5 c/s.), 7.33 (m, 2H, J_{ab}=13.5 c/s., J_{ax}=2.25 c/s, J_{bx}=10.5 c/s.), 8.49 (s, 1H, exchangeable with D_2O), 9.01 (s, 9H).

1,2-diphenyl ethanol (XXXVII f)

Reduction of deoxybenzoin (19.6g., 0.1 mole) with sodium borohydride in an analogous way to above gave 1,2-diphenyl ethanol (15.8g., 80%) as white needles.

B.p. 166-169/10mm.[51];

M.p. 64-65 (from ethanol)[52];

ν_{max}^{nujol}, 3310cm.$^{-1}$;

N.m.r. (τ), 2.68 (s, 5H), 2.77 (s, 5H), 5.13 (t, 1H, J=6½ c/s.), 3.02 (d, 2H, J=6½ c/s.).

2-Phenylethyl thionobenzoate (XXXVIII a).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles) was added cautiously to thiobenzoylthioglycollic acid (2.12g., 10mmoles) in anhydrous t.h.f. (100ml.) with stirring. When effervescence ceased, imidazole (1.36g., 10mmoles) was added, portionwise, with care, followed by 2-phenylethanol (1.22g., 10mmoles). The reaction mixture was refluxed for 5 mins. then cooled. Ice was added cautiously then, after dilution with cold water, the aqueous mixture was extracted with ether. The combined ethereal extracts were washed with water, 2N hydrochloric acid, saturated sodium bicarbonate solution, then water. The solution was dried (Na_2SO_4) then the solvent was evaporated to give a red oil. This was chromatographed three times on 200g. grade III alumina, using 40-60° petroleum ether as eluent. With the aid of a fraction collector, it was possible to separate 2-phenylethyl thionobenzoate (XXXVIII a) (2.0g., 83%) as yellow oil from a red impurity.

ν_{max}^{film}, 1230cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 248, 288 and 420nm. ($\epsilon$=6,600, 9,600 and 120 respectively);

N.m.r. (τ), 1.83 (dd, 2H), 2.67 (m, 8H), 5.14 (t, J= 3½ c/s., 2H), 6.86 (t, J=3½ c/s., 2H).

This was identical to an authentic sample.

1-Phenyl-propan-2-ol thionobenzoate (XXXVIII b).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles), thiobenzoylthioglycollic acid (2.12g., 10mmoles), imidazole (1.36g., 10mmoles) and 1-phenyl-propan-2-ol (XXXVII b) (1.36g., 10mmoles) were reacted in anhydrous t.h.f. (100ml.) as described above. Work-up as usual gave 1-phenyl-propan-2-ol thionobenzoate (XXXVIII b) (1.4g., 55%) as a yellow oil.

ν_{max}^{film}, 1250cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 252, 289 and 417nm. ($\varepsilon$=9,600, 11,530 and 130 respectively);

N.m.r. (τ) 1.85 (dd, 2H), 2.64 (m, 8H), 3.97 (m, 1H) 6.88 (m, 2H), 8.58 (d, J=6½ c/s, 3H)

Analysis, found C, 74.93%, H, 6.17%, S, 12.70%;
$C_{16}H_{16}OS$ requires C, 75.00%, H, 6.25%, S, 12.50%.

1-Phenyl-butane-2-ol thionobenzoate (XXXVIII c).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles), thiobenzoylthioglycollic acid (2.12g., 10mmoles), imidazole (1.36g., 10mmoles) and 1-phenyl-butan-2-ol (XXXVII c) (1.50g., 10mmoles) were reacted in anhydrous t.h.f. (100ml.) as described above. Work-up as usual gave 1-phenyl-butan-2-ol thionobenzoate (XXXVIII c) (1.78g., 66%) as a yellow oil.

ν_{max}^{film}, 1250cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 253, 291 and 421nm. ($\varepsilon$=9,725, 11,250 and 120 respectively);

N.m.r. (τ) 1.82 (dd, 2H), 2.64 (m, 8H), 4.05 (m, 1H), 6.89 (m, 2H), 8.23 (m, 1H), 9.03 (t, 3H);

Analysis, found C, 75.30%, H, 6.72%, S, 11.69%.

$C_{17}H_{18}OS$ requires C, 75.56%, H, 6.67%, S, 11.86%.

3-Methyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII d).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles), thiobenzoylthioglycollic acid (2.12g., 10mmoles), imidazole (1.36g., 10mmoles) and 3-methyl-1-phenyl-butan-2-ol (XXXVII d) (1.64g., 10mmoles) were reacted in anhydrous t.h.f. (100ml.) as described above. Work-up as usual gave 3-methyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII d) (1.70g., 61%) as a yellow oil.

ν_{max}^{film}, 1240cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 256, 293 and 420nm. ($\varepsilon$=9,930, 11,180 and 128 respectively);

N.m.r. (τ) 1.78 (dd, 2H), 2.60 (m, 8H), 4.01 (m, 1H), 6.88 (m, 2H), 7.90 (m, 1H), 8.93 (m, 6H);

Analysis, found C, 76.37%, H, 6.99%, S, 11.10%.

$C_{18}H_{20}OS$ requires C, 76.05%, H, 7.04%, S, 11.26%.

3,3-Dimethyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII e).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles), thiobenzoylthioglycollic acid (2.12g., 10mmoles), imidazole (1.36g., 10mmoles) and 3,3-dimethyl-1-phenyl-butan-2-ol (XXXVII e) (1.78g., 10mmoles) were reacted in anhydrous t.h.f. (100ml.) as described above. Work-up as usual gave 3,3-dimethyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII e) (1.04g., 35%) as yellow needles.

M.p. 51-52° (from methanol);

ν_{max}^{nujol}, 1230cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 254, 293 and 421nm. ($\varepsilon$=9,940, 10,500 and 125 respectively);

N.m.r. (τ) 1.87 (dd, 2H), 2.68 (m, 8H), 3.89 (m, 1H), 6.95 (m, 2H), 8.93 (s, 9H);

Analysis, found C, 76.60%, H, 7.57%, S, 11.00%.
$C_{19}H_{22}OS$ requires C, 76.71%, H, 7.38%, S, 10.74%.

1,2-Diphenylethyl thionobenzoate (XXXVIII f).

Sodium hydride (1g., 50% dispersion in mineral oil, 20mmoles) thiobenoylthioglycollic acid (2.12g., 10mmoles), imidazole (1.36g., 10mmoles) and 1,2-diphenylethanol (XXXVII f) (1.98g., 10mmoles) were reacted in anhydrous t.h.f. (100ml.) as described above. Work-up as usual

gave 1,2-diphenylethyl thionobenzoate (XXXVIII f) (2.8g., 87.5%) as yellow needles.

M.p. 65-66° (from methanol);

ν_{max}^{nujol}, 1230cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 250, 294 and 408nm. ($\epsilon$=9,700, 11,000 and 120 respectively);

N.m.r. (τ) 1.78 (dd, 2H), 2.68 (m, 13H), 3.14 (m, 1H), 6.59 (m, 2H);

Identical to an authentic sample.

Photolysis of 2-phenylethyl thionobenzoate (XXXVIII a).

Anhydrous dichloromethane (400ml.) was degassed by boiling and passing argon for 30 mins. Thionobenzoate (XXXVIII a) (968mg., 4mmoles) was added followed by triethylamine (1.0ml., 8mmoles). The mixture was irradiated with light from a medium pressure mercury lamp using system 'A'. The reaction was followed by u.v. When the reaction was complete, the solution was washed in turn with saturated sodium bicarbonate solution, 2N hydrochloric acid and water, then dried (Na_2SO_4). The solvent was removed by distillation through a short glass column at atmospheric pressure. Chromatography on silica gel GF_{254} plates with 40-60° petroleum ether gave styrene (XXXIX a) (300mg., 71%), identical to an authentic sample.

Photolysis of 1-phenyl-propan-2-ol thionobenzoate (XXXVIII b)

The thionobenzoate (XXXVIII b) (1.024g., 4mmoles) was irradiated in degassed dichloromethane (400ml.) containing triethylamine (0.7ml. 1.2mmoles) using the conditions described above. After washing, the solvent was removed by distillation through a short column of acid-washed silica gel. Elution with 40-60° petroleum ether gave trans-1-phenyl-prop-1-ene (XXXIX b) (255mg., 55%) as a colourless oil, identical with an authentic sample, and unchanged starting material (153mg., 15%). Elution with dichloromethane gave 1,2-diphenyl-3-hydroxy-butan-1-thione (XL b) (10% from absorption maximum at 550nm. in reaction mixture) as an unstable purple oil.

ν_{max}^{film}, 1225cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 229, 234, 248, 316 and 553nm. (ε=8,400, 7,600, 4,600, 12,600 and 76 respectively);

N.m.r. was rather inconclusive, especially in the methyl region which showed a multiplet.

Mass spec. showed a weak peak at 256 and a strong M-18 peak at 238.

The ratio of thioketone/styrene = 15/85.

Photolysis of 1-phenyl-butan-2-ol thionobenzoate (XXXVIII c).

The thionobenzoate (XXXVIII c) (1.08g., 4mmoles) was irradiated under the conditions described above. Work-up in the same way gave trans-1-phenyl-but-1-ene (XXXIX c)

(270mg., 51%) as a colourless oil, identical with an authentic sample, unchanged starting material (101mg., 9.5%) and 1,2-diphenyl-3-hydroxy-pentan-1-thione (XL c) (248mg., 20%) as purple needles.

M.p. 74-77° (from degassed 30-40° petroleum ether under argon);

ν_{max}^{nujol}, 1220, 3300cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 229, 234, 250, 316 and 553nm., (ε=8,100, 7,600, 4,600, 12,650 and 94 respectively);

N.m.r. (τ) 2.05 (dd, 2H), 2.67 (m, 8H), 5.00 (d, J=9 c/s., 1H), 5.43 (m, 1H), 7.23 (broad s, exchangeable with D_2O, 1H), 8.63 (m, 2H), 9.06(t, J=6½ c/s., 3H);

Analysis, found C, 75.36%, H, 6.47%, S, 11.87%.
$C_{17}H_{18}OS$ requires C, 75.56%, H, 6.67%, S, 11.85%.

Ratio of thioketone/styrene = 28/72.

Photolysis of 3-methyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII d)

The thionobenzoate (XXXVIII d) (1.136g., 4mmoles) was irradiated under the condition described above. Work-up in the same way gave trans-3-methyl-1-phenyl-but-1-ene (XXXIX d) (240mg., 41%), identical with an authentic sample, unchanged starting material (180mg., 17.5%) and 1,2-diphenyl-3-hydroxy-4-methyl-pentan-1-thione (XL d) (334mg., 29.4% as purple needles.

M.p. 72-74° (from degassed 30-40° petroleum ether under argon);

ν_{max}^{nujol}, 1220, 3450cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 229, 234, 247, 316 and 553nm. (ε=9,000, 8,500, 5,050, 12,650 and 102 respectively);

N.m.r. (τ) 2.06 (dd, 2H), 2.66 (m, 8H), 4.83 (d, J=9½ c/s., 1H), 5.45 (dd, J=9½ c/s., and 2½ c/s., 1H), 3.51 (broad s, exchangeable with D_2O, 1H), 8.48 (m, 1H), 9.04 (d, J=6 c/s.);

Analysis, found C, 75.42%, H, 6.95%, S, 11.19%.
$C_{18}H_{20}OS$ requires C, 76.05%, H, 7.04%, S, 11.27%.

Ratio of thioketone/styrene = 41.5/58.5.

Photolysis of 3,3-dimethyl-1-phenyl-butan-2-ol thionobenzoate (XXXVIII e)

The thionobenzoate (XXXVIII e) (1.192g., 4mmoles) was irradiated under the conditions described above. Work-up in the same way gave trans-3,3-dimethyl-1-phenyl-but-1-ene (XXXIX e) (177mg., 27%) as a colourless oil, identical with an authentic sample, unchanged starting material (250mg., 21%) and 4,4-dimethyl-1,2-diphenyl-3-hydroxy-pentan-1-thione (XL e) (443mg., 37%) as a purple oil.

ν_{max}^{film}, 1215 and 3460cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 230, 235, 247, 314 and 554nm. (ε=8,000, 7.550, 5,100, 10,000 and 99 respectively);

N.m.r. (τ) 2.12 (dd, 2H), 2.67 (m, 8H), 4.57 (d, J=8 c/s., 1H), 5.66 (d, J=8 c/s., 1H), 6.88 (broad s, exchangeable with D_2O, 1H), 9.14 (s, 9H);

Analysis, found C, 76.51%, H, 7.38%, S, 10.74%.

$C_{19}H_{22}OS$ requires C, 76.44%, H, 7.18%, S, 10.81%.

Ratio of thioketone/styrene = 58/42.

Photolysis of 1,2-diphenylethyl thionobenzoate (XXXVIII f).

The thionobenzoate (XXXVIII f) (1.272g., 4mmoles) was irradiated under the conditions described above. When photolysis was complete, the solvent was removed in vacuo and the residue was treated with excess of methanolic 2,4-dinitrophenylhydrazine. After warming for 5 mins. then cooling to 0°, the 2,4-dinitrophenylhydrazone precipitate was filtered off to give orange platelets (0.63g., 65%) m.p. 236° (from ethyl acetate). This was identified as benzaldehyde 2,4-dinitrophenylhydrazone by direct comparison with an authentic sample.

The filtrate from above was concentrated then chromatographed on silica gel GF_{254}. Elution with dichloromethane gave a second 2,4-dinitrophenylhydrazone (144mg., 10%) m.p. 199° (from ethyl acetate). This was identified as desoxybenzoin 2,4-dinitrophenylhydrazone from the mass spectrum (M^+ 376) and by comparison with an authentic sample.

p-Nitrophenylhydroxamic acid chloride (XLIII).

p-Nitrobenzaldoxime (3.5g) in dry ethyl acetate (20ml.) was treated with dry chlorine gas at 0° for 2 hours. The ethylacetate was removed in vacuo to give p-nitrophenylhydroxamic acid chloride (3.0g) as pale yellow needles.

M.p. 126-128° (from chloroform);

ν_{max}^{nujol}, 870, 955, 1015, 1600 and 3280cm.$^{-1}$.

Oxathiazole (XLI d).

Triethylamine (0.06ml., 0.45mmoles) in anhydrous ether (1ml) was added over ½hr. to a stirred suspension of thioketone (XL d) (128mg., 0.45mmoles) and hydroxamic acid chloride (XLIII) (90mg., 0.45mmoles) in anh. ether (5ml.). The mixture was dissolved in chloroform and washed thoroughly with water. After drying (Na_2SO_4), the solution was reduced in volume then chromatographed on a 20 x 60 x 0.1cm. silica gel GF_{254} plate. Elution with dichloromethane/40-60° petroleum ether 1:1 gave oxathiazole (XLI d) (122mg., 60%) as fine white needles:

M.p. 149-151° (benzene/60-80° petroleum ether);

ν_{max}^{nujol}, 715, 875, 1290, 1360, 1390, 3450cm.$^{-1}$;

λ_{max}^{EtOH}, 281 and 337nm. (ϵ=14,500 and 4,370 respectively);

N.m.r. (τ) 2.0 (dd, J=25, 9c/s., 4H), 2.7 (m, 8H), 3.23 (m, 2H), 4.03 (m, 2H), 7.81 (broad d, J=4 c/s., exchangeable with D_2O, 1H),

8.55 (m, 1H), 9.16 (dd, J=7½, 8 c/s., 6H).

Analysis, found C, 67.18%, H, 5.50%, N, 6.34%, S, 7.10%.
$C_{25}H_{24}O_4SN_2$ requires C, 66.96%, H, 5.36%, N, 6.25%, S, 7.13%;

and another compound as fine yellow needles (80mg., 39%) which had similar properties.

M.p. 153-157° (benzene/60-80° petroleum ether);

ν_{max}^{nujol}, 715, 760, 770, 865, 880, 1025, 1290, 1355, 1385, 3570cm.$^{-1}$;

λ_{max}^{EtOH}, 280, 335 and 377nm. (ϵ=14,700, 4,180 and 567 respectively);

N.m.r. (τ) 1.99 (dd, J=9½, 27 c/s., 4H), 2.65 (m, 8H), 2.95 (m, 2H), 6.07 (m, 2H), 7.19 (d, J=4 c/s., exchangeable with D_2O, 1H), 8.66 (m, 1H), 9.20 (dd, J=6½, 9 c/s., 6H);

Analysis, found C, 66.25%, H, 5.36%, N, 6.30%, S, 7.10%.
$C_{25}H_{24}O_4SN_2$ requires C, 66.96%, H, 5.36%, N, 6.25%, S, 7.13%.

Trans-1-phenyl-prop-1-ene (XXXIX b).

Phosphoryl chloride (20ml.) was added dropwise, with stirring, to a solution of 1-phenyl-propan-2-ol (13.6g., 0.1 moles) in pyridine (200ml.). The reaction mixture was heated under gentle reflux till analytical g.l.c. showed no chloride present. The solution was cooled

and poured on to crushed ice and the product was extracted with ether. The combined ethereal layers were washed with 3N HCl, saturated $NaHCO_3$ and water. After drying (Na_2SO_4) and evaporation of solvent, the crude product was distilled on a spinning band column to give trans-1-phenyl-prop-1-ene (XXXIX b) (7.9g., 68%).

B.p. 73-74°/20mm.[41];

ν_{max}^{film}, 694, 736, 812, 948, 962, 980, 1445, 1495, 1502, 1604cm.$^{-1}$;

λ_{max}^{EtOH}, 250 (17,300)[41];

N.m.r. (τ) 2.73, (s, 5H), 3.66 (m, J_{AB}=16 c/s, 2H), 8.11 (d, J=4.5 c/s., 3H);

G.l.c., retention time (column temperature, 100°; flow rate, 100ml./min.), 7.6mins.

Trans-1-phenyl-but-1-ene (XXXIX c).

In a analogous manner to that described above, trans-phenyl-but-1-ene (XXXIX c) was prepared in 57% yield.

B.p. 91-92°/23mm.[53];

ν_{max}^{film}, 701, 727, 753, 780, 979, 992, 1080, 1385, 1458, 1467, 1502, 1600;

λ_{max}^{EtOH}, 250nm. (ϵ=16,700)[54];

N.m.r. (τ) 2.71 (s, 5H), 3.65 (m, J_{AB}=16 c/s., 2H), 7.74 (m, 2H);

G.l.c., retention time (column temperature, 100°, flow rate, 100ml./min.), 11.4mins.

Trans-3-methyl-1-phenyl-but-1-ene (XXXIX d).

In an analogous manner to that described above, trans-3-methyl-1-phenyl-but-1-ene (XXXIX d) was prepared in 52% yield as a colourless oil.

B.p. 90-91°/13mm.[55];

ν_{max}^{film}, 704, 761, 982, 1394, 1460, 1477, 1502, 1604;

λ_{max}^{EtOH}, 250nm. (ε=16,800)[55];

N.m.r. (τ) 2.70 (s, 5H), 3.74 (m, J_{AB}=16 c/s., 2H), 7.57 (m, 1H) 8.90 (d, J=7 c/s., 6H);

G.l.c., retention time (column temperature, 100°, flow rate, 100ml./min.) 14.0 mins.

Trans-3,3-dimethyl-1-phenyl-but-1-ene (XXXIX e).

In an analogous manner to that described above, trans-3,3-dimethyl-1-phenyl-but-1-ene (XXXIX e) was prepared in 43% yield as a colourless oil.

B.p. 90-91°/10mm.[55];

ν_{max}^{film}, 695, 748, 970, 1270, 1368, 1452, 1467, 1480, 1498, 1604cm.$^{-1}$;

λ_{max}^{EtOH}, 251nm. (ε=14,400);

N.m.r. (τ) 2.82 (m, 5H), 3.72 (m, J_{AB}=16 c/s., 2H), 8.89 (s, 9H);

G.l.c., retention time (column temperature 100°, flow rate 100ml./min.), 15.6 mins.

Cis-1-phenyl-prop-1-ene.

Quinoline (.10ml.) was added to a suspension of 5% palladium on barium sulphate (1.5g.) in ethyl acetate (300ml.). 1-Phenyl-prop-1-yne (11.6g., 0.1 moles) was added and the mixture was hydrogenated in the usual way. Absorption of hydrogen ceased abruptly when 0.1 moles had been taken up. The solution was filtered to remove the catalyst and the solvent was evaporated in vacuo. Distillation of the residue on a 15cm. Vigreux Column gave cis-1-phenyl-prop-1-ene (8.9g., 76%).

B.p. 69-70°/28mm.[41, 57];

ν_{max}^{film}, 702, 769, 808, 917, 1372, 1445, 1495, 1604cm.$^{-1}$;

λ_{max}^{EtOH}, 242nm. (ϵ=13,800)[41];

N.m.r. (τ) 2.80 (s, 5H), 3.52 (m, J_{AB}=12 c/s., 1H), 4.22 (m, J_{AB}=12 c/s., 1H), 8.13 (dd, J_{AX}= 1½ c/s., J_{BX}=7 c/s., 3H);

G.l.c., retention time (column temperature 100°, flow rate 100ml./min.), 5.2 mins.

Cis-1-phenyl-but-1-ene.

Using an analogous method to above, cis-1-phenyl-but-1-yne gave cis-1-phenyl-but-1-ene (69%) as a colourless oil.

B.p. 84-85°/23mm.[53];

ν_{max}^{film}, 712, 774, 782, 813, 932, 1041, 1080, 1458, 1470, 1502, 1604cm.$^{-1}$;

λ_{max}^{EtOH}, 242nm. (ϵ=11,800)[58];

N.m.r. (τ) 2.78 (s, 5H), 3.62 (m, J_{AB}=12 c/s., 1H), 4.39 (m, J_{AB}=12 c/s., 1H), 7.67 (m, 2H), 8.99 (t, J=7½ c/s., 3H);

G.l.c., retention time (column temperature 100°, flow rate, 100ml./min.), 7.6 mins.

Oxidation of 1,2-diphenyl-3-hydroxy-4-methyl-pentane-1-thione (XL d).

The thione (XL d) (986mg., 3½mmoles) in anhydrous dichloromethane (500ml.) was treated with ozone at room temperature. When the purple colour disappeared, the solvent was removed in vacuo. The residue was chromatographed on two 60 x 20 x 0.1cm. silica gel GF_{254} chromatography plates to give 1,2-diphenyl-3-hydroxy-4-methyl-pentan-1-one (XLVII a) (573mg., 62%) as white prisms.

M.p. 120-123° (CH_2Cl_2/60-80° petroleum ether);

ν_{max}^{nujol}, 1678, 3300cm.$^{-1}$;

N.m.r. (τ) 2.01 (dd, 2H), 2.65 (m, 8H), 5.20 (d, J=8½ c/s., 1H), 5.73 (dd, J=2¾, 8½ c/s., 1H), 6.83 (s, exchangeable with D_2O, 1H), 8.54 (m, 1H), 9.04 (dd, J=2¾, 6½ c/s., 6H).

This was then benzoylated with benzoyl chloride (1ml.) and pyridine (5ml.) in the usual way to give 1,2-diphenyl-3-hydroxy-4-methyl-pentan-1-one benzoate (XLVII b) (565mg., 71%) as white needles.

M.p. 162-165° (methanol);

ν_{max}^{nujol}, 1675, 1715cm.$^{-1}$;

N.m.r. (τ) 1.96 (m, 4H), 2.64 (m, 14H), 3.86 (dd, J=2½, 10 c/s., 1H), 4.85 (d, J=10 c/s., 1H), 8.25 (m, 1H), 9.01 (dd, J=6 c/s., 6 c/s., 6H);

Analysis, found C, 80.88, H, 6.53

$C_{25}H_{24}O_3$ requires C, 80.64, H, 6.45.

Baeyer-Villiger rearrangement of (XLVII b).

Ketone (XLVII b) (372mg., 1mmole) and m-chloroperbenzoic acid were heated overnight in anh. dichloroethane 10ml. at 100°. The reaction mixture was cooled and the solid mass which formed was dissolved in a small amount of chloroform. This was then chromatographed on two 60 x 20 x 0.1cm. silica gel GF_{254} plates. Elution with dichloromethane/40-60° petroleum ether (1:1) gave 1-phenyl-3-

methyl-butan-diol dibenzoate (XLIX) (188mg., 49%) as a colourless oil.

$\nu_{max}^{chloroform}$, 1710, 1720cm.$^{-1}$;

N.m.r. (τ) 2.07 (m, 4H), 2.62 (m, 11H), 3.76 (d, J=8 c/s., 1H), 4.39 (dd, J=4, 8 c/s., 1H), 8.18 (m, 1H), 8.89 (dd, 6H).

This was then treated with lithium aluminium hydride in anhydrous ether in the usual way to give threo-3-methyl-1-phenyl-butan-1,2-diol (L) (67mg., 77%).

M.p. 74-75° (hexane/ether).

This was identical to an authentic sample.

Threo-3-methyl-1-phenyl-butan-1,2-diol.

A suspension of silver acetate (1.84g., 11mmoles), trans-3-methyl-1-phenyl-but-1-ene (0.73g., 5mmoles) and iodine (1.27g., 10mmoles) were stirred vigourously for 1½ hours at room temperature in acetic acid (33ml.). The mixture was treated with water (0.2ml.) in acetic acid (5ml.) and heated under reflux for 1 hour. After cooling and filtering, the volatiles were removed at 100° under vacuum. The residue was dissolved in cyclohexane and the solution filtered and stripped of solvent to yield 1.36g. of amber oil. This was dissolved in anhydrous ether (20ml.) and stirred while adding l.a.h. (0.5g.) in small portions. After stirring for a further 10 mins., the excess reagent was destroyed with ethyl acetate and the crude product

isolated in the usual way to give an oil which, on treatment with hexane/ether, afforded threo-3-methyl-1-phenyl-butan-1,2-diol (0.64g., 71%).

M.p. 74-75°.

Erythro-3-methyl-1-phenyl-butan-1,2-diol.

The intermediate amber oil described above was cleaved with 2N NaOH in water to give a non-hydroxyllic oil, probably an epoxide. This was stirred overnight with 0.3ml. formic acid in 10ml. water. Extraction with ether then drying ($MgSO_4$) and evaporating solvent gave erythro-3-methyl-1-phenyl-butan-1,2-diol (0.52g., 58%) which crystallised on standing.

M.p. 102-103° (ether/hexane).

Photolysis of thionobenzoates (XXXVIII a-e) at -78°.

The thionobenzoate (1mmole) in anhydrous degassed dichloromethane (400ml.) at -78° was irradiated, using system 'B', with light from a high pressure mercury lamp. The apparatus was arranged so that the cooling jacket of the lamp did not dip into the solution. The reaction was followed by u.v. When the reaction was complete, formation of the thioketone was induced by letting the solution warm up. The reaction was monitored by u.v. and as soon as the 550nm. peak showed no further increase, the solution was washed with sodium bicarbonate solution and

water. Work-up as previously described for the room temperature experiments gave the following results.

XXXVIII	Yield of thioketone %	Yield of styrene %
(a) R=H	10%*	81%
(b) R=Me	32%*	61%
(c) R=Et	45%	52%
(d) R=i-Pr	55%	42%
(e) R=t-Bu	75%	25%

* Estimated from u.v. spectrum of reaction mixture.

Attempted trapping of intermediate (XLVII d) with diazomethane.

Thionoester (XXXVIII d) (1.3g., 4.5mmoles) in anhydrous dichloromethane (800ml.) was irradiated at -78° as described above. When the reaction was complete, a solution of excess idazomethane in ether was added to the colourless solution which was then allowed to warm up to 0° overnight. Removal of the solvent in vacuo at room temperature gave an oil which was chromatographed on four silica gel GF_{254} plates. Elution with dichloromethane/ 40-60° petroleum ether 1:3 gave styrene (XXXIX d) (450mg., 67%), 1,2-diphenylvinyl methyl sulphide (LVII) (112mg., 11%), identical to an authentic sample, and methyl thiolbenzoate (LVIII) (259mg., 35%).

Meso-hydrobenzoin-mono-thionobenzoate (LX a).

Sodium hydride (3.0g., 50% dispersion in mineral oil, 0.06 moles) was added to a solution of meso-hydrobenzoin (2.14g., 0.01 moles) in anhydrous t.h.f. (250ml.) under dry nitrogen. The mixture was refluxed for 2 hours then cooled. Thiobenzoylthioglycollic acid (2.4g., 0.011 moles) was added portionwise with stirring. When addition was complete, the reaction mixture was warmed for 10 mins., cooled and cautiously diluted with water. The solution was extracted with ether, then the combined ethereal layers were washed with water. After drying (Na_2SO_4), the solvent was evaporated *in vacuo* to give an orange oil. This was chromatographed on grade V alumina (200g.). Elution with 40-60° petroleum ether gave meso-hydrobenzoin-bis-thionobenzoate (LX c) (0.55g., 12%). Elution with dichloromethane gave meso-hydrobenzoin-mono-thionobenzoate (LX a) (2.20g., 66%) as fine yellow needles.

M.p. 107-109° (CH_2Cl_2/40-60° petroleum ether);

ν_{max}^{nujol}, 1227, 3500cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 256, 286, 292 and 419nm. (ϵ=8,400, 9,400, 9,700 and 108 respectively);

N.m.r. (τ) 1.83 (m, 2H), 2.68 (m, 13H), 3.15 (d, 1H, J=5½ cps.), 4.64 (d, 1H, J=5½ cps.), 7.94 (broad s, 1H, exchangeable with D_2O);

Analysis, found C, 75.27%, H, 5.46%, S, 9.27%.

$C_{21}H_{18}O_2S$ requires C, 75.40%, H, 5.39%, S, 9.58%.

Meso-hydrobenzoin-mono-benzoate-mono-thionobenzoate (LX b).

Benzoyl chloride (213mg., 0.18ml., 1.52mmoles) was added dropwise to a stirred solution of meso-hydrobenzoin-mono-thionobenzoate (460mg., 1.38mmoles) in anhydrous pyridine (2.5ml.). When addition was complete, the reaction was stirred for 30 mins. Work-up in the usual way yielded a yellow-orange oil which was chromatographed on a 60 x 20 x 0.1cm. silica gel GF_{254} preparative plate (dichloromethane/40-60° petrol, 1:3) to give meso-hydrobenzoin-mono-benzoate-mono-thionobenzoate (LX b) (452mg., 75%) as yellow needles.

M.p. 205-206.5° (methanol);

ν_{max}^{nujol}, 1225, 1710cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 252, 277, 286, 293 and 419nm. (ε=8,850, 8,850, 10,500, 10,700 and 123 respectively);

N.m.r. (τ) 1.92 (m, 4H), 2.70 (m, 16H), 2.85 (d, 1H, J=5 cps.), 3.32 (d, 1H, J=5 cps.);

Analysis, found C, 76.71%, H, 5.09%, S, 7.25%.

$C_{28}H_{22}O_3S$ requires C, 76.75%, H, 5.05%, S, 7.31%.

Meso-hydrobenzoin-bis-thionobenzoate (LX c).

Thiobenzoylthioglycollic acid (1.7g., 8.0mmoles) in anhydrous t.h.f. (50ml.) was treated with sodium hydride (800mg., 50% dispersion in mineral oil, 16mmoles). When effervescence ceased, imidazole (1.1g., 8mmoles) was added followed by meso-hydrobenzoin (856mg., 4mmoles). The mixture was refluxed for 10 mins. then diluted with water. The material which separated was filtered then washed with water. The filtrate was extracted with ether and the ethereal layer was washed in turn with water, 6N HCl, satd. bicarb., water, then dried (anh. Na_2SO_4) and evaporated. The residue was combined with the filtered material then dissolved in chloroform. The solution was pre-adsorbed on to grade II alumina then chromatographed on a 200gm. column of grade III alumina using 60-80° petrol as eluent. This gave meso-hydrobenzoin-bis-thionobenzoate (LX c) (1.2g., 65%) as yellow needles.

M.p. 193-195°, resolidifies at 197° then remelts at 259-263° (from methanol);

ν_{max}^{nujol}, 1215cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 254, 282 and 420nm. ($\varepsilon$=16,900, 22,200 and 265 respectively);

N.m.r. (τ) 1.90 (m, 4H), 2.78 (m, 17H), 3.36 (d, 1H);

Analysis, found C, 73.82%, H, 4.84%, S, 13.93%.

$C_{28}H_{20}O_2S$ requires C, 74.00%, H, 4.88%, S, 14.08%.

D,l-hydrobenzoin-mono-thionobenzoate (LXI a).

D,l-hydrobenzoin-mono-thionobenzoate was prepared in a similar way to the meso-isomer in 64% yield.

M.p. 94-96° (as fine yellow needles from CH_2Cl_2/40-60° petroleum ether);

ν_{max}^{nujol}, 1230, 3400cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 243, 252, 255, 283, 292 and 420 (ε=7,500, 8,300, 8,050, 9,500, 10,600 and 120 respectively);

N.m.r. (τ) 1.76 (dd, 2H), 2.67 (m, 8H), 3.21 (d, J=7 c/s., 1H), 4.75 (dd, J=3, 7c/s., 1H), 3.40 (d, J=3 c/s., exchangeable with D_2O, 1H).

Analysis, found C, 75.37% H, 5.34%, S, 9.50%.

$C_{21}H_{18}O_2S$ requires C, 75.40%, H, 5.39%, S, 9.58%.

D,l-hydrobenzoin-mono-benzoate-mono-thionobenzoate (LXI b).

This compound was prepared in an analogous manner to the meso-isomer in 72% yield from d,l-hydrobenzoin-mono-thionobenzoate. The product crystallised in yellow needles from petrol (60-80°).

M.p. 125-126.5°;

ν_{max}^{nujol}, 1215, 1712cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 252, 257, 276, 286, 294 and 420nm. (ϵ=9,700, 9,300, 9,300, 11,400, 11,800 and 138 respectively);

N.m.r. (τ) 1.90 (m, 4H), 2.63 (m, 16H), 2.33 (d, 1H, J=8 cps.), 3.34 (d, 1H, J=8 cps.);

Analysis, found C, 76.61%, H, 5.29%, S, 7.24%, $C_{28}H_{22}O_3S$ requires C, 76.71%, H, 5.02%, S, 7.31%.

D,l-hydrobenzoin-bis-thionobenzoate (LXI c).

D,l-hydrobenzoin-mono-thionobenzoate was prepared from d,l-hydrobenzoin (428mg., 2mmoles), as already outlined above, except the product was not recrystallised but passed on to the next stage: Sodium hydride (200mg., 50% dispersion in mineral oil, 4mmoles) was added to thiobenzoylthioglycollic acid (424mg., 2mmoles) in anhydrous t.h.f. (20ml.). When effervescence ceased, imidazole (272mg., 4mmoles) was added followed by d,l-hydrobenzoin-mono-thionobenzoate. The reaction was refluxed for 10 mins, then diluted with water. Work-up in the usual way yielded d,l-hydrobenzoin-bis-thionobenzoate (LXI c) (55mg., 6% from d,l-hydrobenzoin) as yellow prisms (petroleum ether, 60-80°).

M.p. 168-170°;

ν_{max}^{nujol}, 1220cm.$^{-1}$;

$\lambda_{max}^{cyclohexane}$, 253, 290 and 419nm. ($\epsilon$=16,500, 21,600 and 419 respectively);

N.m.r. (τ) 1.77 (m, 4H), 2.61 (m, 17H), 3.25 (d, 1H);

Analysis, found C, 74.03%, H, 4.93%.

$C_{28}H_{22}O_2S_2$ requires C, 74.00%, H, 4.88%.

Photolysis of meso-hydrobenzoin-mono-thionobenzoate.

Thionoester (LX a) (334mg., 1mmole) was dissolved in dichloromethane (1ml.). The solution was diluted to 300ml. with cyclohexane, then triethylamine (1ml.) was added. After degassing the solution, the mixture was irradiated in the usual way with light from a high pressure mercury lamp using system 'A'. The reaction was followed by t.l.c. When starting material had disappeared, the solution was washed with water, 2N hydrochloric acid and water. The solution was dried (Na_2SO_4) and the solvent evaporated in vacuo. The residue was chromatographed on a silica gel GF_{254} plate. Elution with dichloromethane/40-60° petroleum ether, 1:2, gave desoxybenzoin (LXII) (127mg., 65%) as white plates.

M.p. 55-56° (methanol);

ν_{max}^{nujol}, 1695cm.$^{-1}$;

N.m.r. (τ) 1.71 (m, 2H), 2.45 (m, 8H), 5.50 (s, 2H).

Photolysis of d,l-hydrobenzoin-mono-thionobenzoate.

The thionoester (LXI a) was irradiated in an identical manner to above to give desoxybenzoin (LXII) in 60% yield.

Photolysis of meso-hydrobenzoin-bis-thionobenzoate.

The thionoester (LX c) (0.454g., 0.001 mole) was photolysed in anhydrous deoxygenated dichloromethane (500ml.) containing triethylamine (2ml.) using a high pressure mercury lamp using system 'A' with pyrex apparatus. The reaction was followed by t.l.c. to completion. The solvent and triethylamine were removed *in vacuo* at room temperature on a rotary evaporator to yield a brown semi-crystalline oil. This was chromatographed on two 60 x 20 x 0.1cm. silica gel GF_{254} plates. Elution with dichloromethane/40-60° petrol (1:3) gave trans-stilbene (LXVI) (92mg., 51%) as white plates.

M.p. 124° (ethanol);

λ_{max}^{EtOH}, 295nm. (ϵ=27,000);

N.m.r. (τ) 2.75 (s, 10H), 3.39 (s, 2H);

Mass spectrum, M^+ at 180;

cis-stilbene (LXVII) (21mg., 11%) as a colourless oil.

λ_{max}^{EtOH}, 280nm. (ϵ=13,500);

N.m.r. (τ) 2.58 (m, 10H); 2.79 (s, 2H);

Mass spectrum, M^+ at 180;

chloromethanethiol benzoate (LXVIII) (160mg., 41%) as a yellow oil.

ν_{max}^{film}, 1675cm.$^{-1}$;

N.m.r. (τ) 2.04 (dd, 2H), 2.50 (m, 3H), 4.87 (s, 2H);

Mass spectrum, M^+ at 186, $M^+ + 2$ at 186 M/M + 2 = $2\frac{1}{2}/1$

and methanedithiol dibenzoate (LXIX) (84mg., 15%) as white needles.

M.p. 120-121° (ethanol);

ν_{max}^{nujol}, 1666cm.$^{-1}$;

N.m.r. (τ) 2.01 (dd, 4H), 2.51 (m, 6H), 5.30 (s, 2H);

Mass spectrum, M^+ at 288.

Photolysis of d,l-hydrobenzoin-bis-thionobenzoate.

The ester (LXI c) (45.4mg., 0.1mmole) in degassed cyclohexane (50ml.) containing triethylamine (0.2ml.) was irradiated in the manner described above. Work-up in the same way gave diphenyl acetylene (LXIV) (11mg., 62%).

M.p. 61-62° (ethanol);

λ_{max}^{EtOH}, 264, 278 and 296 (ϵ=14,100, 14,800 and 14,000 respectively);

Mass spectrum, M^+ = 178.

Photolysis of meso-hydrobenzoin-mono-benzoate-mono-thionobenzoate.

The ester (XL b) (438mg., 1mmole) in anh. degassed dichloromethane (150ml.) containing triethylamine (2ml.) was irradiated as above. Work-up in the same way gave trans-stilbene (LXVI) (40mg., 22%), cis-stilbene (LXVII) (8mg., 4%) chloromethanethiol benzoate (LXVIII) (58.5mg., 30%) and methanedithiol dibenzoate (LXIX) (72mg., 26%).

Photolysis of d,l-hydrobenzoin-mono-benzoate-mono-thionobenzoate.

Photolysis of (XLI b) gave essentially the same results as (XL b).

Chloromethyl thiolbenzoate (LXVIII).

Thiobenzoic acid (12.2g., 0.1 mole) and paraformaldehyde (300mg., 0.1 mole) were heated at 100° under nitrogen to give Ph-CO-S-CH_2OH (10.5g., 62%). M.p. 46° (Et_2O/ligroin). This was added to PCl_5 with cooling. The reaction mixture was stirred 1½ hours at 40°/0.05mm. The still residue at 0° was shaken with aq. $NaHCO_3$, extracted with ether then the ether extract evaporated to give chloromethanethiol (7.0g., 60%).

B.p. 92°/0.05mm.

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