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The Photochemistry Of Substituted 1,2-dithiole-3-thiones

Hoi-yeung Ng

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THE PHOTOCHEMISTRY
OF
SUBSTITUTED 1,2-DITHIOLE-3-THIONES

by

Hoi-Yeung Ng

Department of Chemistry

Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Canada
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ABSTRACT

Part One of this thesis describes a study of the photochemistry of 4-aryl-1,2-dithiole-3-thiones. Irradiation of 4-p-substituted-phenyl-1,2-dithiole-3-thiones at $\lambda>420$ nm gave coupling photoproducts: 3,3'-bis-1,2-dithiolo-[3,4-b]-benzothiophenyl derivatives. When 4-p-tolyl-1,2-dithiole-3-thione was irradiated at $\lambda>420$ nm in the presence of olefins, vinyl 3-(4-tolyl-1,2-dithiolyl) sulfides were obtained.

Part Two of this thesis describes work done on the photoaddition of 4,5-benzo-1,2-dithiole-3-thione to cyclopentene and tetramethylethylene to form 2-[2-(dithiole-1,3-ylidene)]-3,5-cyclohexadiene-1-thione. The orthothioquinones were found to react with standard dienophiles to give 4+2 adducts. The deep blue orthothioquinones are in thermal equilibrium at ambient temperature with the corresponding colorless dimers (a 1,2:5,6-dibenzo-3,4-dithiacycloocta-1,5-diene or 1,2:5,6-dibenzo-3,7-dithiacycloocta-1,5-diene derivative) formed by 4+4 addition. The equilibria are sensitive not only to temperature but also to light and the nature of the solvent. Thermodynamic studies have yielded energy parameters for the equilibria.

Part Three of this thesis describes work done on the Diels-Alder reaction between α,β-unsaturated thioketones and various aliphatic thioketones to form 1,3-dithianes. The 1,3-dithianes obtained in this study exhibit geometrical isomerisation about the 1,3-dithiolane ring. The isomerisation was studied by means of nmr spectroscopy and was found to be acid catalysed.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

PART I PHOTOREACTION OF 4-ARYL-1,2-DITHIOLE-3-THIONES

PART II THE SYNTHESIS AND THE THERMOCHROMISM OF A METHYLENE MONOTHIOQUINONE SYSTEM

* * *

LIST OF TABLES

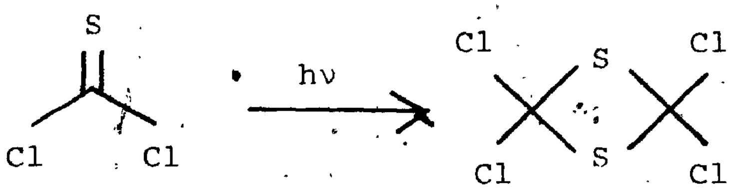
LIST OF FIGURES

PART 1: PHOTOREACTION OF 4-ARYL-1,2-DITHIOLE-3-THIONES

CHAPTER 1

INTRODUCTION

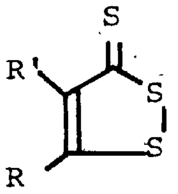
Compared with the amount of work on carbonyl compounds, the photochemistry of thiocarbonyl compounds may be considered to be unexplored. One of the earliest investigations involving thiocarbonyl compounds was Schonberg's study (1) on the photodimerization of thiophosgene, 1. The photochemistry of aromatic thioketones was begun approximately ten years later when the same group (2) investigated the photo-oxidation of substituted thiobenzophenones and related compounds.



1

The photocycloaddition was investigated by Kaiser and Wulfers (3), in 1964, when they irradiated thiobenzophenones in the presence of olefins. Since then intensive and systematic studies in this field have been carried out in Tsuchihashi and Ohno's laboratory as well as in our own (4) with sporadic contributions from other groups.

We were interested to learn whether in an alicyclic ring system, an α,β-unsaturated thione, or equivalent, would react at the thione function or at the ethylenic linkage (as usually occurs with α,β-unsaturated ketones). The system 1,2-dithiole-3-thione, 2, was chosen for our studies because it fulfilled the requirement of being an α,β-unsaturated thione, and was readily accessible.



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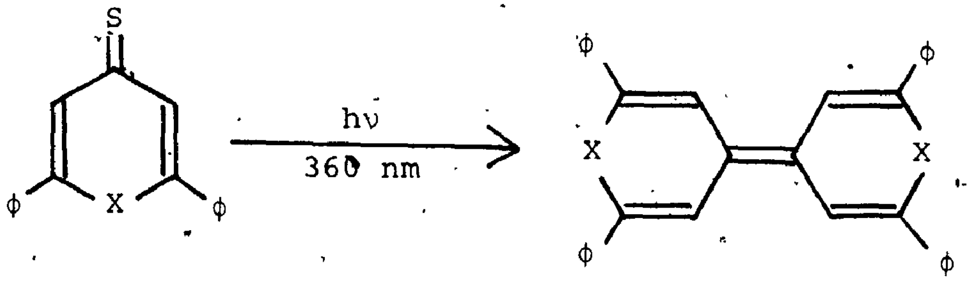
Photocycloaddition

The cycloaddition of enones to multiple bonds is a well-documented reaction (5) and the usefulness of this reaction in organic synthesis has been widely investigated and applied (6). On the other hand, the corresponding reaction with α,β-unsaturated thioketones has not yet been reported. Thus, when thiocholestenone is irradiated in the presence of olefins, it does not give any product which appears to be derived from the addition of the olefin to the olefinic linkage in the thioketone (7). A mixture is obtained involving, apparently, addition to the thiocarbonyl group. A similar result is obtained when thioisophorone is irradiated (8): the addition occurs at the thiocarbonyl function only. Ishibe et al (9) have reported that the irradiation of pyran and thiopyran-thione 3 leads to the



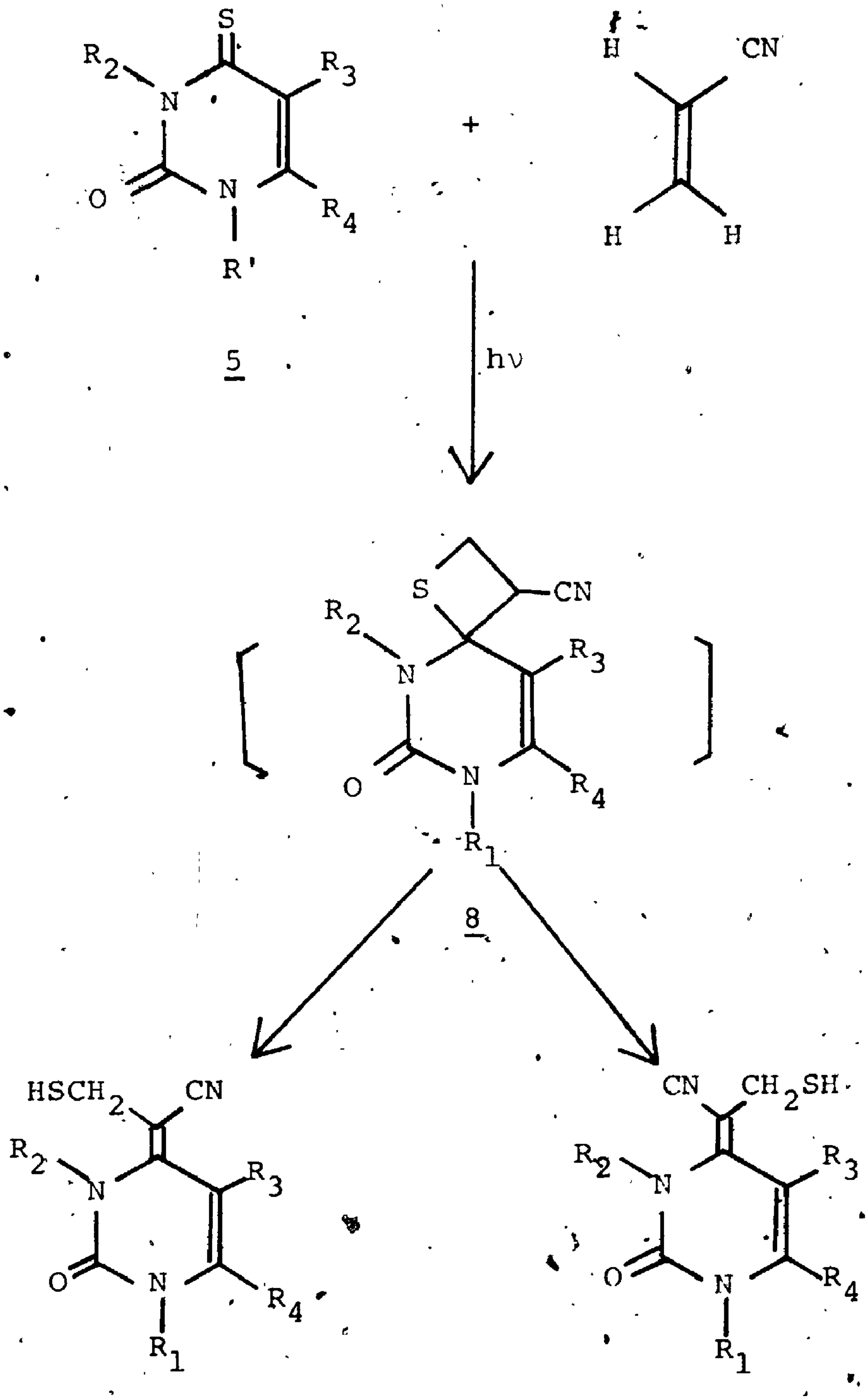
X=S, O

3

4

formation of 4 in high yield. They did not isolate any dimeric product and the mechanism is unestablished, but it would appear that the photochemical reactive site is again the thiocarbonyl function.

Fourrey and coworkers (10) irradiated 4-thiouracil derivatives, 5, in the presence of unsaturated nitriles to obtain a mixture of isomers 6 and 7. They proposed the unstable thietan 8 as an intermediate which then decomposed to the products isolated. Thus, all the α,β-unsaturated thiones here discussed react photochemically with multiple



5

8

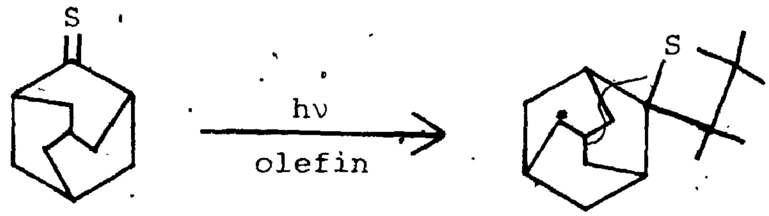
6

7

bonds by means of the C=S linkage: that is, in a manner analogous to that of saturated thioketones.

It has been found that the mode of cycloaddition of olefins to the C=S group of thiobenzophenone varies with the olefin substituent used. In addition, the reaction is in some cases wavelength dependent. When the substituents are not electron withdrawing, 1:1 (thietane) or 2:1 (1:4 dithiane) adducts are formed. With electron withdrawing groups only 1:1 (thietane) adducts are obtained (11, 12).

With the alicyclic thioketone, adamantanethione, the thietan 9 is the major product (13). It has also been



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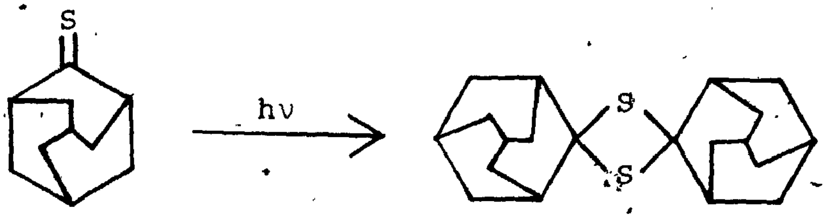
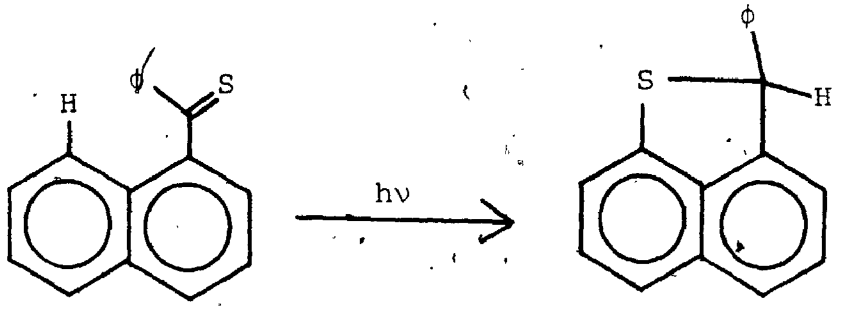
found that when adamantanethione is irradiated in the absence of olefins, the head-to-tail dimer, 10, is obtained



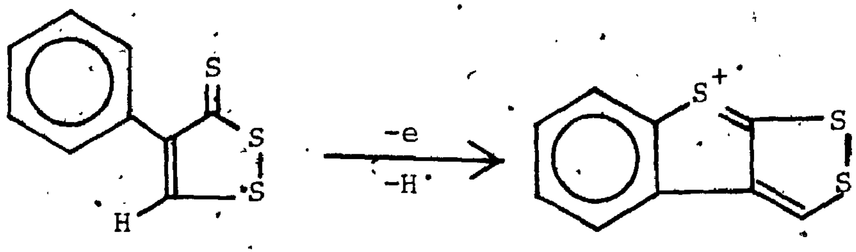
10

quantitatively. Similar reaction products have not yet been observed after irradiation of aromatic thioketones. When an aromatic thione such as 11, which has the position *peri* to the thiocarbonyl group vacant, is irradiated, it cyclizes to give derivatives of thiophane 12 (14) in a



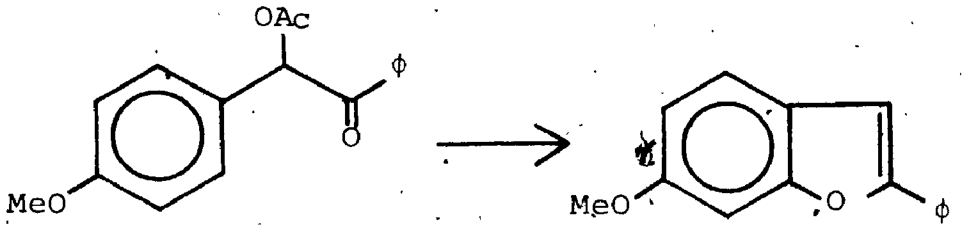
11 12

moderate yield. An ionic species has been proposed as an intermediate in the reaction. Here again, as is so often the case with thiones, no example of such a rearrangement is known in the ketonic series. It is interesting that Pedersen and Møller (15) have shown that the thiocarbonyl function in 4-phenyl-1,2-dithiole-3-thione, 13, cyclizes to



13 14

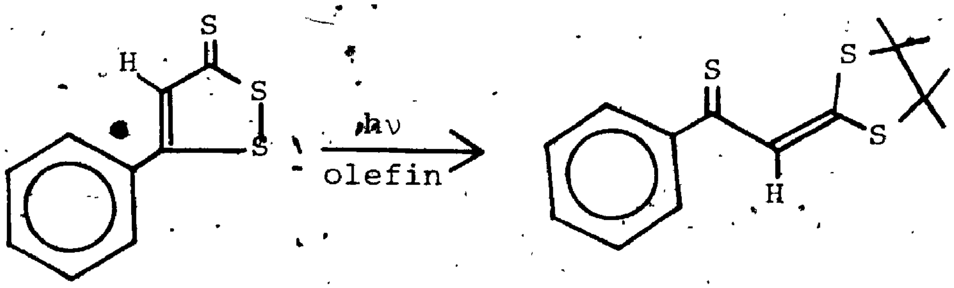
give 14 under electron impact in the mass spectrometer. The proposed structure 14 was supported by labelling experiments. In 4-pentadeuterio phenyl-1,2-dithiole-3-thione, an M-2 peak was present instead of an M-1 peak. These cyclisations, which resemble the photocyclization of 15 to the benzofuran derivative 16 (16), are relevant to



15

16

the work to be discussed. After the present studies had begun, Okazaki (17) reported that 5-phenyl-1,2-dithiole-3-thione, 17, undergoes photoaddition with various olefins to give a 1:1 adduct of type 18 when 254 nm light was used.



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18

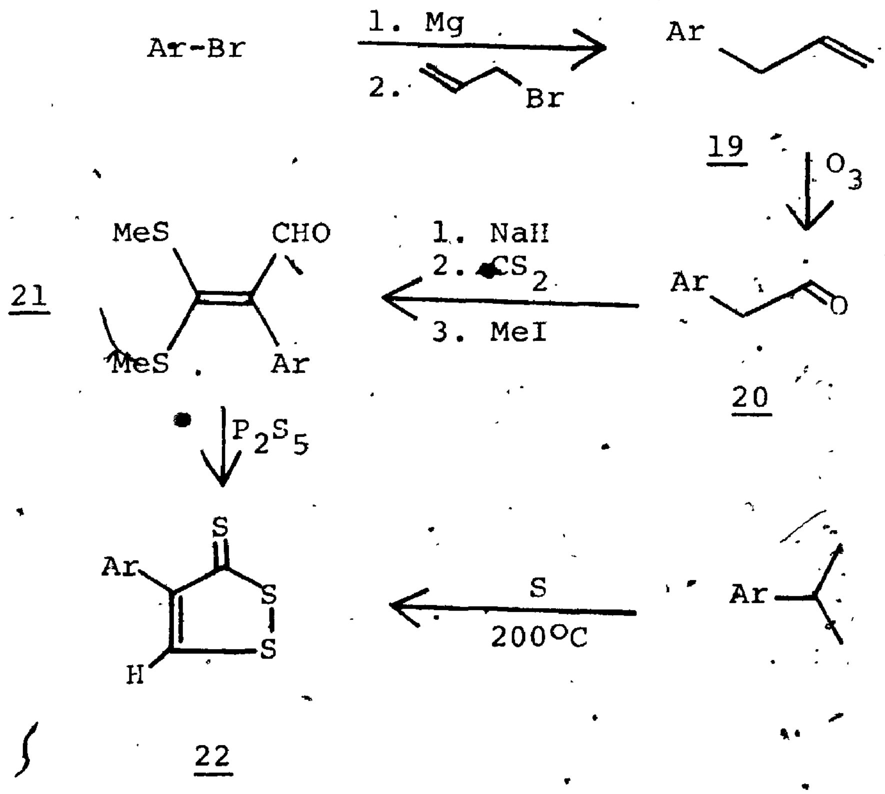
In the present work the studies of the electronic absorption spectrum as well as the photochemical reactions with and without the presence of olefins are reported.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 The Electronic Absorption Spectra of 4-Aryl-1,2-dithiole-3-thiones

4-Aryl-1,2-dithiole-3-thiones were prepared according to Field (18) and Thuillier (19). The synthetic sequences are shown in Scheme 1.

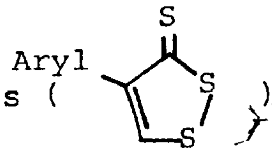


Scheme 1

The uv spectra of 4-aryl-1,2-dithiole-3-thiones in cyclohexane are shown in Table 1. These observations are similar to those reported by Lüttringhaus (20) as well as those reported by Mayer (21). Lozach (22) concluded that the absorption band at 420-430 nm which is characteristic of all these substances belongs to the thione group, but did not discuss the nature of this band. Later on, it was pointed out by Johnstone and Ward (23) that this absorption band is a π-π* transition. The position of the absorption maximum of this band is solvent dependent, and undergoes a hypsochromic shift as the polarity of the solvent is increased (see Table 2). This observation is consistent with previously reported data (21).

The absorption spectra of all the 1,2-dithiole-3-thiones, measured in concentrated benzene solution, show, in addition, a shoulder at around 520 nm which has not previously been reported. The estimated position of the shoulder and its absorption coefficient in the various compounds are shown in Fig. 1 and Table 1. That this low intensity band was not noted earlier may be due to the fact that the spectra have been measured only at wavelengths shorter than 500 nm (21). To learn more about the nature of this weak absorption band, the effect of solvent was studied and the results are shown in Fig. 2. There is a blue shift on changing the solvent from cyclohexane to methanol which is about 30 nm. In view of the low intensity of the band and the large hypsochromic shift on

TABLE 1

Absorption Spectra of 4-Aryl-1,2-dithiole-3-thiones ()

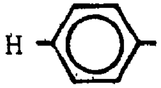
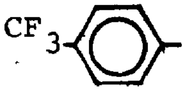
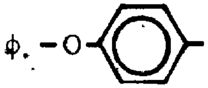
Aryl	Solvent: Benzene $\lambda_{max.}$ in nm (ε)	Solvent: Cyclohexane $\lambda_{max.}$ in nm (ε)
 Me	535 (s) (118)	427 (5900), 335 (5500), 280 (3470), 244 (13800), 222 (17700)
 H	520 (s) (71)	426 (6300), 332 (3480), 285 (3480), 240 (9550)
 F	530 (s) (128)	427 (5900), 333 (5750), 283 (3480), 245 (12000), 215 (s) (16600)
 CF_3	530 (s) (122)	425 (5500), 335 (5700), 295 (3800), 245 (10000), 220 (18600)
 ϕ-O	534 (s) (102)	428 (6610), 334 (6320), 278 (s) (7400), 248 (30200)

TABLE 1 (cont'd)

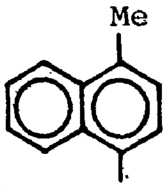
Aryl	Solvent	
	Benzene $\lambda_{max.}$ in nm (ε)	Cyclohexane $\lambda_{max.}$ in nm (ε)
	520 (s) (130)	423 (7440), 334 (7950), 296 (9130), 293 (9130), 284 (102000), 282 (10200), 281 (10100), 279 (10900), 254 (10200)
	525 (s) (100)	423 (4700), 331 (8130), 320 (8330), 301 (10000), 290 (10000), 253 (17000)

TABLE 2

Solvent Effect on the Absorption Spectrum of 4-p-Tolyl-1,2-dithiole-3-thione

Solvent	$\lambda_{max.}$ in nmr (log ε)
Cyclohexane	427 (3.77), 335 (3.74), 280 (3.54), 244 (4.14), 222 (4.25)
Acetonitrile	421 (3.95), 317 (3.66), 280 (3.65), 238 (4.21)
Methanol	423 (3.96), 320 (3.61), 280 (3.61), 240 (4.17)

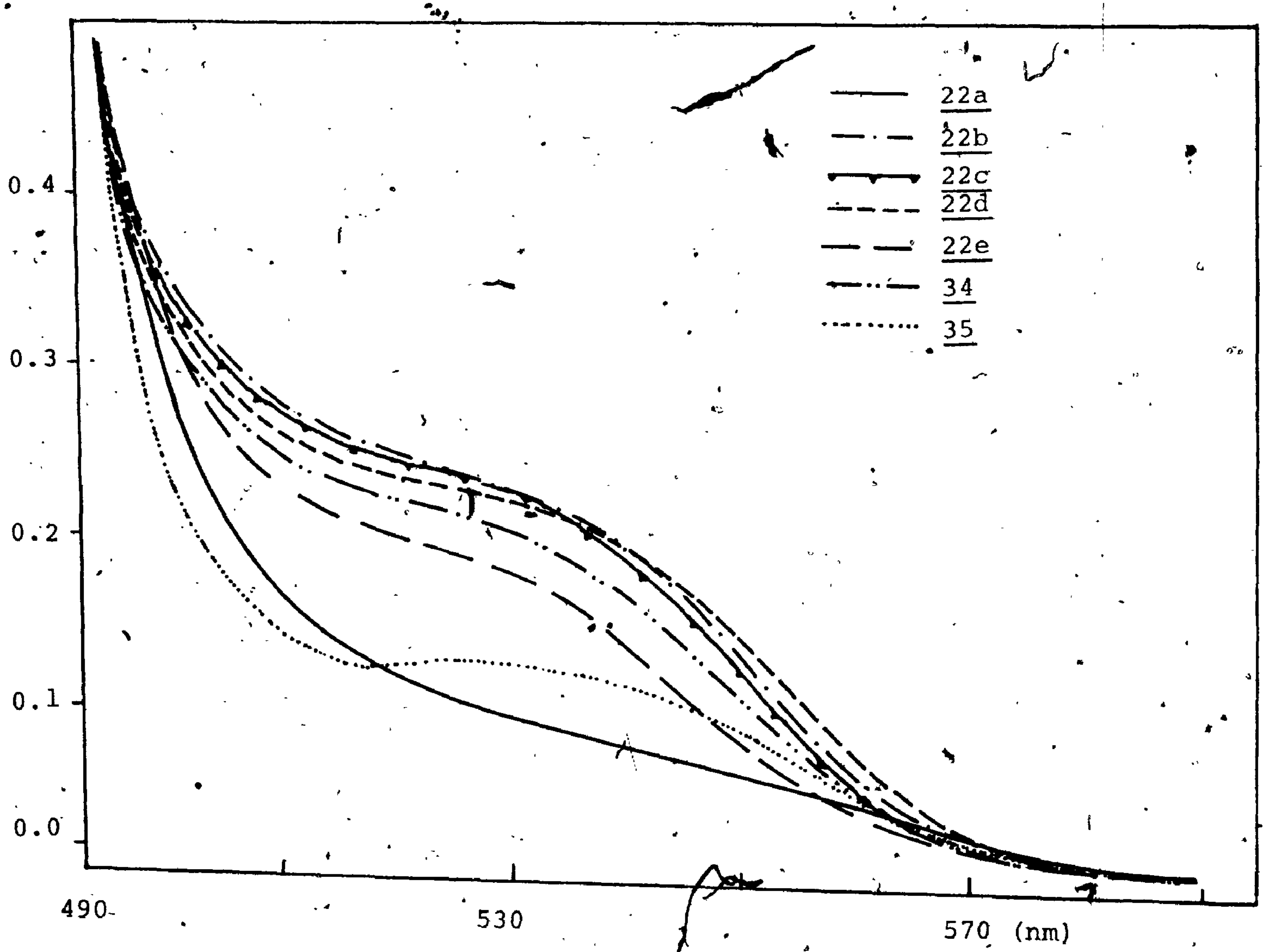
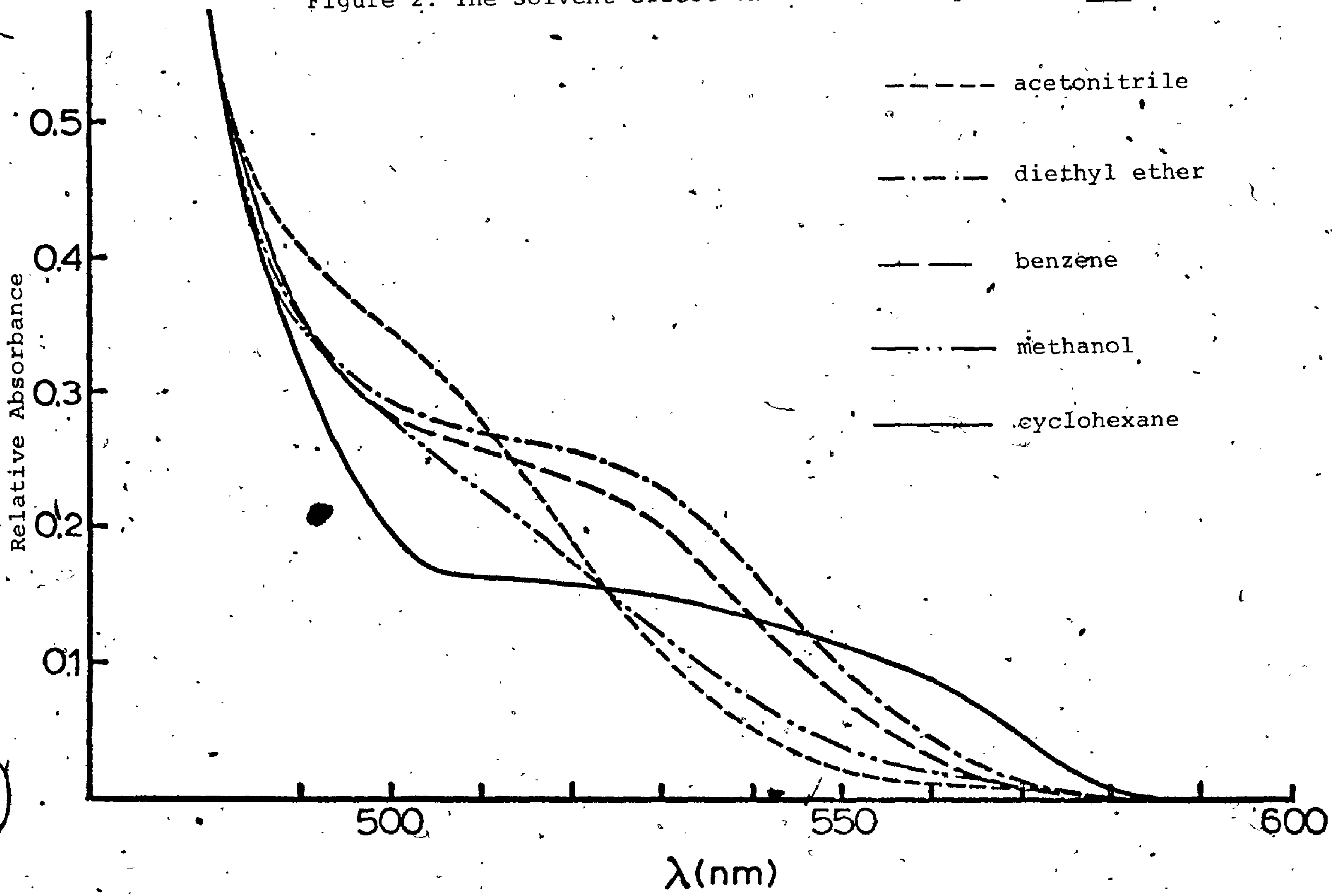


Figure 1. The uv spectra of 1,2-dithiole-3-thiones in benzene (C=1.13m/1).

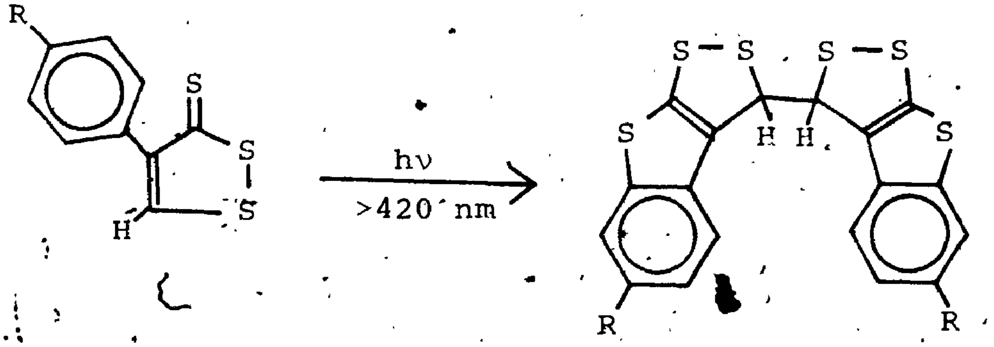
Figure 2. The solvent effect on the uv absorption of 23b.



increasing the polarity of the solvent it is tentatively assigned an $n-\pi^*$ character.

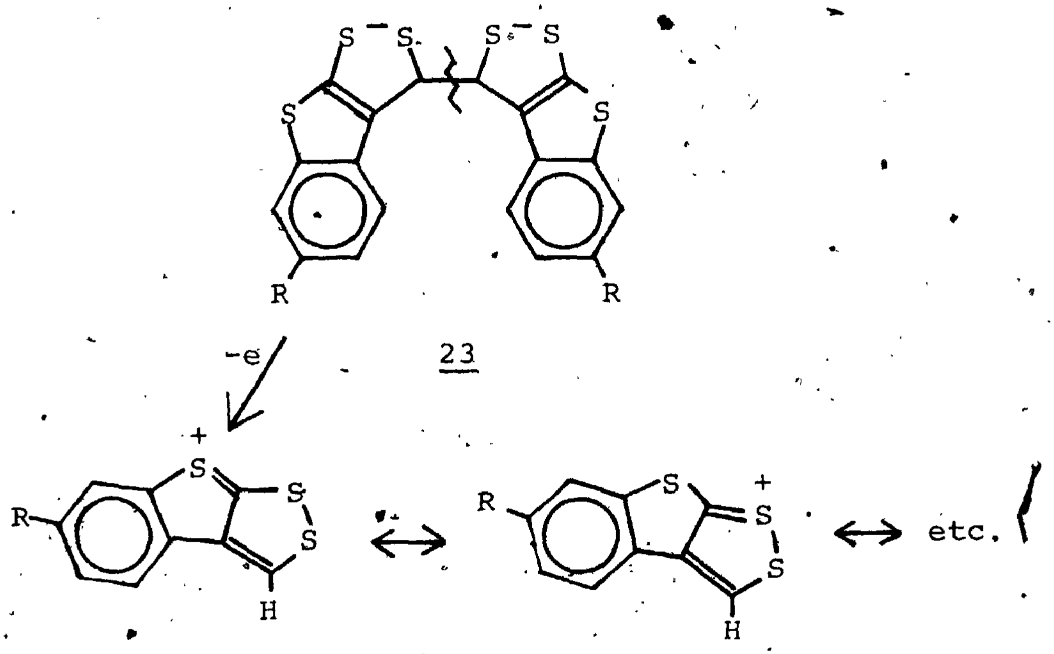
2.2 Structural Determination of the Photoproducts Derived from the 4-Phenyl-1,2-dithiole-3-thione Series

Prior to the investigation of photocycloaddition reactions, 4-aryl-1,2-dithiole-3-thiones were irradiated alone in an inert solvent to examine their photochemical behavior. Irradiation of the 4-aryl-1,2-dithioles, 22, in benzene using light λ>420 nm gave the substances 23 as the major products. The structures of these compounds were deduced from their mass spectra, uv spectra and, in the cases of 23a and 23b, their chemical degradation.



	22		23
a	R=H	a	R=H
b	R=Me	b	R=Me
c	R=C_6H_5-O-	c	R=C_6H_5-O-
d	R=CF_3	d	R=CF_3
e	R=F	e	R=F

The molecular weight of 23b in pyridine was found to be 490 using vapor phase osmometry. The calculated value for 23b was 446*. The mass spectrum confirmed this molecular weight by giving a molecular peak at m/e=446. In addition, all the photoproducts gave a strong peak at m/2 in the mass spectrum. This could arise from 23, by cleavage of the central allylic C-C bond. Aside from the bond weakening because of stabilisation of a radical and a charge by delocalisation and vicinal sulfur, the cation formed might be expected to be particularly stable since it is, in effect, a dithiolium ion 24 (24). A similar facile cleavage in 2- and 3- methylbenzothiophene to give, in this case, a benzothiopyrylium 25 has been reported by Porter (25) and Djerassi (26).



23

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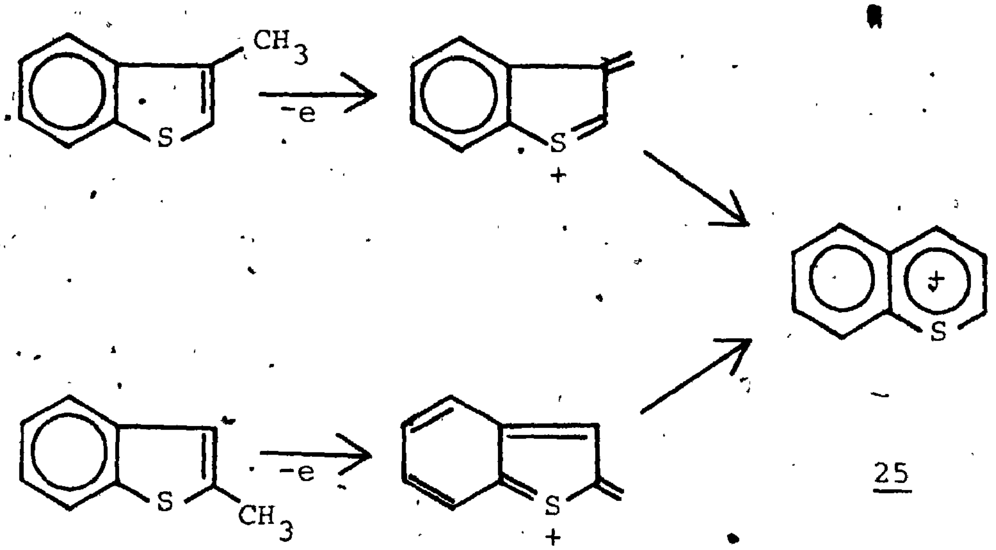
*The poor result may be attributed to the low concentrations, necessitated by low solubility, used in the measurements.



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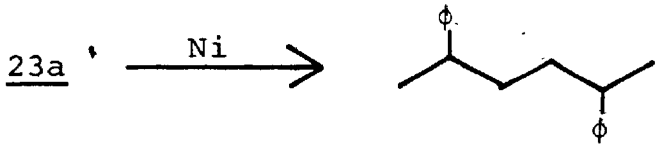
The carbon skeleton of the photoproducts was deduced from partial and complete desulfurisation experiments using Raney nickel. Thus total desulfurisation of 23a gave 2,5-diphenyl-n-hexane, 26, whilst partial desulfurisation of 23b gave three products. That which contained the most hydrogen was assigned the structure 27 which was deduced from spectroscopic data. The mass spectrum of 27 showed a molecular peak at 322 and the 100% peak at 161. The nmr spectrum indicated that the molecule is symmetrical, for it gave only two singlets for the methyl and methylene group at 2.47 and 3.21 ppm respectively. Uv absorption spectra in both methanol and isooctane provided the best evidence for the structure since all the absorption maxima (see Table 3) corresponded with those of 6-methylbenzothiophene (27).

The structures of the other two products, presumbly

TABLE 3

Uv Absorption Spectrum of 27

6-Methyl benzothiophene in isooctane (27)		27 in isooctane	
$\lambda_{max.}$ (nm)	ε	$\lambda_{max.}$ (nm)	ε
302	2100	301	4030
292	2100	294	2960
289	1850	290	4030
282	1650	283 (s)	6450
267	7200	271	12520
260	7800	265	12980
228	36500	233	73380



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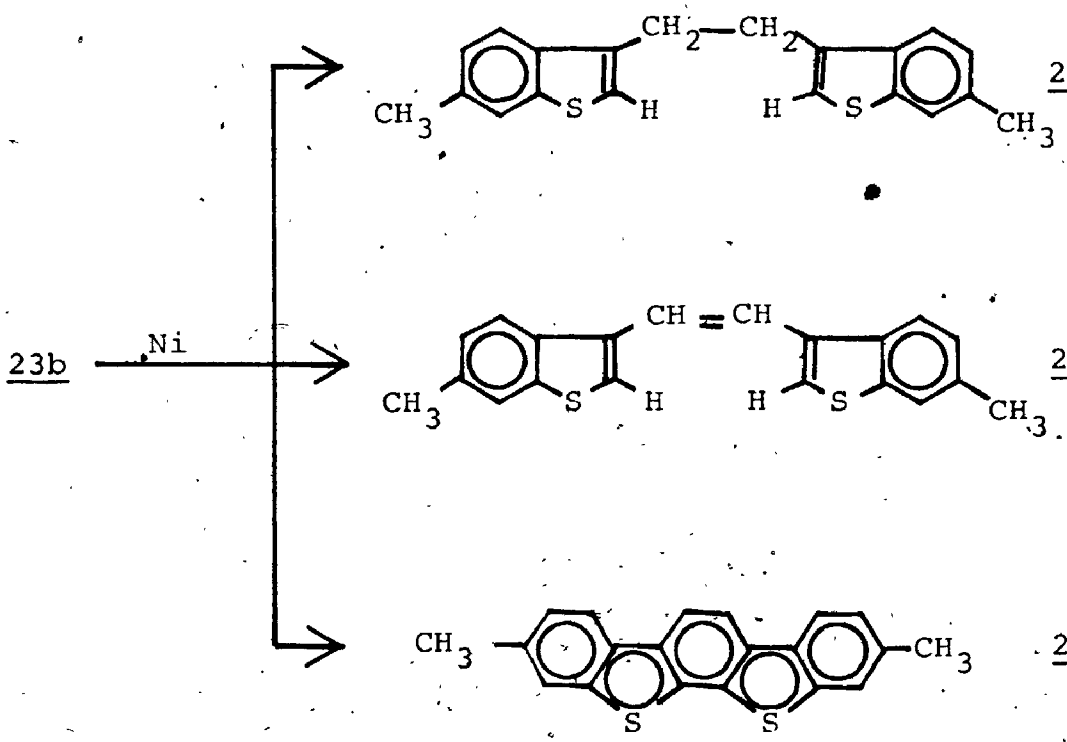


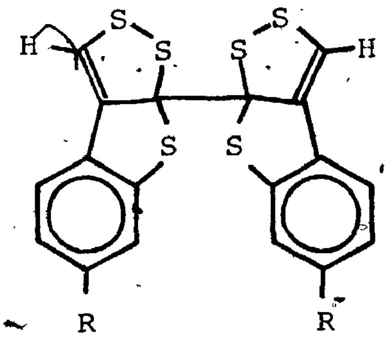
27

28

29

28 and 29, are uncertain. Mass spectra of compounds 28 and 29 showed the 100% peaks at 320 and 318 respectively. The nmr spectra of both compounds showed proton signals in the aromatic region and also singlets for methyl groups at 2.46 and 2.50 ppm respectively.

This evidence suggests the carbon skeleton of the photoproducts, and indicates that they are coupling products. The decision between type 23 and the alternative allylic coupling products of type 30 and 31 is based upon the uv and nmr spectra. Every one of the photoproducts,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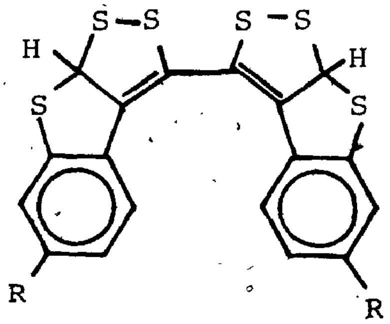

31

23, showed a signal in the region from 4.94 to 5.13 ppm (see Table 4). This signal cannot be attributed to a vinylic proton. For in styrene itself, the corresponding vinyl proton gives a signal at 5.21 ppm (28). The substitution effect of an alkyl sulfide group at the gem-position will shift the signal ~0.5 ppm down filed (29) and so it may be estimated that the signal of the vinyl proton for 30 should appear at 5.7 ppm, that is about 0.6 ppm down field from the observed signal. This would appear to exclude structure 30. Structure 31 for the photoproduct cannot be excluded on the basis of nmr spectral data only. It is rejected for the following reasons. Firstly, it is

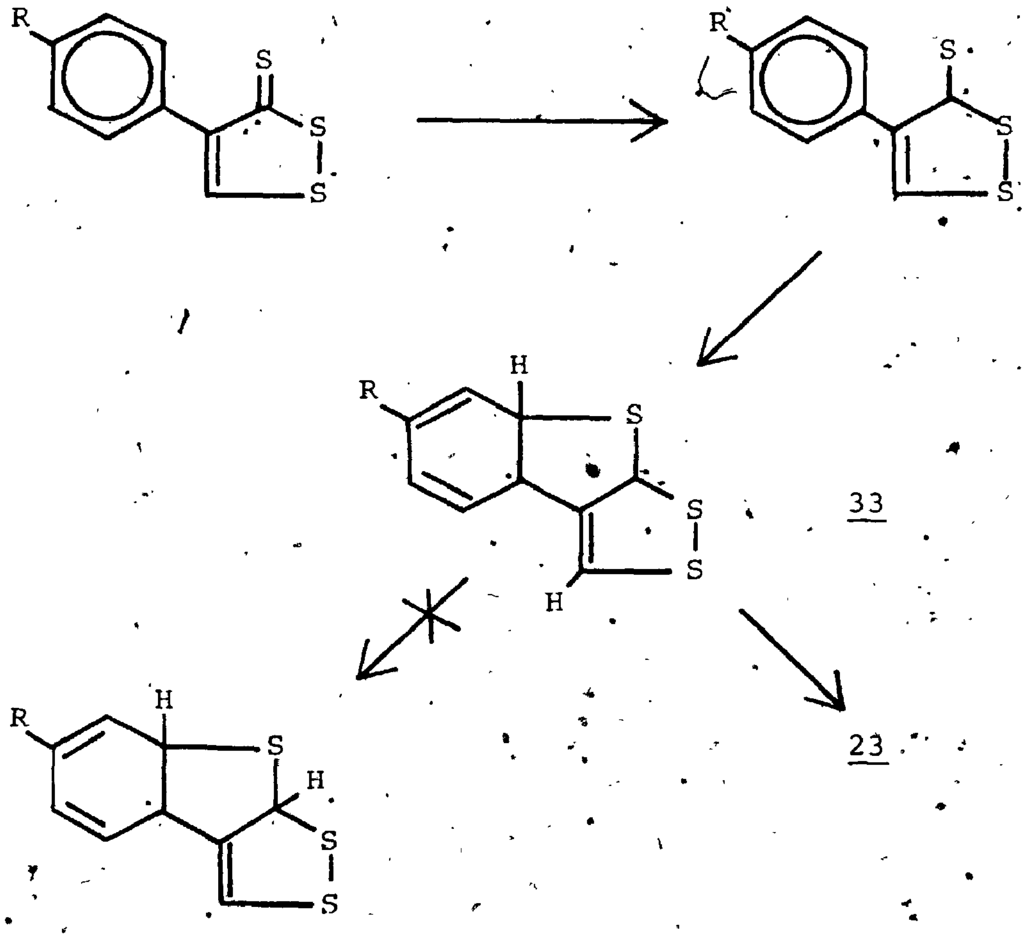
TABLE 4

Chemical Shift of Photoproduct 23 Derived From 22

R	δ
CH_3	4.94
H	5.03
CF_3	5.13
ϕ-O-	4.98
F	not available*

* It was too insoluble for nmr measurement

difficult to visualise the formation of 31. Secondly, a 1,3-hydrogen shift of 23 leading to the formation of 31, seems to be energetically improbable. Such a product may be formed by the coupling of two vinyl radicals, but such a radical 32, in itself, seems most improbable. Its



32

Scheme 2

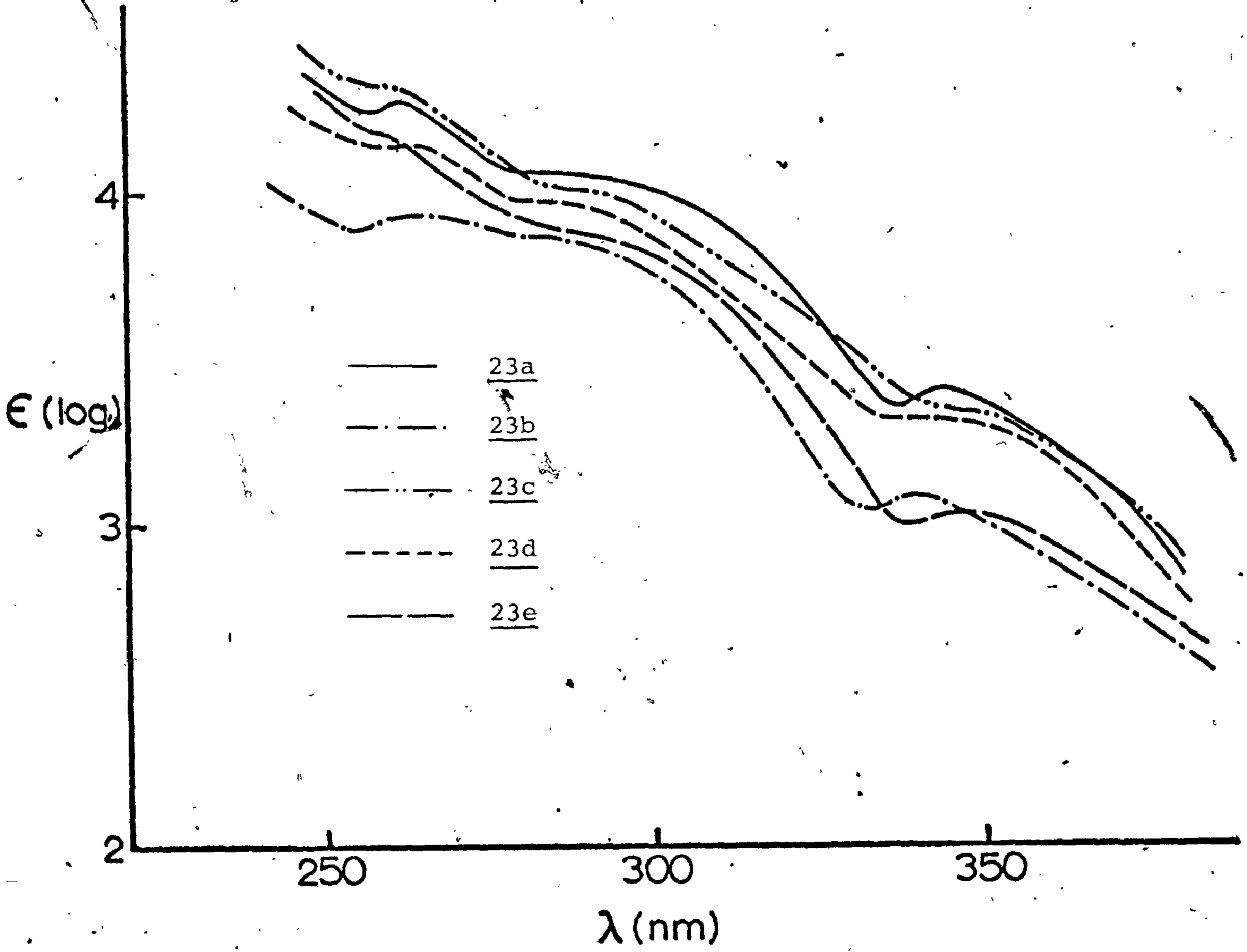
generation would involve the loss of the resonance energy of its precursor, quite aside from other thermodynamic and mechanistic considerations.

Furthermore, the uv absorption spectrum of 31 is expected to be very similar to that of 1,4-diphenyl-1,3-butadiene because both compounds contain the same carbon π-system. The absorption maximum for the latter compound was determined to be 347 nm (ε=34000) (30). The values of maximum absorption and extinction coefficient for the photoproducts obtained are too small for this chromophore to be present. Hence 31 is excluded.

The uv absorption spectra of all the photoproducts are very similar and are instructive (see Fig. 3). The absorption maximum at 340 nm absorption cannot be accounted for by an unsubstituted benzothiophene: this has a maximum at 297 nm (31). But the maximum at 340 nm is consistent with the assigned structure 23. The shift of the maximum from 297 nm to 340 nm could be accounted for by the presence of a disulfide linkage in the system. It has been shown that attachment of a disulfuryl group to a π-system results in a red shift of ~30 nm in the absorption spectrum compared with the absorption spectrum of the parent compound. For instance, the absorption maximum of diphenyl disulfide occurs at 304 nm while that of benzene occurs at ~270 nm (32). A red shift of about 40 nm by the disulfide linkage in the photoproduct 23 is hence very reasonable. Thus based on the uv and nmr spectral data reported here, together with the chemical transformations noted, the assigned structure for 23 appears to be conclusive.

2.3 Irradiation of the 4-Naphthyl-1,2-dithiole-3-thione

Figure 3. The uv absorption spectrum of the photoproduct (<u>23</u>)

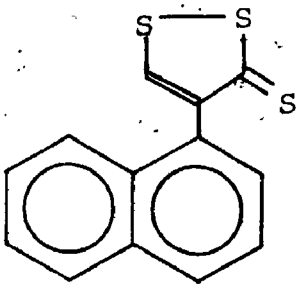


System

In the reaction just described the cyclisation of the thione function on to the aromatic ring bears a superficial resemblance to the thione photocyclisation mentioned in the introduction: in both cases the excited thione attacks the aromatic ring with the formation of a five-membered sulfur containing ring.

The resemblance is, however, superficial. The products obtained by Lapouyade were monomeric whereas the substances observed here are coupling products. The latter have the appearance of being the result of radical processes, whereas the former appear to involve ionic intermediates as was indicated by the incorporation of deuterium from D_2O.

It has been shown by Lapouyade (33) that in the appropriate substance the thione cyclisation could form a six-membered ring. It was, therefore, interesting to find out whether in the present system there was any preference between the formation of a six or a five membered ring since both types of cyclisation were considered possible theoretically. In view of this, 4-(α-naphthyl-)-1,2-dithiole-3-thione, 34, and 4-[1-(4-methyl-naphthyl-)]-1,2-dithiole-3-thione, 35, were synthesised. Owing to their low solubilities, these substances could only be irradiated at a low concentration in benzene ($3x10^{-3}$ mole/liter). The reactions were not clean ones. The only isolable products were 36 and 37 respectively. Many other products of higher polarity were also observed by tlc but since the mixture



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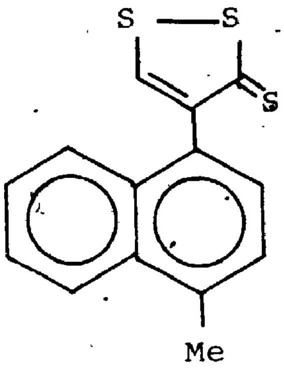
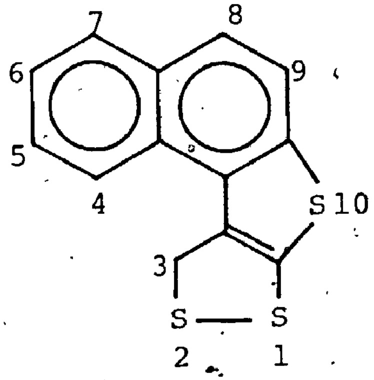


35

was complex, no further attempt was made to separate these products.



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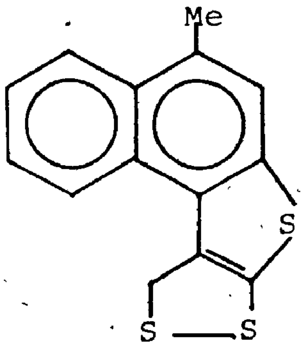
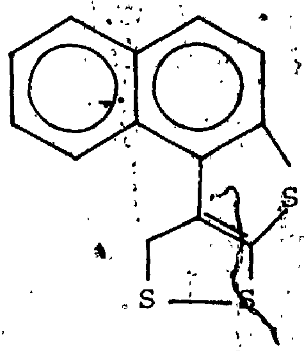


37

The structure proof for 36 (37) is based on the following mass, nmr and uv spectral data. Compound 36 gave a molecular ion at m/e 260. A strong fragmentation peak at m/e 259 indicated the loss of a hydrogen which corresponded to an α-cleavage. Since the compound gave such a strong peak at m/e 259, it is safe to say that the compound is a derivative of thiophene with a substituent at position 2- or 3- of the thiophene ring. A sharp singlet at 4.63 ppm was observed in the nmr spectrum of 36. A similar signal was also observed in the spectra of 23a-e though here the absorption occurred at about 0.5 ppm further down field. We believe these to be protons in similar environments. The difference in chemical shift is probably due to the fact that a proton attached to a tertiary carbon atom frequently shows a signal approximately 0.5 ppm downfield compared with that of a similar proton attached to a secondary carbon atom. The ratio of these proton(s) constituting this signal to that of the aromatic protons was 1:3, indicating the presence of 2 equivalent aliphatic protons in the molecule. This led to two possible structures 36 and 38 for the appropriate photoproduct.



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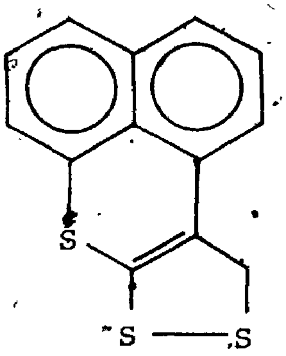
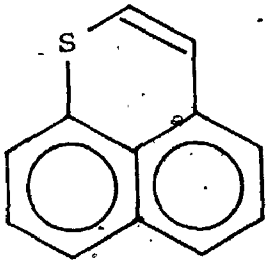


38

An unequivocal decision between these two structures could be made on the basis of uv absorption spectroscopy. The compound 38 is a derivative of 39, 1-thiaphenalene, which is a light orange to bright yellow substance (38, 39). Compound 40 of which 36 is a derivative is colorless. The



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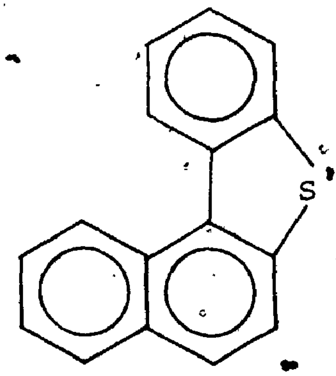

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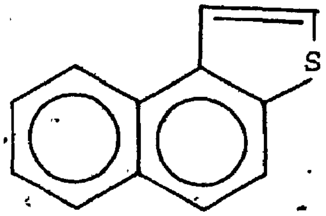


40

photoproduct obtained was almost colorless. The uv spectra of these compounds together with that of 41 (40, 41) are compared in Fig. 4. The spectra of the photoproducts of 36 and 37 consist of major absorption maxima at 245, 285 and 335 nm, correlating well with the uv absorption spectrum of

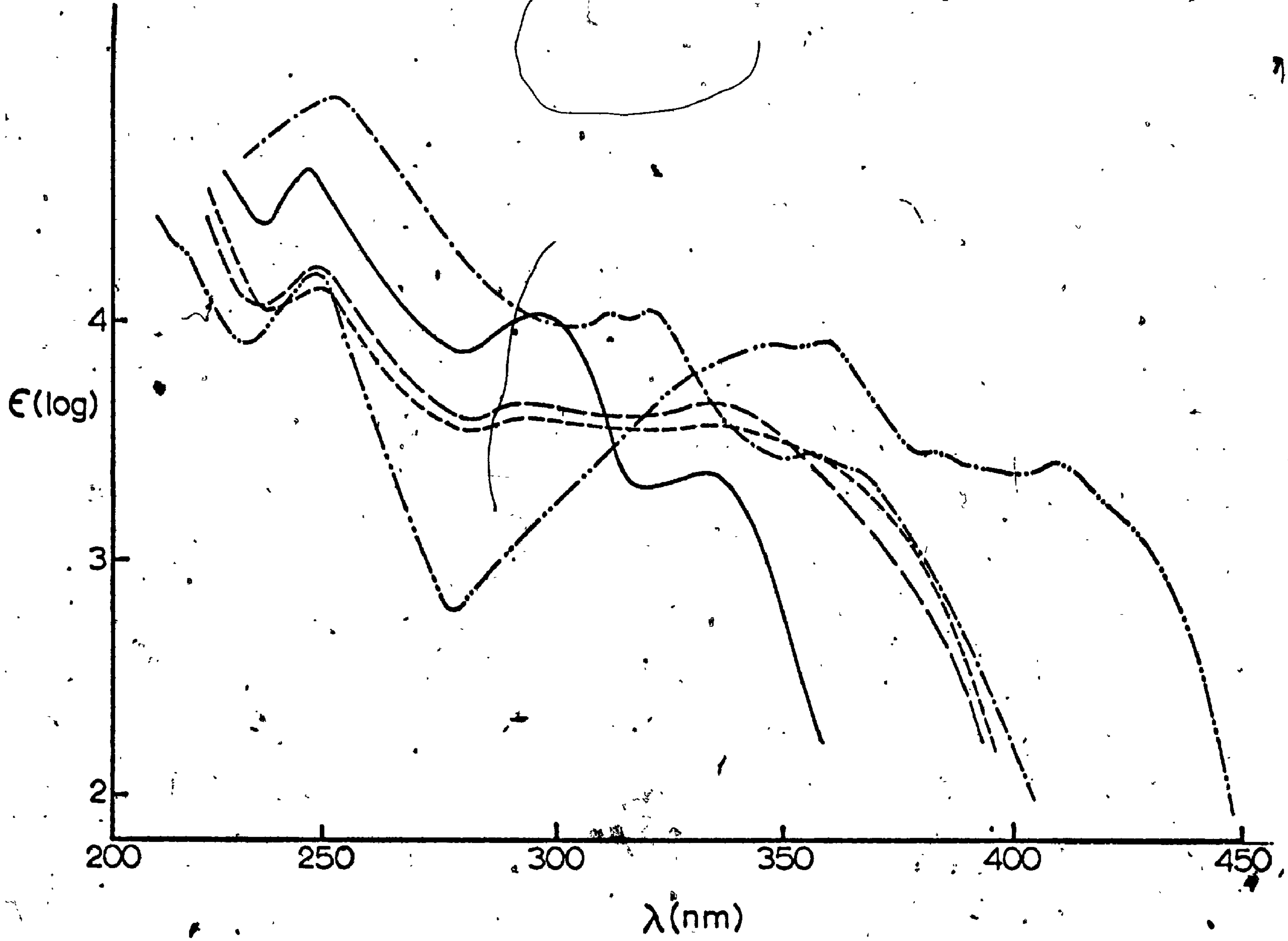


Figure 4. The uv absorption spectra of 36 (— — —), 37 (-----), 39 (—..—), 40 (———) and 41 (—.—).

40 in which the maxima occur at 243, 291 and 330 nm. Structure 38 is ruled out immediately since a maximum is expected at no less than 407 nm. Thus it is concluded that the five membered ring is favored upon cyclisation.

It has been shown that the phenyl series of compounds does not give any (no more than 0.5%) of the monomeric product upon irradiation in benzene at a higher concentration (2.2×10^{-1} mole/liter). The difference in type of reaction product obtained between the phenyl and naphthyl series may well have been due to a concentration factor. To test this possibility, the irradiation of 22b was carried out in benzene at a concentration of 1.5×10^{-3} mole/liter. The irradiation was also carried out in isopropyl alcohol at a concentration of 2.2×10^{-3} mole/liter to determine which conditions facilitated the formation of the monomeric product. However, no corresponding monomeric products were obtained, the major product again being the dehydrogenated coupling product 23b.

Because of the similarity of the absorption spectrum of all the 1,2-dithiole-3-thiones studies, it is assumed that the reaction in both of the phenyl and the naphthyl-1,2-dithiole-3-thione series occurs via a $n\pi^*$ transition, a state which is responsible for the photoreaction in most of thioketones (14, 42). Although the high intensity $\pi\pi^*$ band at 420 nm absorbs most of the absorbed light, a fast internal conversion to the $\pi\pi^*$ state may occur due to the very small energy gap separating these two states. The multiplicity and the reaction mechanism were not investigated. But it may be assumed that the electrophilic half-vacant n orbital of the sulfur atom of the n-π* state of the thiones attacked the electron rich phenyl ring to form a diradical intermediate, 33, (see Scheme 2). This intermediate may couple or extract hydrogen to form a coupled or cyclised product depending on the substituent at the 4-position.

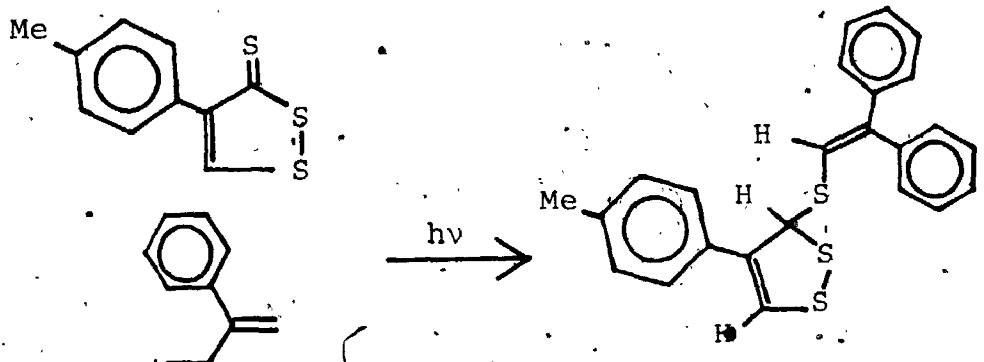
2.4 Photoreaction between Olefins and 4-p-Tolyl-1,2-dithiole 3-thione

It was one of our original purposes to see whether olefins would cycloadd to the 1,2-dithiole-3-thione system to form a cyclobutane derivative. Although a number of different olefins was used in this study, none of them reacted cleanly with 4-p-tolyl-dithiole-3-thione.

A. Addition of 4-p-Tolyl-1,2-dithiole-3-thione to 1,1-Diphenyl-ethylene

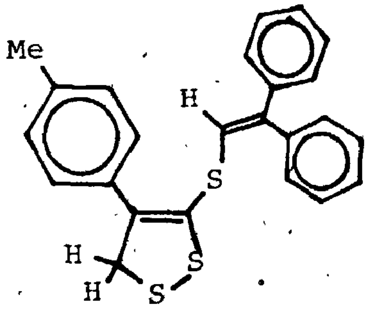
Irradiation (λ>420 nm) of 4-p-tolyl-1,2-dithiole-3-thione in the presence of 1,1-diphenyl-ethylene gave a complex reaction mixture. No cycloaddition product was isolated.

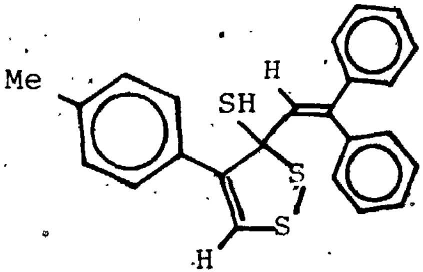
The major isolable product was the adduct 42 (60%) whose structure was established on the basis of spectroscopic measurements and chemical transformations. The mass spectrum of the product showed the expected molecular ion,



42

peak at m/e=404. The nmr spectrum showed two singlets at 4.40 and 6.50 ppm each singlet corresponding to one proton: neither was exchangeable for deuterium with D_2O. These observations excluded the alternative structures 43 or 44. The exclusion of 43 is based on the number of protons each



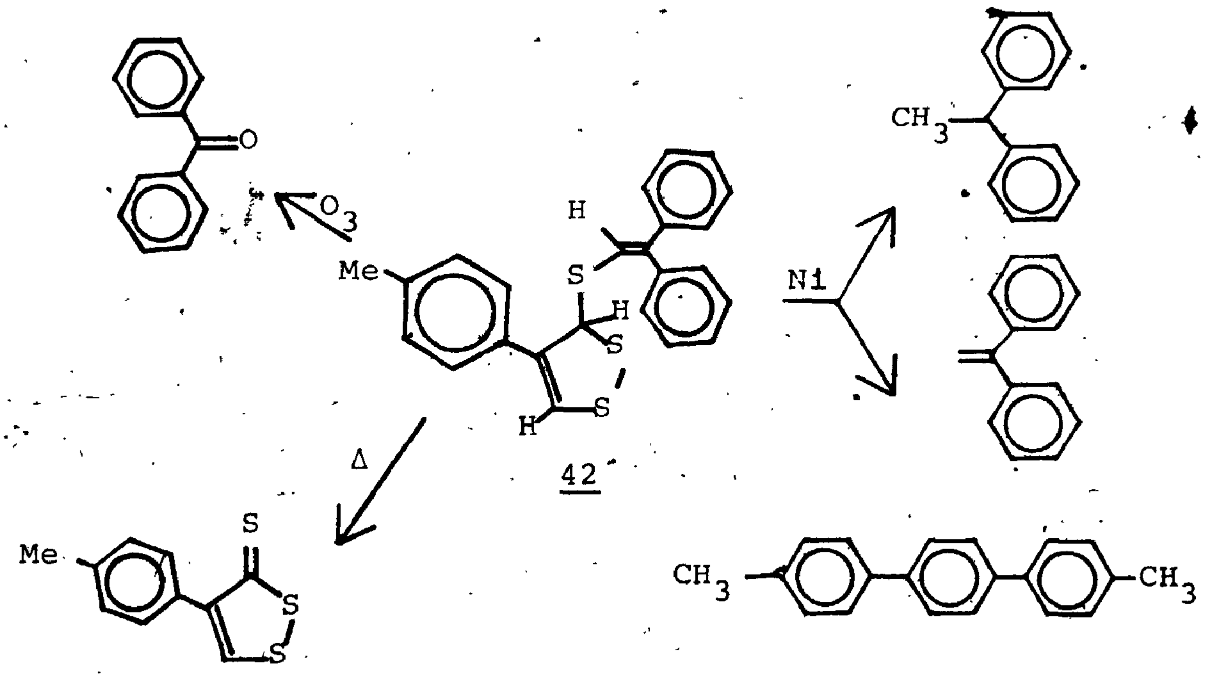


43

44

singlet contains. For 43, one of the singlets must integrate for 2 protons. The elimination of 44 as the correct structure was due to the fact that the protons were not exchangeable and there was no absorption peak at around 2750 cm^{-1} in the ir spectrum. These are two distinct characteristics of a thiol group. The vinyl proton in the five membered ring appeared in the aromatic region and could not be seen at all. Its presence was revealed by integration.

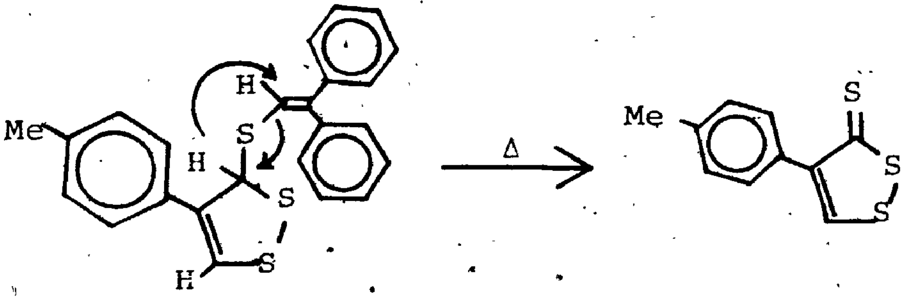
Upon ozonolysis, 42 gave a carbonyl compound together with some other, unidentified products. The carbonyl compound was shown to be benzophenone by comparison of its ir spectrum and m.p. of the 2,4-dinitrophenylhydrazone derivative with those of an authentic specimen. W$_3$ Raney nickel reduction in methanol yielded 1,1-diphenylethylene in 20% yield. When the reduction was carried out in benzene with a more active W$_3$ Raney nickel, it gave 1,1-



diphenylethylene, 1,1-diphenylethane and 1,1-dimethyl-p-terphenyl in 15, 3.5 and 5% yields respectively.

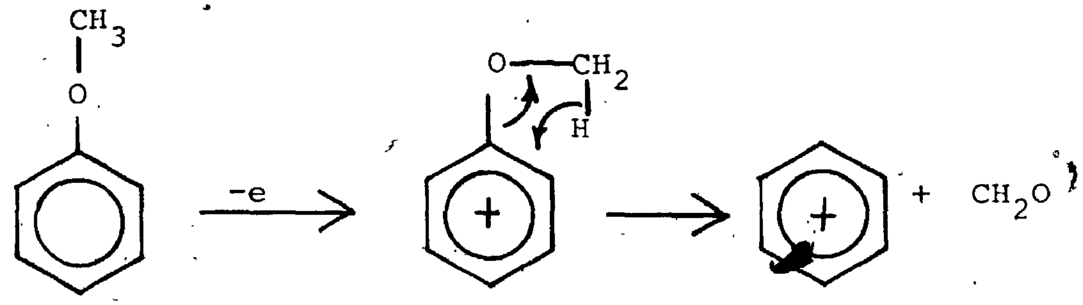
The different results obtained from the desulfurization may be attributed to the different reactivity of the Raney nickel used. It seems that when a higher hydrogen content nickel is used the desulfurisation proceeds at a much greater rate. At the same time reduction takes precedence over coupling.

Thermal decomposition of 42 under vacuum at 178° for 12 hours afforded the starting 4-p-tolyl-1,2-dithiole-3-thione in 46% yield. The mechanism of the transfer of the hydrogen atom to form the thione group is not clear. It may be assumed that a 1,3-hydrogen shift followed by the cleavage of the vinyl-sulfur bond occurs as shown in the drawing. Unfortunately, such a rearrangement has not yet



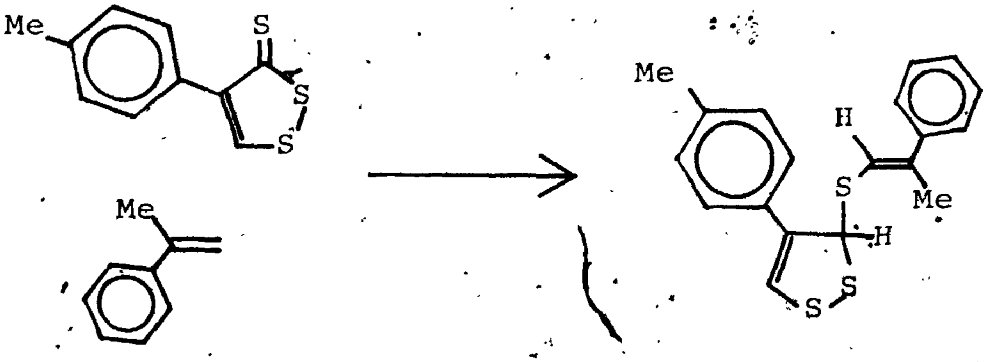
42

been reported. However, an analogous fragmentation of anisole in a mass spectrometer via a four-membered cyclic transition state has been postulated (43).



B. Addition of 4-p-Tolyl-1,2-dithiole-3-thione to α-Methyl Styrene

When a benzene solution of 4-p-tolyl-1,2-dithiole-3-thione was irradiated (λ>420 nm) in the presence of α-methyl styrene, the 1,1-adduct 45 was produced in 10% yield. The structure of the adduct was determined from spectroscopic data and by comparison of its physical data with that of 42. It showed a molecular peak at m/e=342. The nmr spectrum showed a doublet of 3 protons at 1.88 ppm



45

with a coupling constant 1.0 Hz, a singlet of 3 protons at 2.34 ppm, a singlet of 1 proton at 4.30 ppm, a quartet of 1 proton at 6.21 ppm with a coupling constant of 1.0 Hz and 10 protons in the region of 7.07-7.15 ppm.

The methyl group on the double bond was assigned to be trans to the hydrogen [i.e. E-isomer (44)]. The assignment cannot be derived from the magnitude of the coupling constant with the adjacent proton alone. The value obtained in the present case (1.0 Hz) is inconclusive although cisoid coupling constants are usually greater than this. The trans relation between the proton and methyl group was suggested by the actual chemical shift of the proton, using the method of chemical shift estimation established by Pascual and his coworkers (29). This method is based on the fact that substituents on a double bond induce different chemical shifts when cis or trans to a particular olefinic proton. It is possible to estimate the chemical shift for the cis (Z) and trans (E) configuration using the value 5.28 ppm for the chemical shift of an ethylene proton and appropriate standard values derived from substituent coefficients for the phenyl, methyl and sulfide groups. The values estimated by this method are 5.92 ppm for the Z-isomer and 6.32 ppm for the E-isomer, the latter value agreeing better than the former with the experimental value.

C. Irradiation of 22b in the Presence of Electron Rich

Olefins

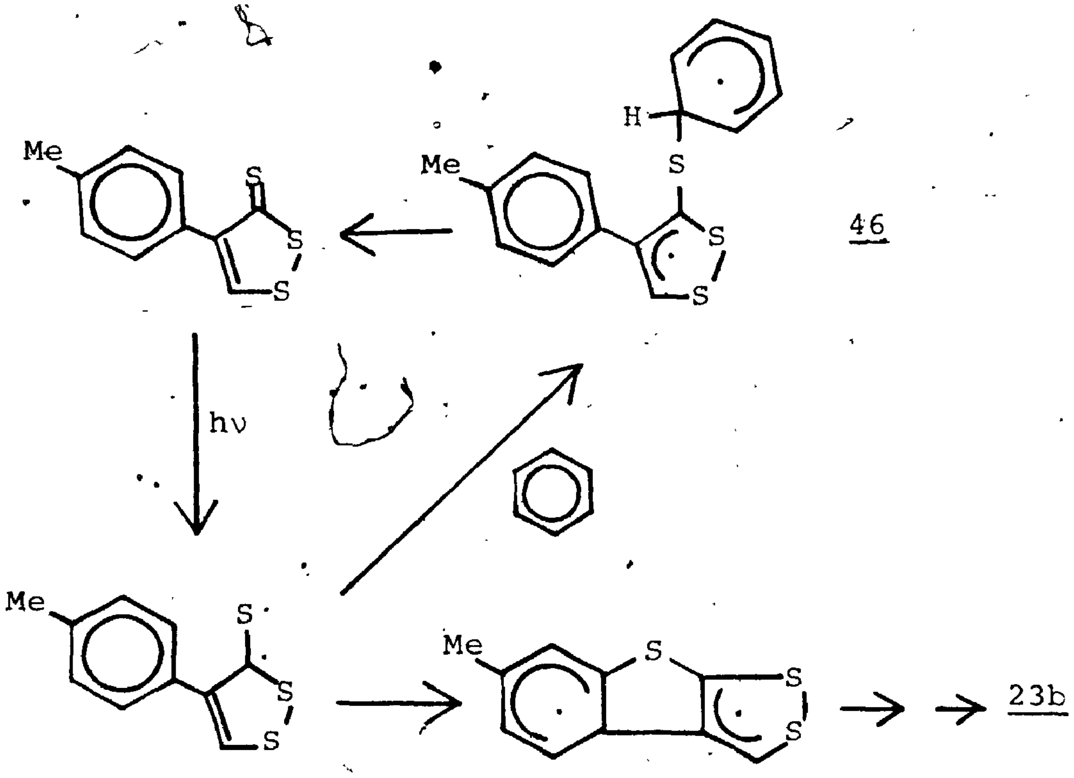
When 22b was irradiated (λ>420 nm) in the presence of electron rich olefins, namely: cyclohexene and ethylvinyl ether, the reaction proceeded at a much faster rate than that with 1,1-diphenylethylene or α-methylstyrene. Unfortunately, the reaction was so messy that no definite spot could be seen on tlc. The reaction was not further investigated.

D. Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione, 22b, in cis-1,2-Dichloroethylene

When 22b was irradiated (λ>420 nm) in cis-1,2-dichloroethylene, 23b was formed. The rate of formation of 23b in the presence of cis-1,2-dichloroethylene was faster than that in benzene solution. Tlc showed only the presence of the starting materials and 23b.

The results may be explained by the electrophilic nature of the nπ* state of the excited C=S group. When benzene is used as solvent, the electrophilic sulfur atom may react intermolecularly with the solvent to form the diradical 46 or it may attack the tolyl group intramolecularly to form 33 (see Scheme 3).

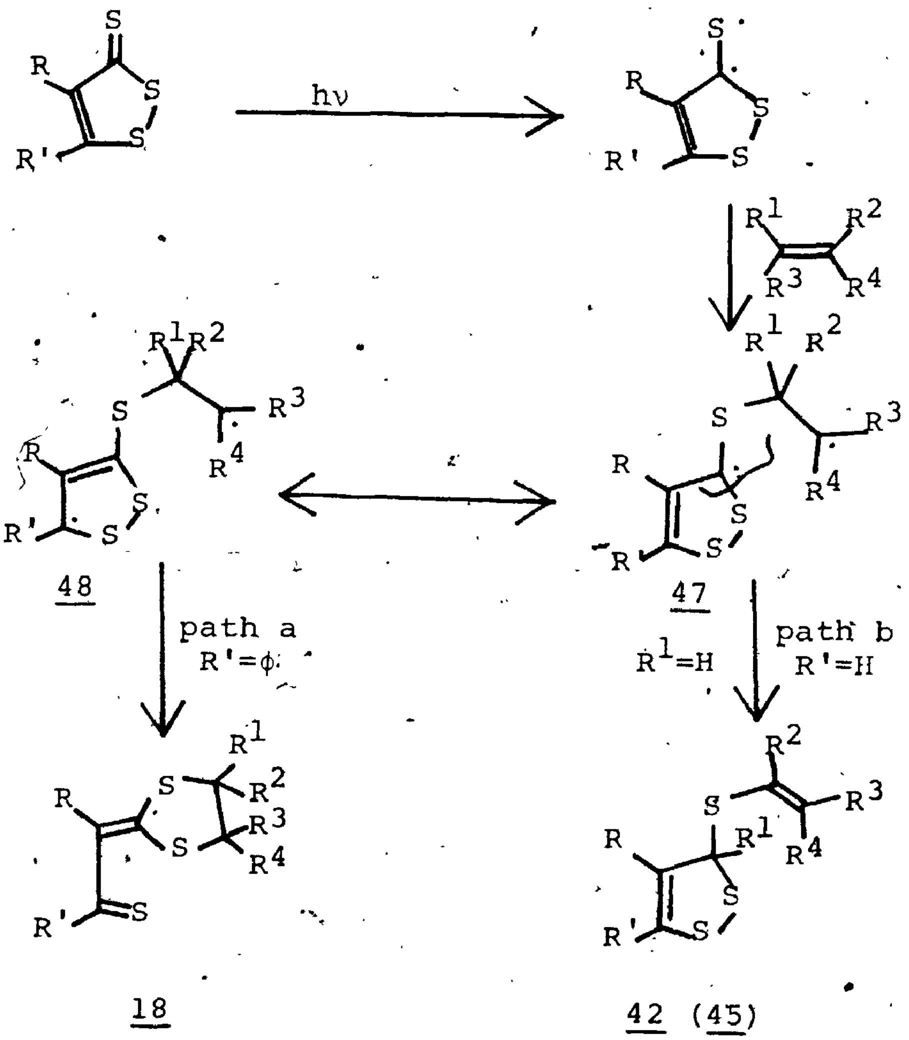
The diradical 46 may revert back to the starting thione and benzene. An analogous reaction route has been suggested as the major path of deactivation of carbonyl triplet states with nπ* electronic character (45-47). In our case, with benzene as solvent, the intermolecular



Scheme 3

process may compete successfully with the intramolecular pathway and this may account for the slow rate in the formation of 23b.

An oversimplified mechanism of reaction between 4-p-tolyl-1,2-dithiole-3-thione and different olefins is presented in the following sequence. Upon irradiation, an excited state of the C=S group of the 1,2-dithiole-3-thione is produced. The excited state is nπ*, a state also responsible for the coupling and cyclisation reactions (see sections 2.2 and 2.3). Addition to the olefins through the electron deficient sulfur site of the nπ* state may occur, in the same way as the addition of adamantanethione to olefins (42), to form a diradical. This diradical intermediate may be represented by two resonance forms 47 and 48. When the intermediate possesses an aromatic substituent at the 5 position (R'=Ph) cleavage of the disulfide linkage occurs with the formation of 2-thiobenzoyl-methylene-1,3-dithiolanes (path a) (see Scheme 4). In the absence of the



Scheme 4

phenyl group at the 5-position, hydrogen transfer takes precedence, with the formation of adducts of type 42 and 45 (path b).

2.5 Summary

Irradiation of aryl-1,2-dithiole-3-thiones results in the formation of the coupling products, 23, and the naphthothiophenes 36 (37). This observation parallels the cyclization of thiobenzoyl polycyclic aromatic compounds reported by Lapouyade and de Mayo (14). Irradiation of 4-p-tolyl-1,2-dithiole-3-thione with olefins leads only to a vinyl 3-(4-p-tolyl-3H-1,2-dithiolyl)-sulfide (42,45) and not to a cycloaddition product. From these results, it may be concluded that an α,β-unsaturated thioketone or its derivative behaves differently from an enone and that the preferred site of photoreaction is the thione group.

EXPERIMENTAL

GENERAL

All melting points were measured on a Reichert apparatus and are uncorrected. Infrared spectra (ir) were obtained using a Beckman IR-10 or IR-20A spectrophotometer. Ultraviolet spectra (uv) were recorded on a Cary model 14 spectrophotometer and the unit for the molar absorption extinction (ε) is liter x mole^{-1} x cm^{-1}. Proton nuclear magnetic resonance (nmr) spectra were measured on a Varian T-60 or a Varian HA-100 spectrometer unless otherwise specified. Chemical shifts are reported as δ values in parts per million from TMS. The coupling constants (J) are given in cycles per second (Hz) and the multiplicity of each absorption is denoted as follows: s=singlet, d= doublet, t=triplet, q=quartet and m=multiplet. The ^{13}C spectra were taken on a Varian XL-100-15 instrument. The peak positions were measured using internal TMS as reference. Mass spectra data were determined on a Varian M-66 spectrometer. The first m/e values are given for the molecular ions while the other values are for the major fragments in the spectra. Elemental analyses were performed by the Gygli Microanalytical Laboratory, Toronto, Ontario. Precise mass determinations were carried out on a Varian M-66 spectrometer (multiple determinations) using appropriate halogen compounds as internal calibrants.

CHEMICALS

α-Methyl styrene (Eastman) and 1,1-diphenylethylene (Eastman) were distilled under nitrogen on a 40 cm spinning band column.

Cyclohexene (Aldrich) was refluxed under nitrogen over sodium for 1.5 hours, then distilled through a 30 cm Vigreux column. It was passed through a column of alumina (Woelm neutral) prior to use.

Ethyl vinyl ether (Aldrich) was refluxed under nitrogen and over sodium for 2 hours, then distilled through a 10 cm Vigreux column.

Maleic anhydride (Baker) was recrystallised from ether. 1,1-dichloroethylene (Pfaltz and Bauer) was distilled once. 1-Bromonaphthalene (Aldrich), 1,bromo-4-methyl naphthalene (Pfaltz and Bauer), p-bromophenyl phenyl ether (Pfaltz and Bauer), 4-bromobenzotrifluoride (Aldrich), 4-bromofluorobenzene (Pfaltz and Bauer) were used without purification. Cumene and p-cymene (Aldrich) were distilled once. Benzene (Fisher) (for preparative irradiation) was purified by irradiation of spectroanalyed benzene with chloranil for 7 days and subsequent distillation under nitrogen using a Vigreux column. Silica gel for column chromatography was supplied by British Drug Houses while that for tlc was supplied by Mondray.

Preparation of α-Isopropylnaphthalene

1-Bromonaphthalene (30 gm) was reacted with magnesium metal (3.5 gm) in ether (50 ml). After 3 hours, the reaction mixture was cooled and an excess of acetone was added. The reaction mixture was then stirred for 4 hours at room temperature. At the end of this time 10% sulfuric acid (20 ml) was added to the mixture which was heated on a steam bath for one hour. It was then extracted with benzene and washed with sodium bicarbonate solution. The organic layer was dried and solvent was removed. The residue was heated with 85% phosphoric acid (5 ml) at 140° for thirty minutes. This mixture was extracted with benzene (50 ml), washed with sodium bicarbonate solution and water. The crude product was hydrogenated in methanol using platinum oxide (100 mg) as catalyst. After the uptake of hydrogen had ceased, the solution was filtered and solvent was removed. The product was distilled at 135°/12 mm Hg [Lit. 132°/12 mm Hg (48)] in 90.1% yield; nmr (CCl_4), 1.00 (d, J=3.5, 6H), 3.20 (m, J=3.5, 1H) and aromatic protons.

Preparation of 1-Methyl-4-isopropylnaphthalene

The procedure for preparing α-isopropylnaphthalene was followed. Hence, 1-bromo-4-methylnaphthalene (10 gm) gave 1-methyl-4-isopropylnaphthalene (6.5 gm, 78%), b.p. 140-5°/12 mm Hg [Lit. 135-45°/12 mm Hg (49)].

Preparation of 4-Aryl-1,2-dithiole-3-thione

Compounds A-D were prepared according to the method of Fields (18). A mixture of 2-arylpropane (0.03 moles), sulfur (0.04 moles) and quinoline (0.5 ml) was refluxed for 24 hours. The mixture was kept at 0° for 24 hours to allow the thione to crystallize. The red solid was collected and chromatographed on 200 gm of silica gel (BDH) using petroleum ($60-80^{\circ}$)-benzene (4:1) as eluent. The resulting orange solid was recrystallized from an appropriate solvent. The spectral data obtained for the aryl-1,2-dithiole-3-thione are given as follows:

A. 4-p-Tolyl-1,2-dithiole-3-thione (22b)

Yield = 25%; m.p. (cyclohexane) $100-102^{\circ}$ [Lit. $122-3^{\circ}$ (18) or 102° (50)]; ir ($CHCl_3$) 3050, 3000, 1335, 1315, 1145, 1010, 850 cm^{-1}; nmr ($CDCl_3$) 2.40 (s, 3H), 7.0-7.4 (q, 4H), 8.20 (s, 1H); uv (see Table 1); mass spectrum m/e 224 (90), 223 (100).

B. 4-Phenyl-1,2-dithiole-3-thione (22a)

Yield = 30%; m.p. (cyclohexane) $120-1^{\circ}$ [Lit. 123° (18)]; nmr ($CDCl_3$) 7.3-7.6 (m, 5H), 8.3 (s, 1H); uv (see Table 1); mass spectrum m/e (%) 210 (85), 209 (100).

C. α-Naphthyl-1,2-dithiole-3-thione (34)

Yield = 10%; m.p. (benzene) $204-6^{\circ}$ [Lit. 198° (51)]; nmr (CS_2) 7.32-7.93 (m, 7H), 8.28 (s, 1H); uv (see Table 1); mass spectrum m/e (%) 260 (95), 259 (100).

Calcd. for $C_{13}H_8S_3$: 259.9788. Found: 259.9765

D. 4-[1-(4-Methyl-naphthyl)]-1,2-dithiole-3-thione (35)

Yield = 7%; m.p. (benzene) 195-6°; nmr (CS_2) 2.62 (s, 3H), 7.20-8.00 (m, 6H), 8.20 (s, 1H); uv (see Table 1); mass spectrum m/e (%) 274 (90), 273 (100).

Calcd. for $C_{14}H_{10}S_3$: 273.9945. Found: 273.9949.

Compounds E-G were prepared according to Thuillier and coworkers (19) in the following sequence of reactions (shown in Scheme 1):

i. Preparation of Allyl Arene, 19

This was prepared by a coupling reaction between allyl bromide and the corresponding Grignard reagent. The pure product was obtained by vacuum distillation.

ii. Preparation of Aryl-acetaldehyde, 20, from Allyl Arene

Ozonolysis of the allyl arene, 19, was carried out in methylene chloride at -78°. The ozonide was decomposed by stirring with zinc dust in acetic acid to give the aldehyde which was distilled at reduced pressure under a nitrogen atmosphere.

iii. Preparation of 2-Aryl-3,3-bis(methylthio)-2-propenal, 21

The reaction was carried out under nitrogen and it was protected from moisture by a calcium chloride tube.

Sodium hydride (0.13 mole) was added to dimethylsulfoxide (50 ml). The aldehyde, 20, (0.065 mole) was added to the stirred mixture over a period of 20 minutes and the temperature was kept at 20°. Carbon disulfide (0.054 mole) was then added and the mixture became dark red. Methylation was performed after 30 minutes by adding methyl iodide (0.13 mole), the stirring being continued for 3 hours. The reaction mixture was taken up in water and extracted with benzene. The organic portion was washed 10 times with salt water and was dried. The yellow residue obtained was separated by preparative tlc using benzene as eluent.

iv. Preparation of 4-Aryl-1,2-dithiole-3-thione, 22

A solution of 2-aryl-3,3-bis(methylthio-)-2-propenal, 21, (5 gm) in xylene was added over a period of 20 minutes to a stirred suspension of phosphorus pentasulfide (25 gm) in boiling xylene (500 ml). The reaction mixture was refluxed for one hour. It was decanted while hot, was diluted with ether and allowed to stand for 5 hours before it was filtered. The filtrate was washed with dilute sodium hydroxide solution and brine. After evaporation of solvent, the residue was recrystallized.

E. 4-p-Fluoro-phenyl-1,2-dithiole-3-thione (22e)

1. the allyl arene, 19e

   yield = 69%; b.p. 156-160° [Lit. 157-160° (52)].

2. the acetaldehyde, 20e

yield = 79%; b.p. 64-66°/6 mm Hg [Lit. 63-5°/5-6 mm Hg (53)]; nmr (CCl_4) 3.48 (d, J=1.5, 2H), 6.8-7.1 (m, 4H), 9.50 (d, J=1.5, 1H).

3. the propenal, <u>21e</u>

yield = 42%; b.p. 175°/2 mm Hg; ir (CCl_4) 3040, 1878, 1643, 1480, 1257, 1220, 1020 cm^{-1}; nmr ($CDCl_3$) 2.03 (s, 3H), 2.38 (s, 3H), 7.0-7.3 (m, 4H), 10.2 (s, 1H); ^{19}F nmr ($CDCl_3$) 2544; uv (methanol) $\lambda_{max.}$ 327, 253 nm (ε= 11100, 4500); mass spectrum m/e 242.

4. the thione <u>22e</u>

yield = 50%; m.p. (hexane) 152-3°; ir ($CHCl_3$) 3020, 1610, 1314, 1200, 1135, 850 cm^{-1}; nmr ($CDCl_3$) 7.08 (m, 2H), 7.50 (m, 2H), 8.2 (s, 1H) ^{19}F nmr ($CDCl_3$) 2540; uv (see Table 1); mass spectrum m/e (%) 228 (82), 227 (100).

Calcd. for $C_9H_5FS_3$: 227.9547. Found: 227.9547.

F. <u>4 - p-Perfluoromethyl-phenyl-1,2-dithiole-3-thione (22d)</u>

1. the allyl arene, <u>19d</u>

yield = 74% b.p. 166-70° [Lit. 168-70° (52)].

2. the acetaldehyde, <u>20d</u>

yield = 62%; b.p. 84-88°/8 mm Hg [Lit. 81.5-82.5°/7.5 mm Hg (54)].

3. the propenal, <u>21d</u>

yield = 90%; b.p. 120-2°/0.5 mm Hg; ir (CCl$_4$) 3080, 2945, 1667, 1615, 1335, 1177, 1109, 954, 848, 710 cm^{-1}; nmr (CCl$_4$) 2.12 (s, 3H), 2.45 (s, 1H); uv (methanol) $\lambda_{max.}$ 327, 280, 250 nm (ε=10900, 5300, 5500); mass spectrum m/e 292.

4. the thione, 22d

yield = 52%; m.p. 144-145.5°; ir (CHCl$_3$) 2998, 1610, 1318, 1299, 1277, 1128, 995, 822 cm^{-1}; nmr (CDCl$_3$) 7.63 (s, 4H), 8.33 (s, 1H); uv (see Table 1); mass spectrum m/e (%) 278 (85), 277 (100).

Anal. calcd. for $C_{10}H_5F_3S_3$: C, 43.18; H, 1.81; F, 20.49; S, 34.51. Found: C, 43.11; H, 2.01; F, 20.24; S, 34.77.

G. 4-p-Phenoxy-phenyl-1,2-dithiole-3-thione (22c)

It was obtained in 22%, m.p. 123-4°; nmr (CDCl$_3$) 6.92-7.50 (m, 9H), 8.20 (s, 1H); uv (see Table 1); mass spectrum m/e (%) 302 (100), 301 (80).

Anal. cald. for $C_{15}H_{10}S_3O$: C, 59.61; H, 3.34; S, 31.76. Found: C, 59.55; H, 3.49; S, 31.78.

Preparation of 2,5-Diphenyl-n-hexane (26)

2,5-Dihydroxy-2,5-diphenyl-n-hexane was prepared according to Freeman (55). Recrystallization from n-hexane gave white crystals, m.p. 135-40° [Lit. 135-50°]; ir (CCl$_4$) 3600, 3400 cm^{-1}; nmr (CCl$_4$) 1.5 (d, 3H), 1.77 (s, 2H), 2.35

(s, 1H), 7.2 (s, 5H). 2.5-Diphenyl-2,5-hexadiene was prepared according to the method of Shvartsberg and coworkers (56). Hence, 1.7 gm 2,5-diphenyl-hexa-2,5-diol gave 0.8 gm 2,5-diphenyl-2,5-hexadiene (m.p. 136-8°). Hydrogenation of this diene over platinum oxide gave a colorless oil, 2,5-diphenyl-n-hexane, in 50% (0.4 gm) yield, ir (CCl_4) 3100, 3080, 1600, 1493, 1450, 1375, 1325, 905 cm^{-1}; nmr (CCl_4) 1.13 (d, 6H), 1.50 (m, 4H), 2.50 (m, 2H), 7.0 (s, 10H); mass spectrum m/e 238.

Preparation of W$_3$ Raney Nickel

Sodium hydroxide (5 gm) in water (20 ml) was placed in a 250 ml flask equipped with a magnetic stirrer and a thermometer. The solution was cooled to -5° in a salt-ice bath. Raney nickel aluminum alloy (4 gm) was added in small portions over a period of thirty minutes. During the addition the temperature never rose above 5°. The ice bath was then removed and the temperature was raised to 50° over a period of 50 minutes on a steam bath. The sodium hydroxide solution was then decanted and the Raney nickel divided into two equal portions. Each was put into a centrifuge tube and was washed 40 times with water, 5 times with ethanol and 5 times with acetone. The Raney nickel was refluxed in acetone for 6 hours. The acetone was decanted and the Raney nickel was washed 4 times with ethanol.

Preparative Irradiations

A typical example was the irradiation of 4-p-tolyl-1,2-dithiole-3-thione (22b) in benzene at room temperature.

(1) Irradiation of 4-p-tolyl-1,2-dithiole-3-thione

A solution of 4-p-tolyl-1,2-dithiole-3-thione (0.0015 mole/liter and 0.22 mole/liter, i.e. 33 mg/100 ml and 1.1 gm/20 ml) in benzene was degassed by the freeze-thaw method (three cycles) in a pyrex tube. The solution was irradiated in the sealed tube through a Corning 0-73 filter (420 nm cut off) for 6 days. The yellow solid (0.5 gm) deposited on the wall of the irradiation cell was collected and washed with benzene (20 ml). It was recrystallized from chloroform (250 ml) to give pale yellow crystals, 23b, in 44% (0.48 gm) yield; m.p. 252-4^{o} (dec.); ir (CS_2) 3040, 2930, 1345, 1328, 1218, 1098, 1005, 1049, 975 cm^{-1}; nmr (CS_2) 2.43 (s, 3H), 4.94 (s, 1H), 7.17 (d, J=8, 1H), 7.40 (s, 1H) 7.67 (d, J=8, 1H), uv (2-propanol) $\lambda_{max.}$ 340, 309, 262, 225 nm (ε= 1160, 3800, 9200, 15200); mass spectrum m/e 446, 233, 218. Molecular weight determination: the molecular weight was found to be 490 (determined in pyridine using a Hewlett Packard 310 Vapour Pressure Osmometer and benzil as calibrant) while the value for 23b is 446.

Anal. Calcd. for $C_{20}H_{14}S_6$: C, 53.82; H, 3.16; S, 43.02.
Found: C, 53.68; H, 3.16; S, 43.07.

Tlc analyses of the filtrate showed that it contained a complicated mixture, one of the major components being 23b.

No further analyses of the mixture were undertaken.

Raney Nickel Desulfurization of 23b

A solution of 23b (333 mg) in ethanol (600 ml) was added to Raney nickel (2 gm) (prepared from 4 gm Raney nickel aluminum alloy) in ethanol (5 ml). The solution was refluxed for 3 days, after which time the ethanol was filtered through Celite and the Raney nickel was wahsed twice with two 30 ml portions of hot ethanol. The ethanol was evaporated and the residue was chromatographed on 100 gm silica gel using petroleum (60-80) as eluent to give three compounds.

The first compound was a white solid, 27, in 21% (57 mg) yield; m.p. (chloroform) 139-40°; nmr ($CDCl_3$) 2.47 (s, 3H); 3.21 (s, 2H); 6.89 (s, 1H); 7.09 (d, J=8, 1H); 7.55 (d, J=8, 1H); 7.58 (s, 1H); uv (see Table 3); mass spectrum m/e 322 and 161.

Anal. calcd. for $C_{20}H_{18}S_2$: C, 74.52; H, 5.65; S, 19.83. Found: C, 74.06; H, 5.98; S, 20.00.

The second compound was also a solid, 28, in 8.6% (26 mg) yield, m.p. (chloroform) 157-9°; nmr ($CDCl_3$) 2.46 (s, 6H), 7.0-8.0 (m, 10H), mass spectrum m/e 320.

Calcd. for $C_{20}H_{16}S_2$: 320.0693. Found: 320.0691.

Third compound was a white solid, 29, obtained in 2.2% (8 mg) yield, m.p. (chloroform) 285-95°, (sublimed); nmr (CS_2) 2.5 (s), 7.5-8.2 (m); uv (MeOH) $\lambda_{max.}$ 342, 318, 307 (s), 294, 283, 262, 259, 255, 253, 247, 244 nm (ε=231, 1880, 1388, 1938, 1215, 1700, 1780, 1866, 1909, 2490, 2580); mass spectrum m/e 318.

Calcd. for $C_{20}H_{14}S_2$: 318.0536. Found: 318.0421

(2) Irradiation of 4-Phenyl-1,2-dithiole-3-thione (22a)

This thione (1.25 gm) gave the product, 23a, (350 mg, 30% yield) m.p. (choroform) 234-6°; nmr (CS_2) 5.03 (s, 1H), 7.13-7.95 (m, 4H); uv (CH_2Cl_2) $\lambda_{max.}$ 340, 310, 298, 283, 262 nm (ε=2470, 9100, 10100, 11200, 19500).

Anal. calcd. for $C_{18}H_{10}S_6$: C, 51.69; H, 2.41; S, 45.90.
Found: C, 51.90; H, 2.28; S, 46.22.

Desulfurization of 23a

The procedure used for the reduction of 23a was identical to that for 23b except that the Raney nickel was not deactivated. When the ethanol was evaporated, an oil was obtained which was shown to contain only one component. The product 2,5-diphenyl-n-hexane, 26, was a colorless oil and was obtained in 78% yield. The retention time, ir, nmr and mass spectra were identical with those of 2,5-diphenyl-n-hexane, 26.

(3) Irradiation of 4-p-Fluoro-phenyl-1,2-dithiole-3-thione (22e)

Irradiation of this thione (85 mg) in benzene (20 ml) gave compound (20 mg), 23e, m.p. (CS_2) 340-5°; uv (CH_2Cl_2) $\lambda_{max.}$ 342, 308 (s), 282, 258 nm (ε= 1000, 5200, 7800, 17500; mass spectrum m/e (%) 454 (1), 388 (100) and 358 (7), 192 (16).

Anal. calcd. [illegible] $C_{18}H_8F_2S_6$: C, 47.59; H, 1.77; S, 42.26. Found: C, 47.64; H, 1.97; S, 41.84.

(4) Irradiation of 4,p-Perfluoromethyl-1,2-dithiole-3-thione (22d)

Irradiation of this thione (100 mg) in benzene (20 ml) gave 23d, in 25% yield (25 mg), m.p. (CS_2) 250-2°; ir (CS_2) 1320, 1261, 1165, 1129, 1089, 1068, 818 cm^{-1}; nmr (CS_2) 5.13 (s, 1H), 7.53 (dd, J=2 and 0.5, 1H), 7.80 (d, J=0.5, 1H) 8.02 (d, J=2, 1H); uv (CH_2Cl_2) $\lambda_{max.}$ 256 nm (ε=2700, 7300, 9500, 11300); mass spectrum m/e (%) 554 (2), 488 (100), 458 (20), 444 (20), 426 (32), 278 (25).

Anal. calcd. for $C_{20}H_8F_6S_6$: C, 43.34; H, 1.45; S, 34.64. Found: C, 43.21; H, 1.37; S, 34.64.

(5) Irradiation of 4,p-Phenoxy-phenyl-1,2-dithiole-3-thione (22c)

Irradiation of the thione (100 mg) in benzene (20 ml) yielded 23c (35 mg), m.p. (MeOAc) 200-2°; nmr (CS_2) 4.98 (s, 1H), 6.78-7.20 (m, 8H), 7.76 (d, 1H); uv (CH_2Cl_2) $\lambda_{max.}$ 345, 290, 260 nm (ε=2060, 1200, 22600); mass spectrum m/e 602.

Anal. calcd. for $C_{30}H_{18}O_2S_6$: C, 59.80; H, 3.01; S, 31.87. Found: 59.75, H, 3.36; S, 31.77.

(6) Irradiation of 4-α-Naphyl-1,2-dithiole-3-thione (34)

A solution of the thione (78 mg) in benzene (80 ml) was irradiated for 2 days. The complex reaction mixture was separated on a preparative tlc plate to give 36 as the only isolable product in 20% yield, m.p. (benzene) 189-91°; nmr (CS_2) 4.63 (s, 2H), 7.30-7.80 (m, 5H), 8.30 (m, 1H); uv (CH_2Cl_2) $\lambda_{max.}$ 334, 282 nm (ε=4450, 4150); mass spectrum m/e (%) 260 (100), 259 (70), 228 (25), 227 (28) and 192 (10).

Calcd. for $C_{13}H_8S_3$: 259.9789. Found: 259.9777.

(7) Irradiation of 4-[1-(4-Methyl-naphthyl-)]-1,2-dithiole-3-thione (35)

A solution of the thione (40 mg) in benzene (15 ml) was irradiated for 3 days to give 37 (8 mg) separated from preparative tlc, m.p. (CH_2Cl_2-C_6H_{12}) 192-5°; nmr (CS_2) 2.80 (s, 3H), 4.75 (s, 2H), 7.5-8.2 (m, 4H), 8.60 (m, 1H); uv (CH Cl) $\lambda_{max.}$ 365, 337, 286, 248 nm (ε=3300, 3600, 3700, 14400), mass spectrum m/e 274.

Calcd. for $C_{14}H_{10}S_3$: 273.9945. Found: 273.9966.

(8) Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione in Isopropanol

A solution of the thione (2.24×10^{-3} mole/liter) in isopropanol was degassed and was irradiated in the usual manner for 3 days. The nmr spectrum of the crude reaction product showed that there were no other peaks in the region between 4.0-6.5 ppm except the one at 4.95δ. The only isolable product was 23b.

(9). Short Wavelength Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione

4-p-Tolyl-1,2-dithiole-3-thione (100 mg) in cyclohexane (40 ml) was degassed in a quartz tube. The resulting solution was irradiated at 254 nm with a Rayonet reactor at room temperature for 6 days. There was a layer of insoluble substance attached to the wall of the quartz tube. The solution was concentrated and chromatrographed on a preparative plate to give 35 mg of the starting thione and 5 mg 23b.

Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione and 1,1-Diphenyl-ethylene

A solution of 4-p-tolyl-1,2-dithiole-3-thione (740 mg) and 1,1-diphenyl-ethylene (8 ml) in benzene (10 ml) was saturated with nitrogen and irradiated with light of wavelengths greater than 420 nm for 3 days. The reaction yielded a complex mixture (tlc) which was separated on silica gel (200 gm) using petroleum (60-80°)-benzene as eluent. Apart from the unreacted 1,1-diphenylethylene, the 1,1 adduct 42 was obtained in 64% yield, m.p. (n-hexane/chloroform) 188-9°; ir ($CHCl_3$) 3060, 3040, 3000, 1610, 750, 730, 700, 675, 500 cm^{-1}; nmr ($CDCl_3$) 2.35 (s, 3H), 4.40 (s, 1H), 6.50 (s, 1H), 7.10 (m, 15H); uv (C_6H_{12}) $\lambda_{max.}$ 310, 280 (s), 230 (s), nm (ε=13230, 12000, 19990); mass spectrum m/e (%) 404 (1), 390 (40), 224 (100), 223

(95), 212 (93), 211 (90), 209 (85), 180 (15), 179 (20). Anal. calcd. for $C_{24}H_{20}S_3$: C, 71.26; H, 4.99; S, 23.74. Found: C, 71.27; H, 5.27; S, 23.77.

Thermal Decomposition of 42

Compound 42 (6.6 mg) was sealed under vacuum (0.1 mm Hg) in a pyrex tube and was heated at 178° for 12 hours. The reaction mixture was then dissolved in chloroform. 4-p-Tolyl-1,2-dithiole-3-thione was separated by preparative tlc in 46% yield. It had a melting point 100-1° which did not depress that of an authentic sample.

Raney Nickel Desulfurisation of 42

A suspension of 42 (100 mg) and Raney nickel (1 gm, previously deactivated in acetone for 6 hours) in methanol (20 ml) was refluxed for 12 hours. The oily residue was vacuum distilled to give two fractions, the fraction with a lower boiling point being 1,1-diphenylethylene in 20% (12 mg) yield. The nmr spectrum and the retention time of this product were identical with those of an authentic specimen.

The higher boiling point fraction was obtained in 5 mg yield. The nmr showed peaks at 2.4, 5.2, 5.5, 6.4 and in the aromatic region. No further investigations were made.

When the desulfurisation was carried out in benzene using a large amount of Raney nickel (deactivated for only 2 hours), the reaction mixture contained more than 2 compounds. The crude product, on standing, gave a solid, 4,4'-dimethyl-p-terphenyl in 5% yield, m.p. 253-7° [Lit. 255-7° (57)], uv (MeOH) $\lambda_{max.}$ 283 nm (log ε=4.3) [Lit. $\lambda_{max.}$ (EtOH) 283 nm [log ε= 4.0 (58)]. The residual liquid was separated by vpc (10% SE 30, 165°). The first compound emerging from the column was 1,1-diphenylethane in 3.5% yield. Identification was by comparison of its retention time and mass spectrum with an authentic sample. The second compound was 1,1-diphenylethylene in 15% yield. The retention time and the nmr spectrum were identical with that of an authentic sample.

Ozonolysis of 42

A solution 42 (25 mg) in chloroform (10 ml) was ozonized at -20° until the solution turned blue. 50% Aqueous acetic acid (5 ml) and zinc dust (20 mg) were added to the solution which was gradually warmed up to room temperature (usually took 30 minutes). The solution was then stirred for 12 hours. The reaction mixture was filtered and the chloroform layer was separated and washed successively with sodium bicarbonate solution and water. The residue obtained after evaporation of the solvent was separated on a preparative tlc plate using petroleum (60-80) -benzene (1:1) as eluent. The band with Rf value ≈ 0.4 was collected to give 5 mg benzophenone, m.p. 46-7° [Lit. 48-48.5° (59)], ir (CCl_4) 1660 cm^{-1}; the 2,4-dinitrophenylhydrazone derivative melted at 238-9° and gave no depression in melting point with an authentic specimen.

Apart from benzophenone, there were at least four more spots on the plate. No further attempts were made to identify them.

Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione and α-Methyl-styrene

A solution of 4-p-tolyl-1,2-dithiole-3-thione (0.65 gm) and α-methyl-styrene (3 ml) in benzene (75 ml) was irradiated in a pyrex tube for 3 days. The reaction product was chromatographed on a silica gel column using a petroleum (60-80)-benzene mixture as eluent. The only isolable product was 45 (10% yield) m.p. 168-9°; nmr ($CDCl_3$) 1.88 (d, J=1.0, 3H), 2.34 (s, 3H), 4.30 (s, 1H), 6.21 (q, J=1.0 Hz, 1H), 7.07 (s, 5H), 7.15 (s, 5H); uv (cyclohexane) $\lambda_{max.}$ 275, 225 nm (ε=8950, 12700); mass spectrum m/e 342. Anal. calcd. for $C_{19}H_{18}S_3$: C, 66.66; H, 5.30; S, 28.04. Found: C, 66.76; H, 5.04; S, 28.04.

Irradiation of 4-p-Tolyl-1,2-dithiole-3-thione in cis-1,2-Dichloroethylene

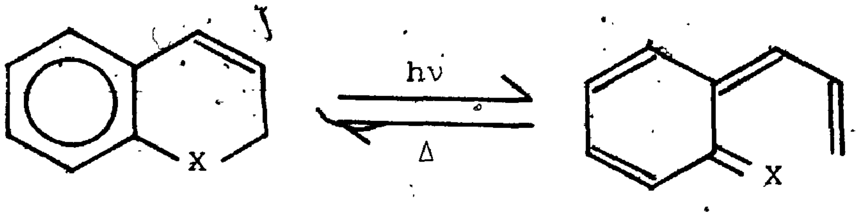
A degassed solution of 4-p-tolyl-1,2-dithiole-3-thione (634 mg) in cis-1,2-dichloroethylene (20 ml) was irradiated (λ>420 nm) for 28 hours. Tlc showed that no starting thione was left. The other spot apart from cis-1,2-dichloroethylene was 23b; m.p. 250-2°.

PART 2: THE SYNTHESIS AND THE THERMOCHROMISM OF A METHYLENE MONOTHIOQUINONE SYSTEM

CHAPTER 1

INTRODUCTION

Compounds containing an ortho quinoid moiety in the molecule are usually interesting to both theoretical (60) and organic chemists and are frequently proposed as intermediates in thermolytic and photolytic reactions (61-64). Such intermediates are usually too reactive to be isolated but can be trapped as adducts by suitable reagents (61, 63) or else they may react inter- or intra-molecularly to form dimeric (65, 66) or monomeric products (67, 68). Another interesting feature associated with some ortho quinoid systems is that they exhibit reversible photochromism as represented by the equilibrium between 49 and 50 (68-71).

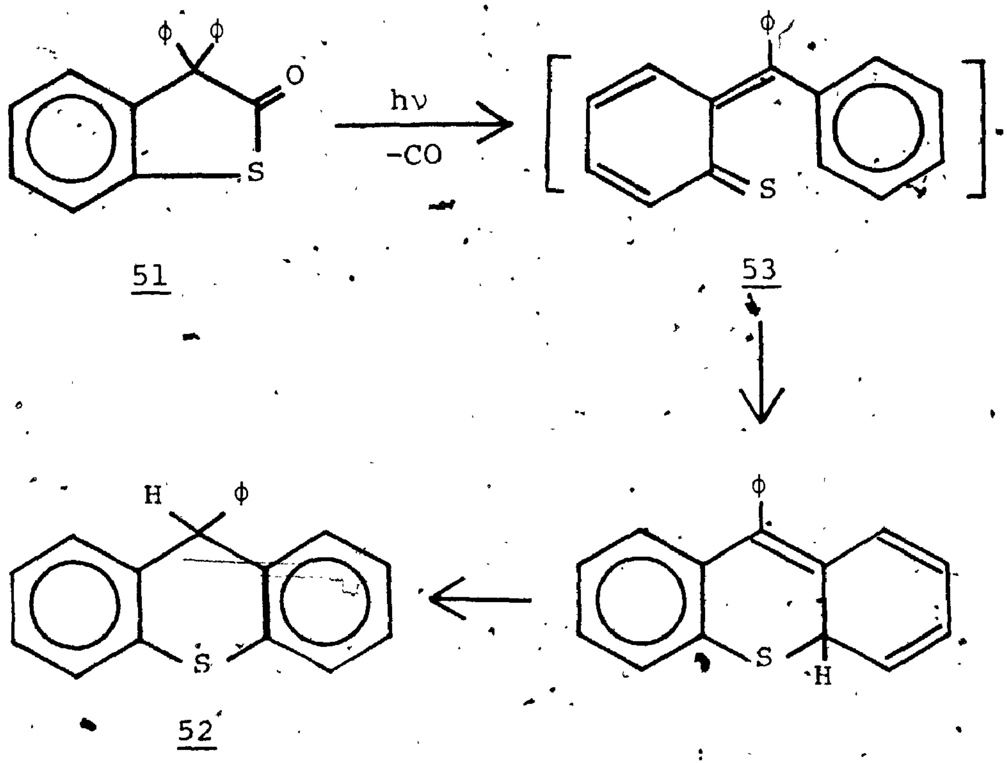


49 50

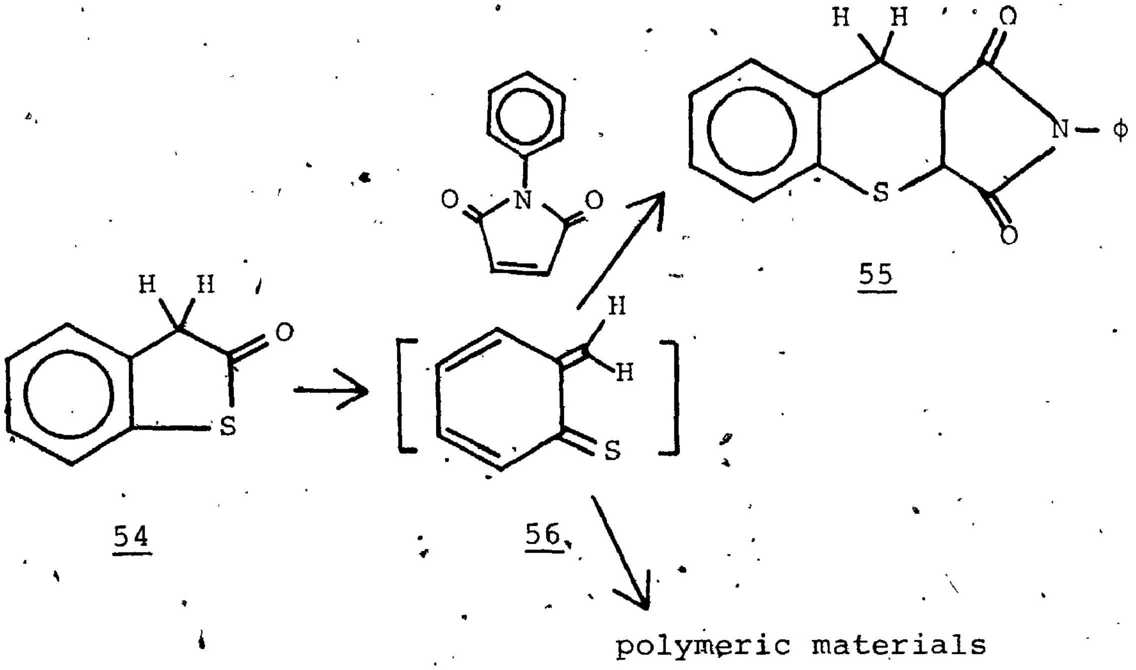
X=O, S, NR, CH_2, Se

The quinoid 50 has never been isolated and this may be due to the fact that the extra double bond serves as an intramolecular dienophile which undergoes an electrocyclic reaction reverting back to 49 when the irradiating light is removed.

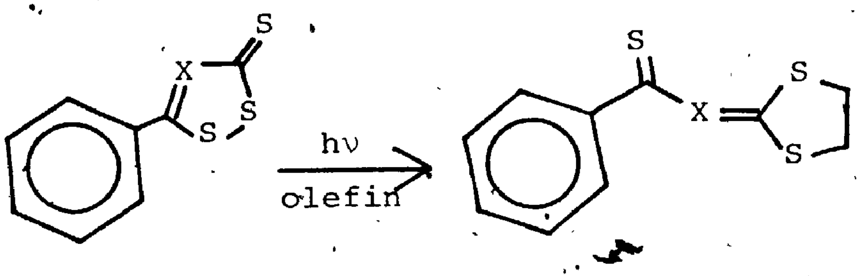
Nasielski and his coworkers (72, 73) photolysed the thiolactone 3,3-diphenyl-2-(3H)-benzo[b] thiophenone, 51, and obtained 52 via the proposed quinoid intermediate 53. The formation of 52 was suggested to go through an electro-



cyclization of 53 followed by a sigmatropic rearrangement. When the non-substituted 2-benzo[b]-thiophenone 54 was photolysed only polymeric materials were formed. The adduct 55 was formed if 54 was photolysed in the presence of N-phenylmaleimide. Again the thio-quinoid intermediate, 56, escaped isolation.



For some time, we have been engaged in the study of the photochemistry of thioketones (74, 75) and their derivatives (76, 77). We became interested in synthesizing an α,β-unsaturated thioketone in an ortho quinoid system. During this period, Inamoto and his coworkers (78, 17) generated a stable substituted α,β-unsaturated thioketone 57 by photochemical means. Since the result was very encouraging and the reaction was very similar to the one we had been studying (see Part 1), the photo-reaction between 4,5-benzo-1,2-dithiole-3-thione and olefins (cyclopentene and tetramethylethylene) was investigated because in this system, a thioortho-quinoid system may be produced. The results obtained are described in the following sections.



57

X = N or CH

CHAPTER 2

RESULTS AND DISCUSSION

2.1 The Ultraviolet Absorption Spectrum of 4,5-Benzo-1,2-dithiole-3-thione

4,5-Benzo-1,2-dithiole-3-thione, 58, belongs to the family of 4-substituted 1,2-dithiole-3-thiones described in Part 1. The whole spectrum (Fig. 5) agrees well with that reported by Mayer and collaborators (21), except for an extra absorption at 527 nm with an extinction coefficient of 109. It is quite reasonable to assume that this weak absorption is of the same nature (nπ*) as that shown at this wavelength by the 4-substituted 1,2-dithiole-3-thiones.

2.2 Structure Determination of Photoproducts Derived from the Addition of Cyclopentene and Tetramethylethylene with 4,5-Benzo-1,2-dithiole-3-thione

Irradiation (through a pyrex tube) of an ether solution of 4,5-benzo-1,2-dithiole-3-thione in the presence of cyclopentene and tetramethylethylene under nitrogen gave adducts 59 and 60 respectively. These two reactions did not occur in the absence of light.

When 59 was refluxed in a solution of carbon tetrachloride for 12 hours it gave back the starting 4,5-

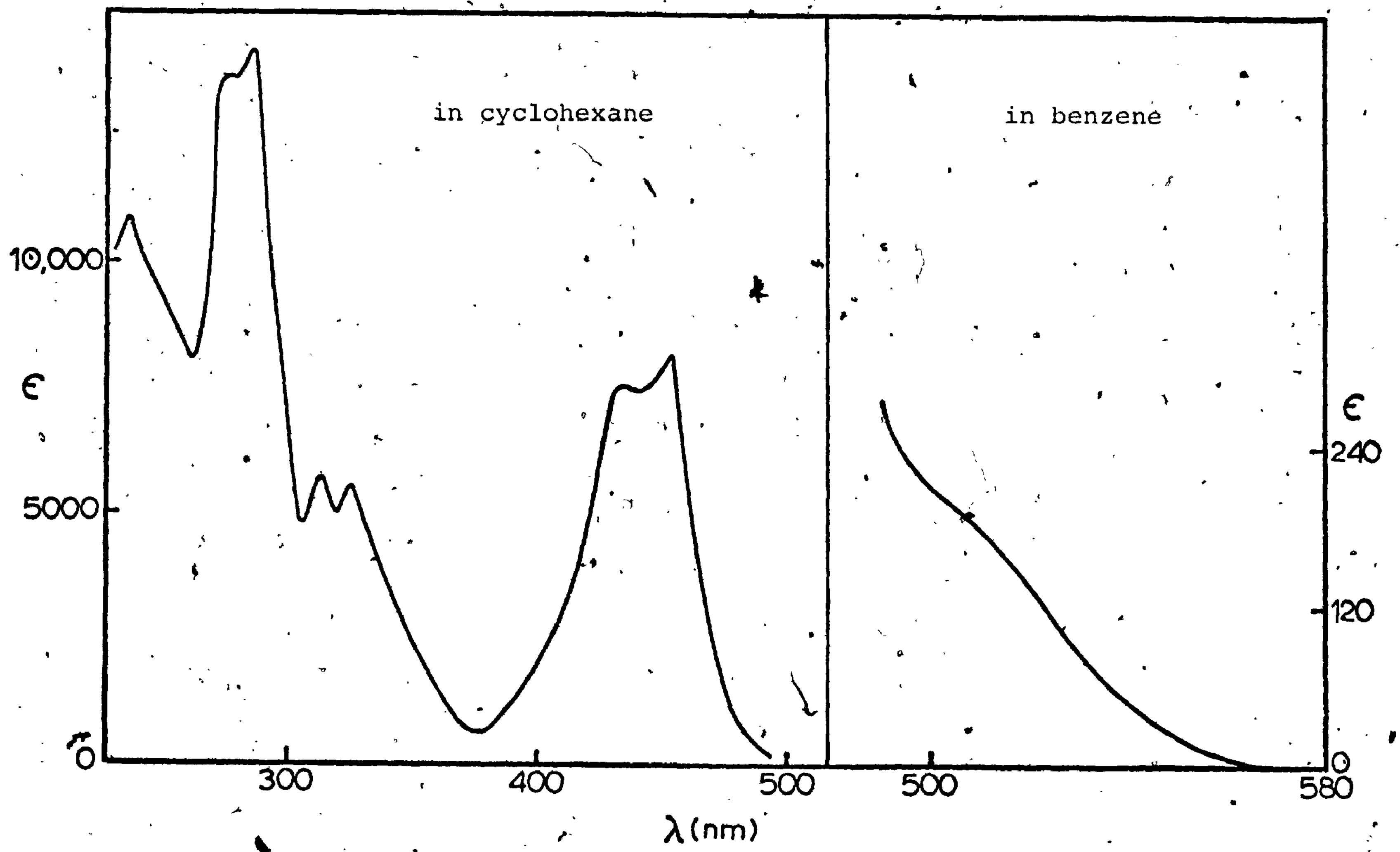
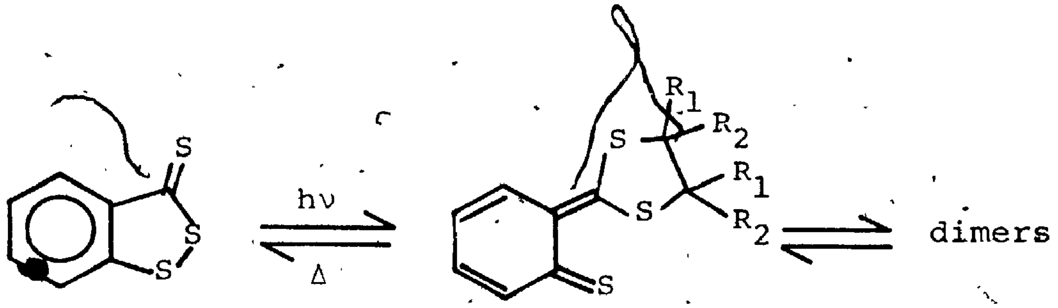


Figure 5. The uv absorption spectrum of 4,5-benzo-1,2-dithiole-3-thione.



58

59 R_1=H, R_2R_2=$-(CH_2)_3-$ 59a

60 R_1=R_2=Me 60a

benzo-1,2-dithiole-3-thione in 50% yield. This indicates that the addition was thermally reversible.

The adduct 59 was obtained as a colorless solid while 60 was blue. Both solids gave blue solution at room temperature in benzene. In the case of 59, the color of a solution in benzene became lighter as the temperature was lowered and eventually was lost at about 5°. The same intensity of color could be restored if the solution was warmed up to room temperature. The cycle of this color change could be repeated for many times without any decomposition, as shown by tlc. The same change could not be observed visually in 60 but the change of the intensity of the blue color with temperature could be easily shown by absorption measurement at 585 nm. Again, the cycle could be performed repeatedly. This clearly indicated that an equilibrium of some sort was present in the system. The nature of this equilibrium will be dealt with in the following section.

The molecular weight of 59 in chloroform measured by osmometry was concentration dependent (Fig. 6). Cryoscopic determination of the molecular weight in benzene gave a value of 496±10 showing that the equilibrium involved an association which was dimeric. The theoretical value for the dimer was 502. The molecular weight of 60 was also measured by osmometry at one concentration (5.8 mg/ml) in chloroform with a resulting value of 498 (calc. value for the dimer was 536).

An optical method for measuring the concentration of monomer was used (see section 2.3) and the equilibrium constants at 24.5° determined over a wide range of concentration using various possible equilibra. Only for the system $A_2 \rightleftharpoons 2A$ was the equilibrium constant constant (see Appendix 1,2) indicating that this was the nature of the equilibrium existing in solution. The values for the equilibrium constants for the cyclopentene and tetramethylethylene adducts are indicated in Table 5 & 6. Hence, a process of the type $A_2 \rightleftharpoons 2A$ was conclusively proven by the results of these observations.

(A) The Structure of the Monomers

Diels-Alder addition of 59 to N-phenylmaleimide and to acetylene dicarboxylic acid dimethyl ester gave the adducts 61 and 62. The structure of adduct 61 was deduced

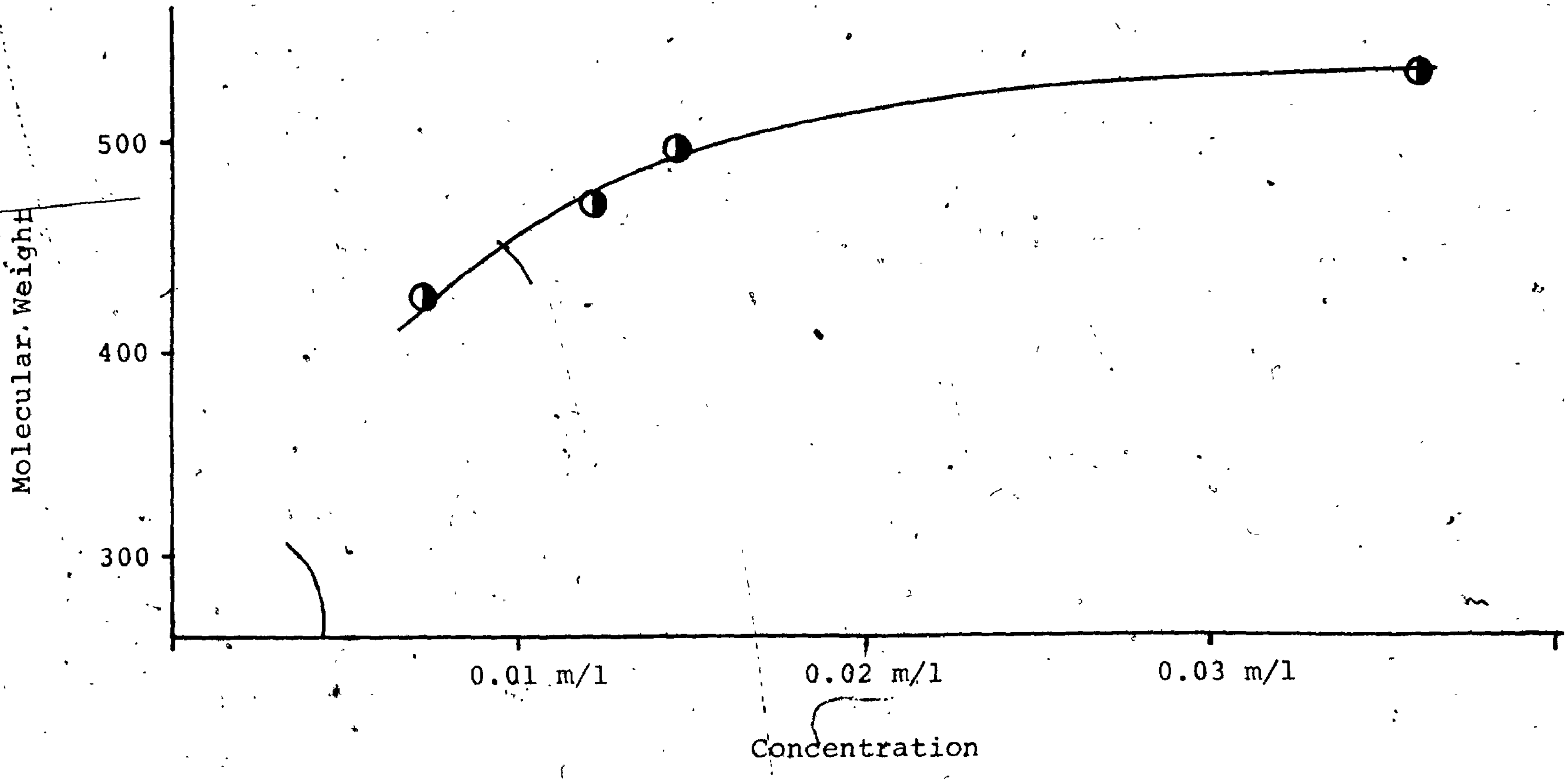


Figure 6. Concentration dependence of molecular weight of 59 in chloroform.

TABLE 5

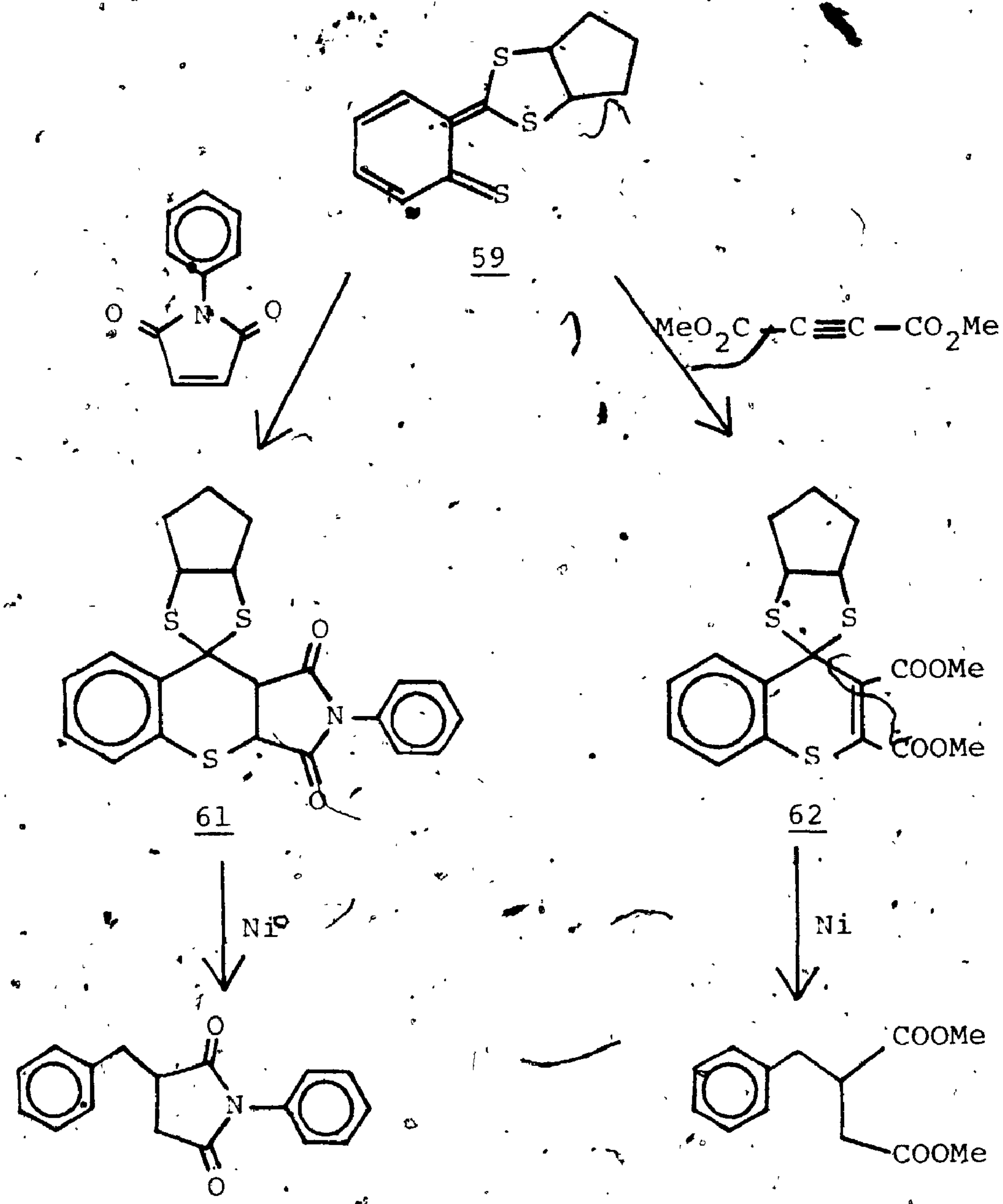
Equilibrium Constant of 59 in Chloroform at 24.5°C

Conc. (mg/50 ml)	Equil. Const. (mole/liter)
3.38	8.45×10^{-6}
2.08	8.83×10^{-6}
0.406	8.75×10^{-6}
0.161	8.89×10^{-6}
0.027	8.46×10^{-6}
0.00108	9.14×10^{-6}
0.000065	6.50×10^{-6}
Average	8.43×10^{-6}

TABLE 6

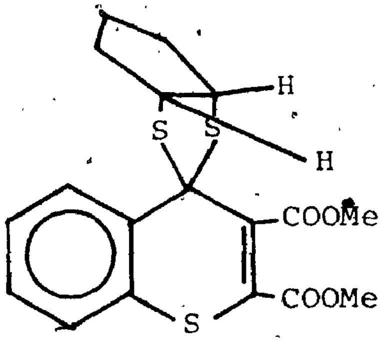
Equilibrium Constant of 60 in Benzene at 24.5°C

Conc. (mg/50 ml)	Equil. Const. (mole/liter)
3.43	1.89×10^{-4}
2.05	1.90×10^{-4}
1.23	1.87×10^{-4}
0.37	2.02×10^{-4}
0.074	1.73×10^{-4}
Average	1.88×10^{-4}

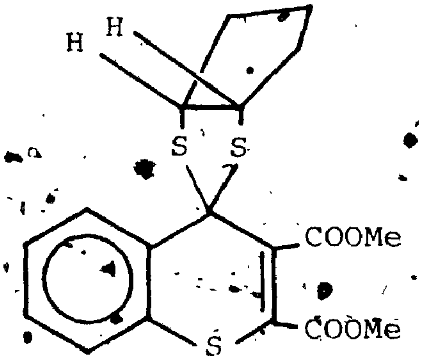


from spectroscopic data and the result of Raney nickel reduction. Integration of the nmr spectrum showed that 61 was consistent with the structure of a 1:1 adduct between 59 and N-phenylmaleimide. The integration indicated that there were nine aromatic protons, a singlet at 4.93 ppm of 2 protons which could be resolved into 2 doublets with a coupling constant of 9 Hz when $Eu(fod)_3$ was added, a multiplet of 2 protons between 4.1-4.4 ppm and a multiplet of 6 protons between 1.5 and 2.4 ppm. The mass spectrum confirmed that it was a 1:1 adduct. The absence of any absorption in the 500-600 nm region indicated the absence of any thiocarbonyl group. This reaction was, therefore, analogous to the already described (55) trapping of an ortho quinoid intermediate with N-phenylmaleimide. The structure assignment of the adduct 61 was further confirmed by Raney nickel reduction to give 2-benzyl-N-phenylsuccinimide; m.p. 128-30°C. The ir and mass spectra of this product were identical to that of 2-benzyl-N-phenylsuccinimide sythesised from 2-benzylsuccinic acid and aniline.

Adduct 62 was obtained as a gummy solid. The fact that it could not be induced to crystallise suggested that it might be a mixture. Indeed, two geometrical isomers are possible for 62 (assuming only as fusion). In one isomer the cyclopentyl ring is bent towards the phenyl ring (structure 62a) while it turns away from the phenyl ring in the other isomer 62b. Attempts to separate these two isomers by vpc and tlc methods were unsuccessful. The structure of 62, however, was determined in the same way as that of 61. The ir spectrum showed an α,β-unsaturated ester absorption at 1721 cm^{-1}. The mass spectrum demonstrated that 62 was a 1:1 adduct. This was confirmed by the Raney nickel desulfurization to dimethyl benzylsuccinate.



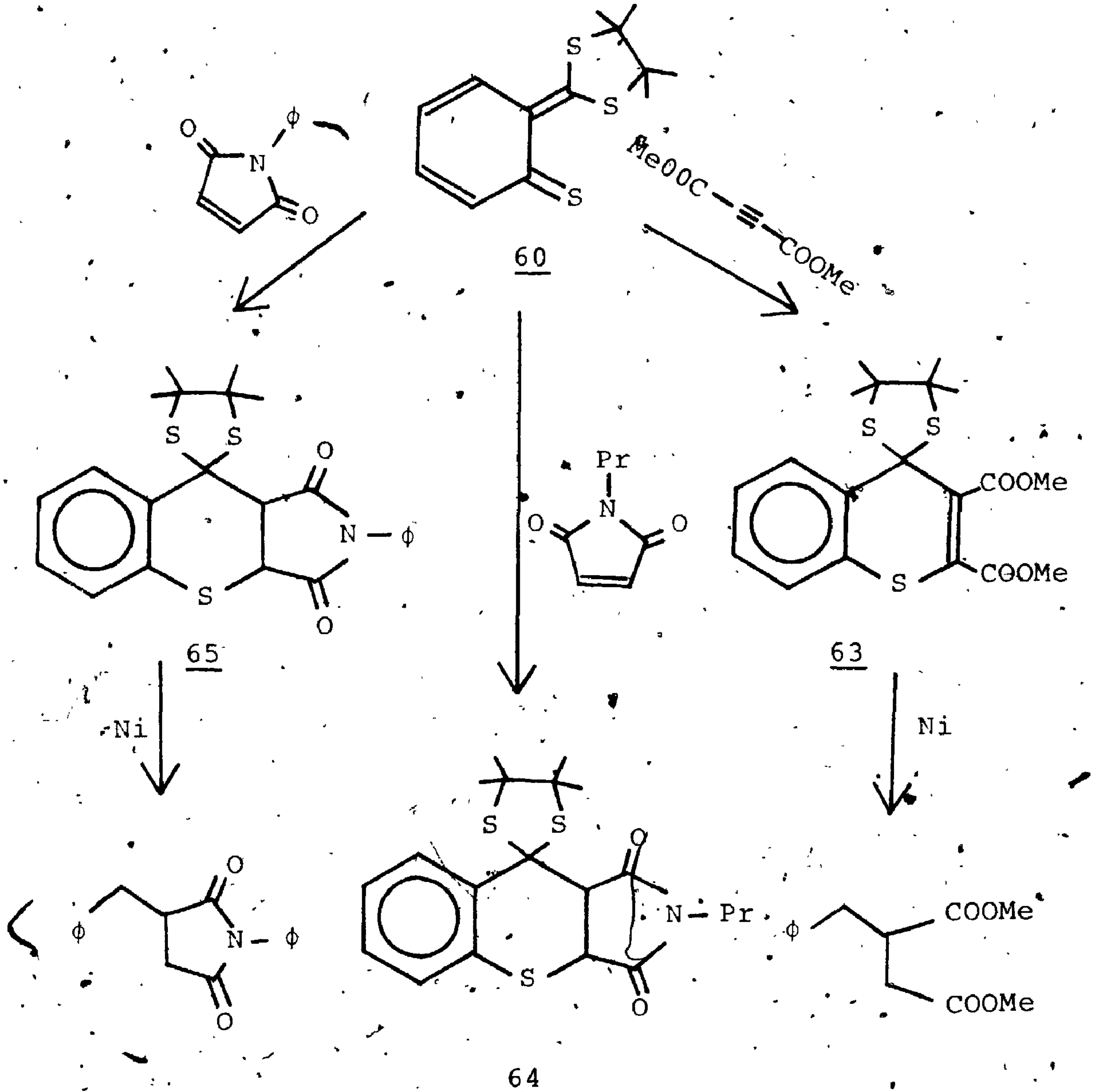
62a



62b

Similarly, the determination of the structure of the monomeric 60 was achieved by the trapping experiments with acetylene dicarboxylic acid dimethyl ester, N-n-propylmaleimide and N-phenylmaleimide to form adducts 63, 64 and 65 respectively. The structure of adduct 63 was shown to be consistent with that of a 1:1 adduct by analysis of the nmr data. The nmr spectrum showed a multiplet of 4 protons in the aromatic region (phenyl protons), 2 singlets of 3 protons each at 3.75 ($-COOCH_3$) and 3.78 ppm ($-COOCH_3$) and 2 singlets of 6 protons each at 1.44 and 1.32 ppm [$-C(CH_3)_2-C(CH_3)_2-$]. The ir spectrum showed an α,β-unsaturated ester absorption peak at 1721 cm^{-1}. The carbon skeleton of 63 was determined by desulfurisation with Raney nickel to dimethyl benzylsuccinate.

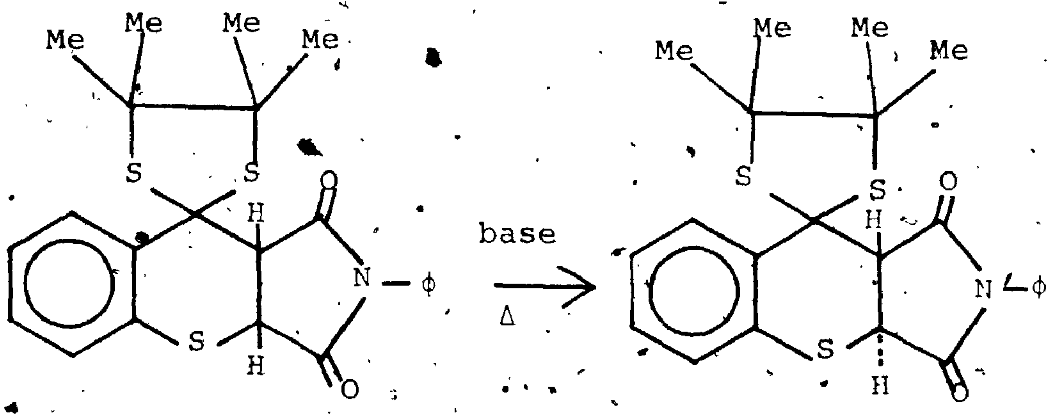
The structure of adduct 64 was deduced from its spectroscopic properties. Its ir spectrum showed a


60
65
63
64
MeOOC
COOMe
Pr
Ni
Ni
φ
N
S
O

carbonyl absorption at 1724 cm^{-1} and its mass spectrum showed the molecular ion peak at m/e 407. The nmr showed that 64 was a 1:1 adduct. The methylene groups of the normal propyl chain gave signals at 3.20 and 1.1 ppm respectively. The terminal methyl group absorbed at 0.4 ppm. A chemical shift for this methyl group at such high field is unusual. However, a similar chemical shift (0.7 ppm) has been reported, without explanation, for N-n-butylsuccinimide (79). The existence of a special ring current in N-alkyl substituted succinimide ring has been demonstrated by Matsuo (80). Nonetheless this, in itself, is insufficient explanation since, in any likely conformation, the terminal methyl group is far away from the succinimide ring. The interpretation remains unknown and no detailed study has been made.

The elucidation of the structure of 65 was the same as for the adduct derived from 59 with the same dienophile. The nmr spectrum of 65 showed that it was a 1:1 adduct. Compound 65 was desulfurised by freshly prepared Raney nickel to give 2-benzyl-N-phenylsuccinimide.

Attempted desulfurisation of 65 by a four-year-old Raney nickel sample resulted in partial isomerisation to 66. Compound 66 was identified by comparison of the spectroscopic data with that of 65. Both 65 and 66 had the same molecular ion and ir spectrum. However, their Rf values and melting points were different. The assignment of the steric relationship between the two methine protons was



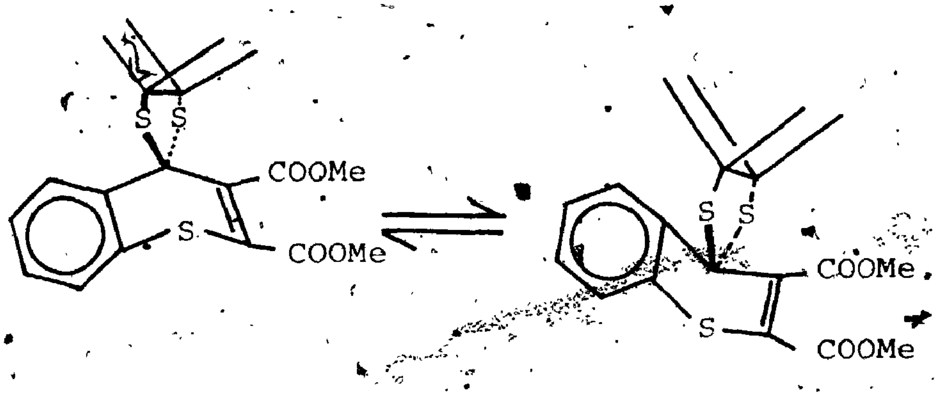
65

66

based on nmr data. The coupling constant of the methine protons was 9 Hz in 65 and 19 Hz in 66. The values of these two coupling constants were in good agreement with the values for the cis- and trans relationship of the two methine protons in the two isomers of the lactone of 3-(2-hydroxycyclohexyl)-propionic acid in which the coupling constant is 7.5 Hz for the cis isomer and 18 Hz for the trans isomer (81). Moreover, the Diels-Alder reaction always gives a cis adduct which is consistent with what we had obtained. The mechanism of isomerisation is not certain, but presumably, a trace amount of base in the Raney nickel acted as catalyst.

The nmr spectrum of all the adducts 64, 65 and 66 gave 4 singlets for the 4 methyl groups while it showed only 2 singlets in 63. In the first three compounds, it is obvious that all of the methyl groups are non-equivalent.

In 63 the molecule exists in a boat-like conformation in which the four methyl groups are also different from each other. However, this boat-like conformer is in equilibrium with another identical boat conformer. These 2 conformers are represented as 63a and 63b.



63a 63b

The interconversion between these conformers is rapid in the nmr time scale at room temperature. The net result is that the 4 different methyl groups on the 1,3-dithiolane ring are seen as 2 different sets of protons in the spectrum. Indeed, it was shown by the variable temperature nmr technique that the interconversion could be stopped at low temperature. The nmr spectrum (see Fig. 7) of 63 was measured in carbon disulfide between +30° and -110°, the two signals corresponding to the four methyl groups being broadened as the temperature went down. After

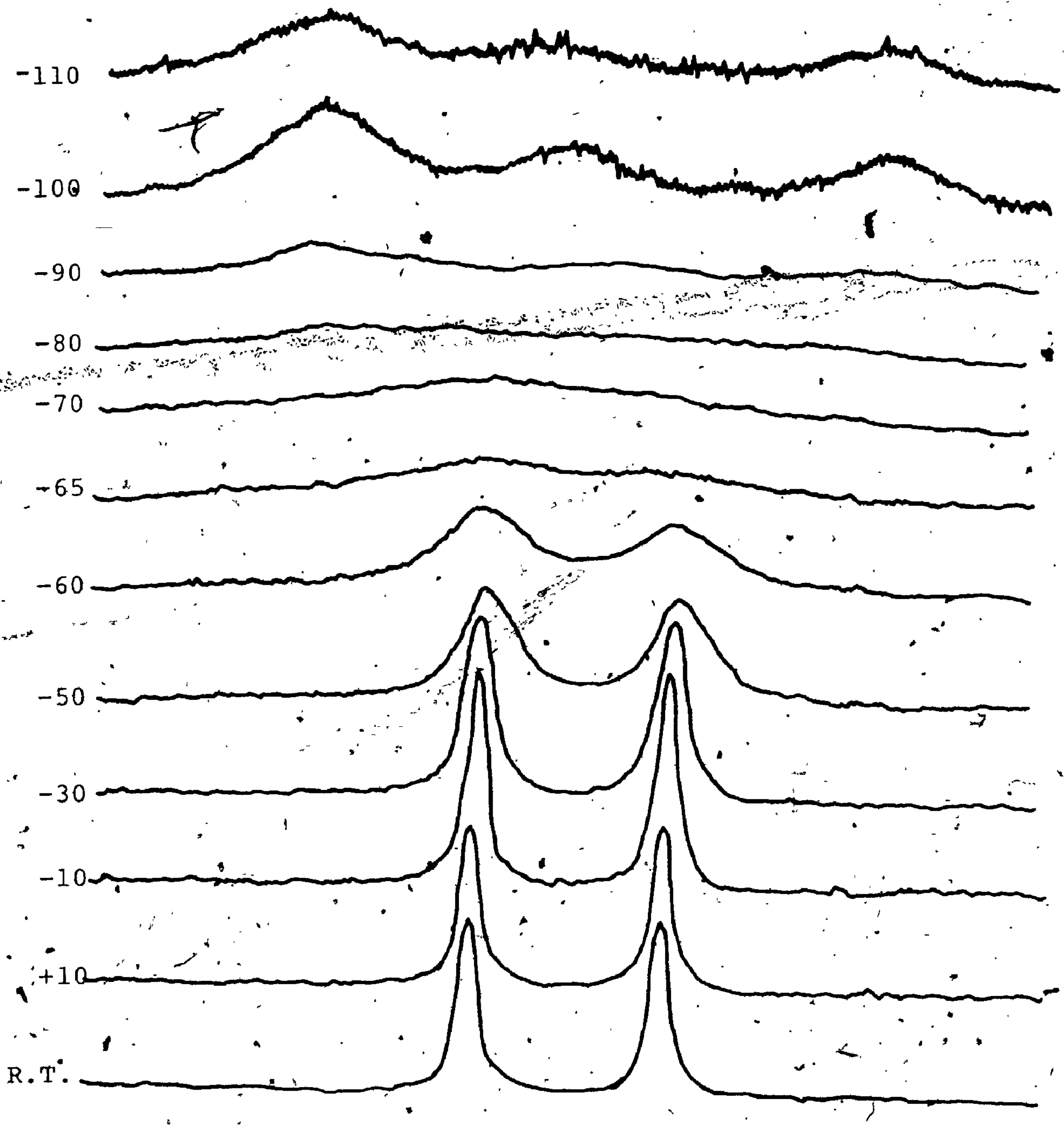


Figure 7. Variable temperature nmr of 63 in carbon disulfide.

passing through the coalescence temperature (-70±5°), four signals appeared as expected. Unfortunately, owing to the high viscosity of the solution, the signals did not become sharp even at -110°. The activation energy, $\Delta G^{\ddagger}$, for the boat-to-boat flip was calculated as follows (82, 38). The rate of flipping K' at the temperature of coalescence T_c was calculated from equation (1)

$$k'=\pi\Delta\nu/\sqrt{2} \tag{1}$$

where $\Delta\nu$ is the frequency separation of the resolved signals at low temperature. The value of $\Delta G^{\ddagger}$ was derived from the Eyring equation (2)

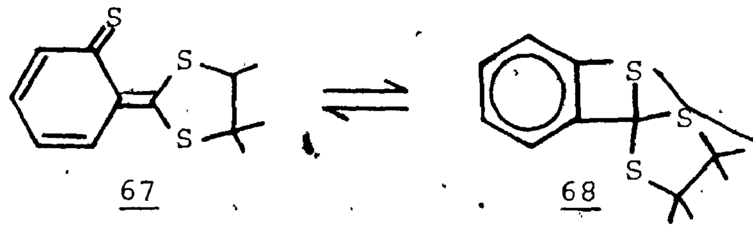
$$k'=\kappa\frac{KT_c}{h}\exp\left(\frac{-\Delta G^{\ddagger}}{RT_c}\right) \tag{2}$$

where κ is an unit transmission, R is the gas constant, h is Planck's constant, k is the Boltzmann constant. Equation (2) is transformed to (3) for the purpose of calculation.

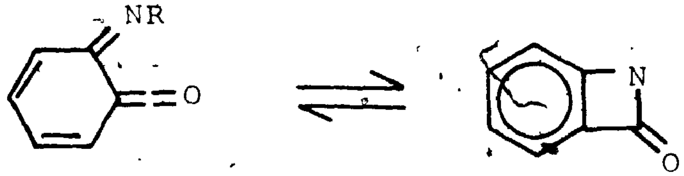
$$\Delta G^{\ddagger}=2.303\ RT_c(10.319-\log k'+\log T_c) \tag{3}$$

Thus the activation energy for this flipping was found to be about 9.3 Kcal/mole at the coalescence temperature specified above.

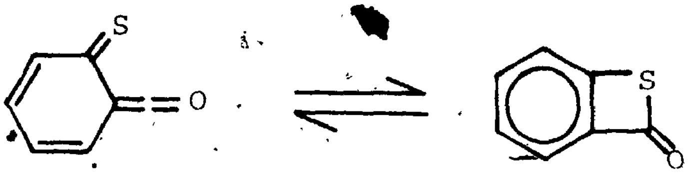
We have thus proposed that the monomers be of thioortho quinoid structure 67. This might, however, be an over-simplified representation since another species may be possible. There is the possibility of a tautomerisation between 67 and the thietene 68 shown in Scheme 5. A similar valence tautomer 70 and 72 had been postulated in ketenimine, 69, (84) shown in Scheme 6 as well as in ketenthione, 71, which is shown in Scheme 7 (85, 86).



67 ⇌ 68 Scheme 5



69 ⇌ 70 Scheme 6



71 ⇌ 72 Scheme 7

(B) The Structure of the Dimer 59a and 60a

From the molecular weight measurement and the nature of the equilibrium (Section 2.2), the associated species which formed from the monomer had to be a dimer.

A number of possibilities could be envisaged for the structure of the dimers. The Diels-Alder reaction 4+2 has been demonstrated with alicyclic thiones (see Part 3). However, the structure for a compound arising from such a reaction could be eliminated because the ultraviolet absorption of the dimer was below 300 nm. The uv spectrum of 59a in ether at $-15^{\circ}C$ (Fig. 8) showed an absorption essentially below 300 nm. Any 4+2 or 2+2 adduct must leave

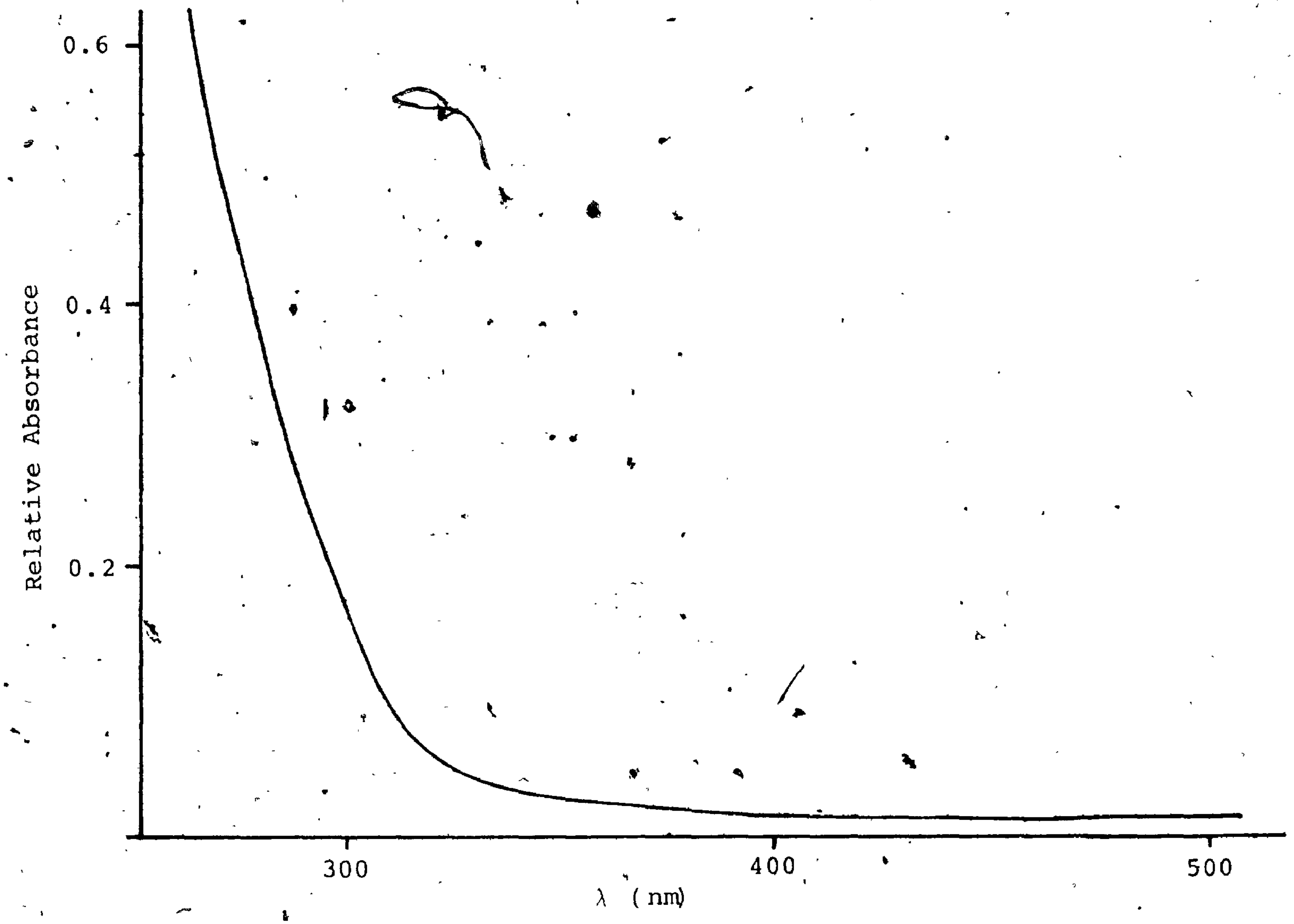
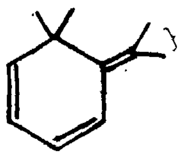


Figure 8. Uv spectrum of <u>59</u> in Et_2O at $-15^{\circ}C$, $C=8.4\times10^{-5}$ mole/liter.

either an extended conjugated system, 73, absorbing above 350 nm (87) or should contain a spectroscopically recognisable thiocarbonyl group. 4+2 adducts were also excluded



73

by the ^{1}H and ^{13}C nmr spectra (see Experimental and Fig. 9) which clearly indicated symmetry and no other unsaturation apart from the aromatic ring. The ^{13}C nmr gave only 13 carbon atom signals which was one half of the total carbon atoms in the molecule. This led to the conclusion that the molecule was symmetrical. The most probable structure for the dimer is a 4+4* eight membered ring dimer 59b (60b) or 59c (60c).

On desulfurisation with Raney nickel at a relatively low temperature, the dimer derived from cyclopentene (59a) gave a small yield (4%) of bibenzyl. The finding suggested a head-to-head dimer (59b, 60b) was the right structure. However, Chapman and McIntosh (85) suggested a transannular coupling might occur during the desulfurisation of 74 to

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*A similar 4+4 system has been reported on the dimerisation of dithietenes. Equilibrium between monomer and dimer in this system was also demonstrated but at a much higher temperature (88).

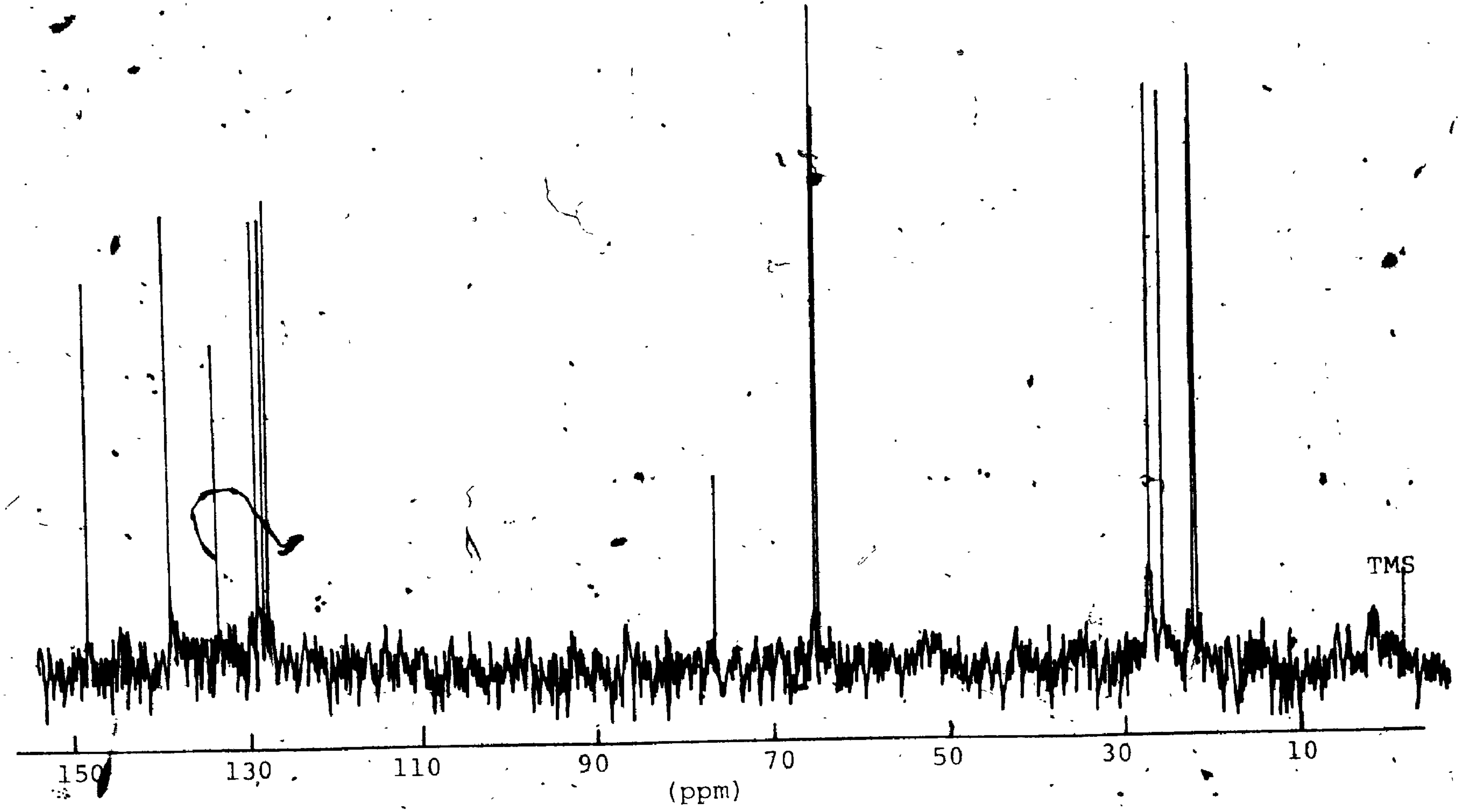

Figure 9. The ^{13}C nmr spectrum of 60 in deuterated methylene chloride.

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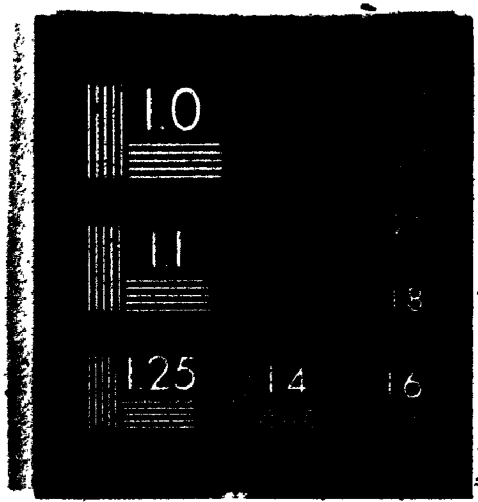

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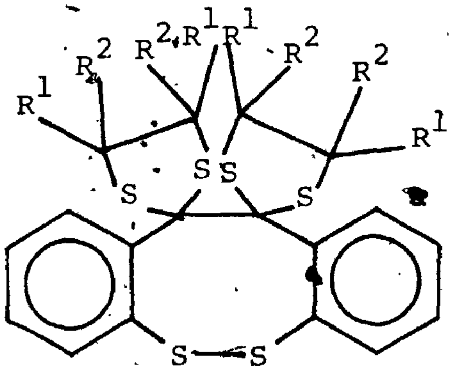
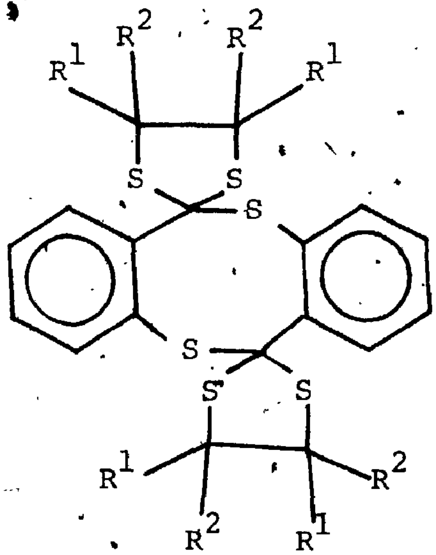




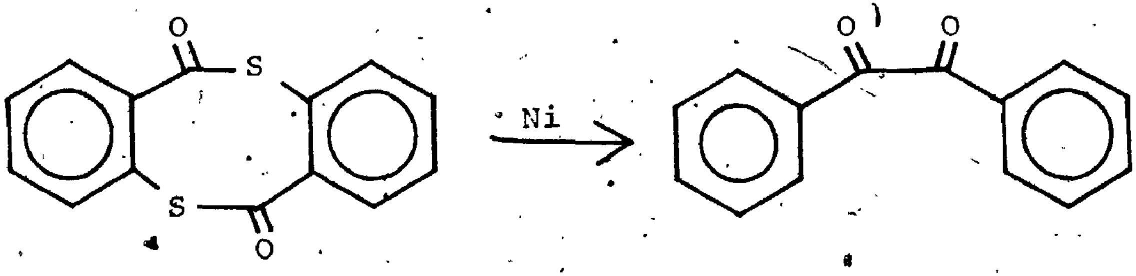
59b R^1=H, R^2R^2=$-(CH_2)_3-$

60b R^1=R^2=Me

59c R^1=H, R^2R^2=$-(CH_2)_3-$

60c R^1=R^2=Me

give benzil. Although the systems are not analogous — 59 and 60 do not have sp^2 carbon in the eight membered ring — complications prevented us from drawing a definite



74

conclusion from the desulfurisation result.

Since dimer derived from tetramethylethylene (60a) showed 4 methyl signals in the ^{1}H nmr spectrum, it follows that conformation equilibration, necessarily possible via the monomer if not in the dimer itself is slow on the nmr time scale at 32°C. It was shown by Dreiding molecular models that flipping between the two possible conformations, namely: the tub form and the chair form must go through a very high energy barrier in the head-to-head dimer since there is serious interaction in the transition state.

It was found that the free energy change in the monomer-dimer interconversion was not the same for the two equilibria and differed by 3.3 Kcal/mole (see Section 2.5). This large difference is probably steric in origin because it seems unlikely, on chemical grounds and from a consideration of bond energies, that the two dimers could differ in regiospecificity. Such a steric effect is hard to rationalise with a head-to-tail structure (59c, 60c) for the dimer. This taken with the desulfurisation result leads us to accept the head-to-head structure.

2.3 The Visible and Ultraviolet Absorption Spectra of 59 and 60

Since the monomer was in equilibrium with the dimer in solution, to measure the absorption maxima and the molar absorption coefficients of the individual species posed problems. However, the absorption spectrum of the dimer, 59a, could be measured at low temperature in ether, as shown in Fig. 8. This absorption is attributed to the dimer by the fact that it did not give any absorption at 585 nm which was characteristic for the monomer.

The spectrum of the pure monomer could not be obtained. Nevertheless, the spectrum of the equilibrating solution of the adduct derived from cyclopentene showed a broad peak centered at 585 nm together with a peak at 346 nm and a shoulder at 260 nm in a wide range of solvents. These absorption bands were assigned to the monomer only.

It was important to measure the molar absorption extinctions for the monomers in order to study some of the thermodynamic properties of the equilibrium. This was done by the method developed by Keussler and Lüttke (89, 90) for the monomer-dimer equilibrium in arylnitroso compounds. For the equilibrium

$$A_2 \rightleftharpoons 2A$$

we may define the dimer dissociation constant

$$K_c = C_m^2 / C_d$$

where C_m and C_d are the molar concentrations of the monomer and dimer, respectively. The total molar concentration of the compound computed as monomer is

$$C = C_m + 2C_d$$

If α is the fraction of the adduct present as monomer, then

$$\alpha=C_m/C$$

and it follows that

$$K_c=2C\alpha^2/(1-\alpha) \qquad (4)$$

If Ai is the absorbancy of the solution at a total adduct concentration C and ℓ is the path length, we may define an effective molar absorbancy index

$$\varepsilon=Ai/\ell c$$

It follows that

$$\varepsilon=\alpha\varepsilon_m+(1-\alpha)\varepsilon_d/2 \qquad (5)$$

where ε_m and ε_d are the absorption extinctions of the monomer and dimer respectively. Since the absorbance is monitored at 585 nm at which the dimer does not absorb, the equation (5) becomes

$$\alpha=\frac{\varepsilon}{\varepsilon_m}$$

Equation (4) may be transformed to give

$$K_c=2C\left(\frac{\varepsilon}{\varepsilon_m}\right)^2/\left(1-\frac{\varepsilon}{\varepsilon_m}\right)$$

$$(\varepsilon_m-\varepsilon)K_c=2\frac{\varepsilon^2}{\varepsilon_m}C$$

$$\varepsilon=K\varepsilon^2C+\varepsilon_m$$

where $K=\frac{-2}{\epsilon_m K_c}$

ϵ_m at 585 nm could be obtained by plotting ϵ vs $\epsilon^2 x C$ at different concentrations followed by extrapolation to zero concentration. The molar extinction coefficient were determined in benzene and chloroform at 24.5°C. The results which are obtained by the least squares methods are shown in Table 7-9 as well as Figs. 10-12.

Owing to the low degree of dissociation of the dimer, 59a, in benzene, a reliable value would be obtained only when the spectrum was measured at a very low concentration. This was found to be impossible to achieve with our apparatus. However, the molar absorption extinction of 60a at λ=585 nm in both solvents and that of 59a in chloroform were very similar (see Table 7-9). It was assumed that the molar absorption extinction of 59a in benzene and that in chloroform would be similar. Thus the value of the absorption extinction for 59a in benzene was obtained as 5250 by using a conversion factor 52000:5000.

The absorption band in the visible region for both 59 and 60 seems quite interesting because of its high intensity. Most of the aliphatic (91-93) and aromatic thioketones (94) show a low intensity absorption at long wavelength. The value on extinction of this absorption is less than 100 in the case of aliphatic thioketones while it is in a magnitude of hundreds in the aromatic thioketones. Such absorption has been attributed to a

TABLE 7

Concentration Dependent Molar Absorbancy Index for 59 in Chloroform at 24.5°C at 585 nm

Conc. (mole/liter) (as monomer)	Molar Absorbancy Index
2.48×10^{-4}	652
1.61×10^{-4}	832
3.22×10^{-5}	1675
1.28×10^{-5}	2427
5.36×10^{-6}	3060
2.14×10^{-6}	4020
8.58×10^{-7}	4730
5.14×10^{-8}	5440
0.00 (extrapolated)	5456±150

TABLE 8

Concentration Dependent Absorbancy Index of 60 at 585 nm in Benzene at 24.5°C

Conc. (mole/liter) (as monomer)	Molar Absorbancy Index
2.56×10^{-4}	2269
1.53×10^{-4}	2690
9.21×10^{-5}	3105
2.76×10^{-5}	4097
5.53×10^{-6}	4705
0.00 (extrapolated)	5004±100

TABLE 9

Concentration Dependent Absorbancy Index of 60 in Chloroform at 24.5°C at 585 nm

Conc. (mole/liter) (as monomer)	Molar Absorbancy Index
2.47×10^{-4}	4635
4.94×10^{-5}	5101
2.47×10^{-5}	5180
9.88×10^{-5}	4959
0.00 (extrapolated)	5254±100

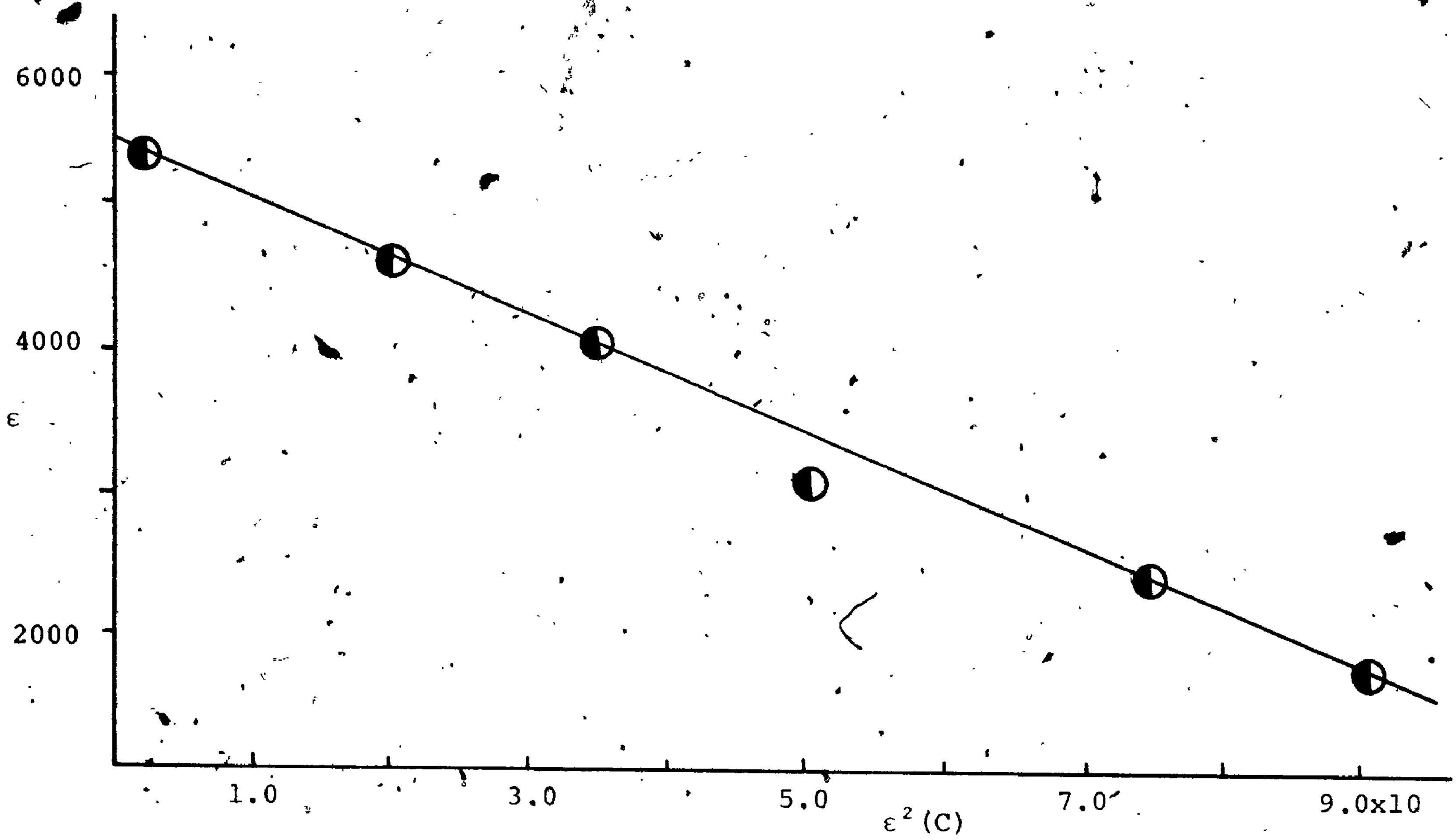


Figure 10. The $\varepsilon^2(C)$ vs ε for 59 in chloroform measured at $\lambda=585$ nm

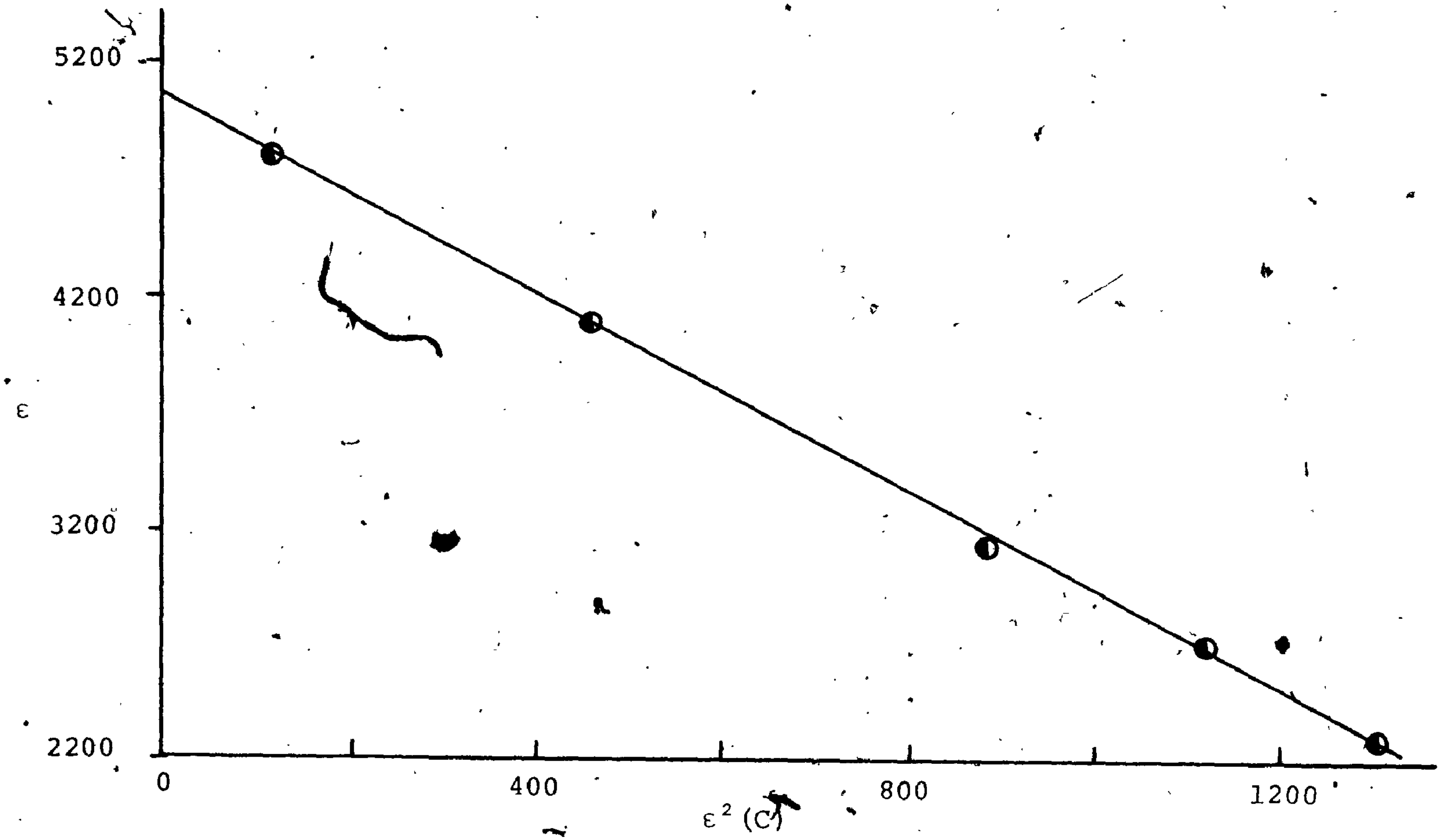


Figure 11. The ε^2(C) vs ε plot for <u>60</u> in benzene measured at λ=585 nm.

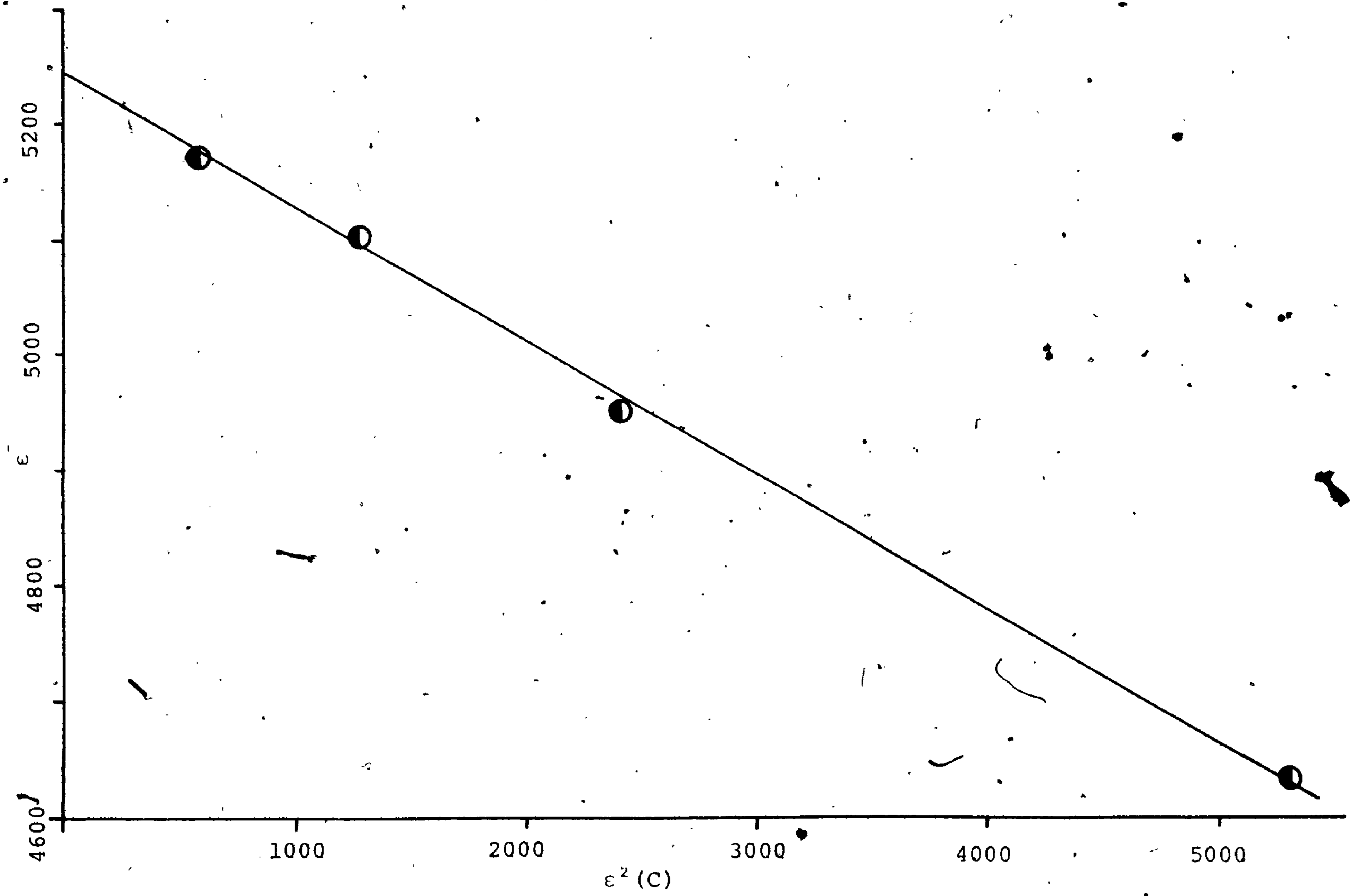
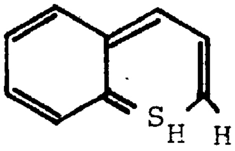


Figure 12. The $\varepsilon^2(C)$ vs ε plot for <u>60</u> in chloroform measured at λ=585 nm

nπ* (singlet) transition (94). This low intensity band is not compatible with the high intensity band observed in 59 and 60 in which the absorption extinction was about 2 to 3 orders of magnitude larger than that of an ordinary thioketone. However, high intensity bands of this type are not uncommon in some α,β-unsaturated thioketones (17, 95). Becker (96) also reported a high intensity absorption band centered at 570 nm for 75 and subsequently this absorption band was assigned to an ππ* transition. Since the band we obtained for the adducts was quite similar to that reported



75

for 75 and since its absorption maximum was not much shifted by polar solvents (see Table 10) it seems probable that this might also be a ππ* transition.

It is interesting to point out that both the compounds 75 and the adducts obtained in this study gave similar absorption maxima for the C=S group although they differed in one conjugated C=C bond. This may be due to the presence of a sulfide group which is conjugated with the π-system in the molecule. It has been demonstrated that the effect of such a sulfide group is roughly equivalent to that of a C=C bond (97). In general, it seems that the effect of a second sulfide group is about

TABLE 10

Solvent Fffect on the Uv Absorption Maximum of the C=S Group in 59

Solvent	$\lambda_{max.}$ (nm)
acetonitrile	580
methanol	583
chloroform	585
methylene chloride	585
benzene	585
methylene chloride/ n-hexane	585
methylene chloride/ acetonitrile (3:2)	583

one half as much as that of the first group (98).

2.4 Solvent Effect on the Equilibrium 59a and 59

The ultraviolet and visible absorption spectra of 59 in solvents of different polarity have been determined. Those in methylene chloride hexane mixture are shown in Fig. 13. It may be seen that the extinction of the band at 585 nm, solely attributed to the monomer, decreases with decreasing polarity of the solvents. This indicates that the monomer is more polar than the dimer.

The displacement of the equilibrium in favor of the monomer 59 at higher temperatures in methylene chloride is shown in Fig. 14. The same displacement could also be obtained on irradiation with short wavelength (254 nm) light. Upon irradiation, the absorbance at 585 nm increased and reverted slowly to its original value after the light source was removed (Fig. 15). This showed that the shift of equilibrium from the dimeric form to the monomeric form could be effected by light. This photochromic phenomenon was not further pursued.

2.5 Thermodynamic Parameters

Equilibrium constants were measured by means of ultraviolet spectroscopy at 585 nm in both benzene and chloroform over a temperature range of at least 42^{o}C. The absorption at this wavelength was converted into the molar absorption extinction ε (absorbancy index). The percent

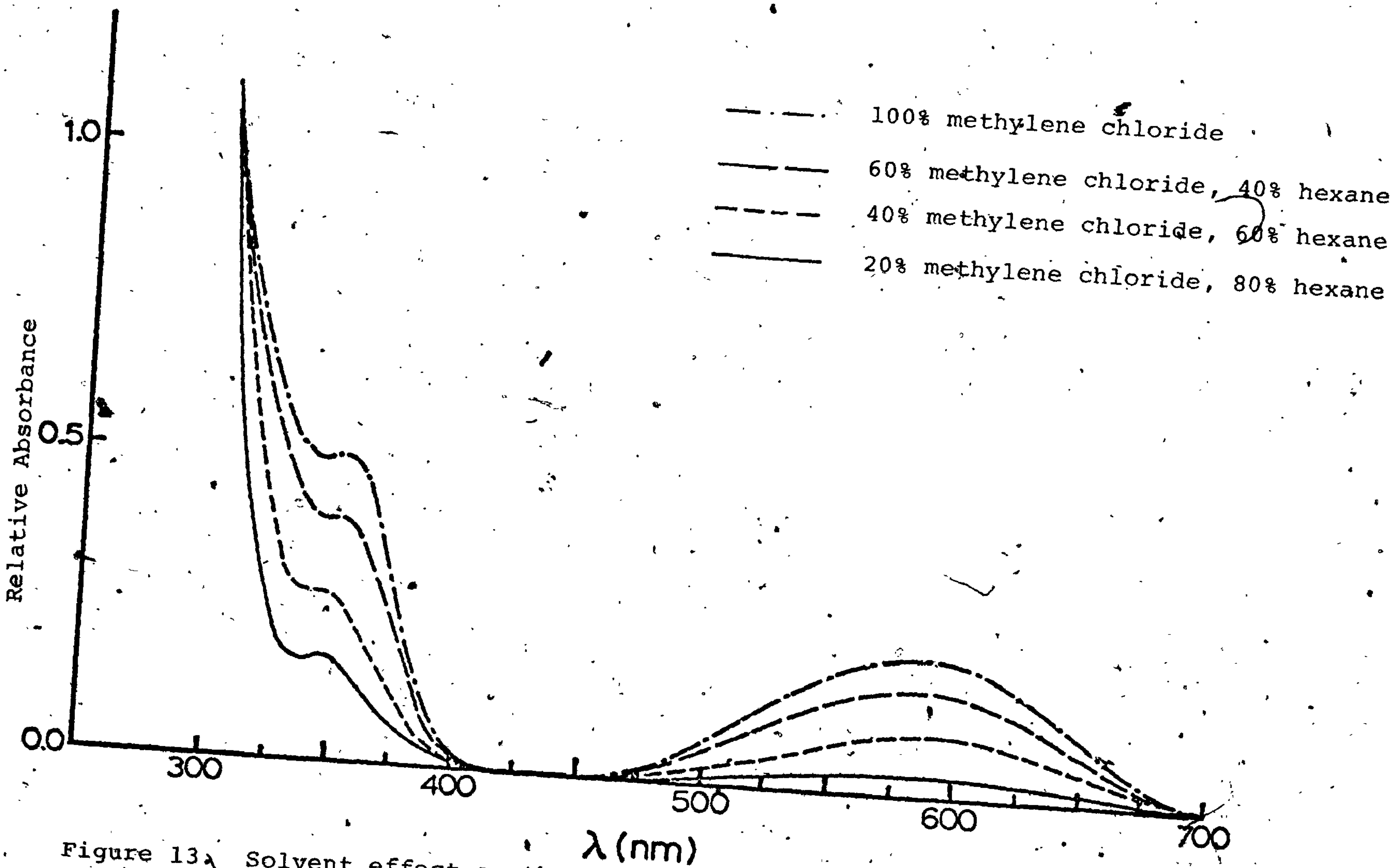


Figure 13. Solvent effect on the absorption spectrum of 59.

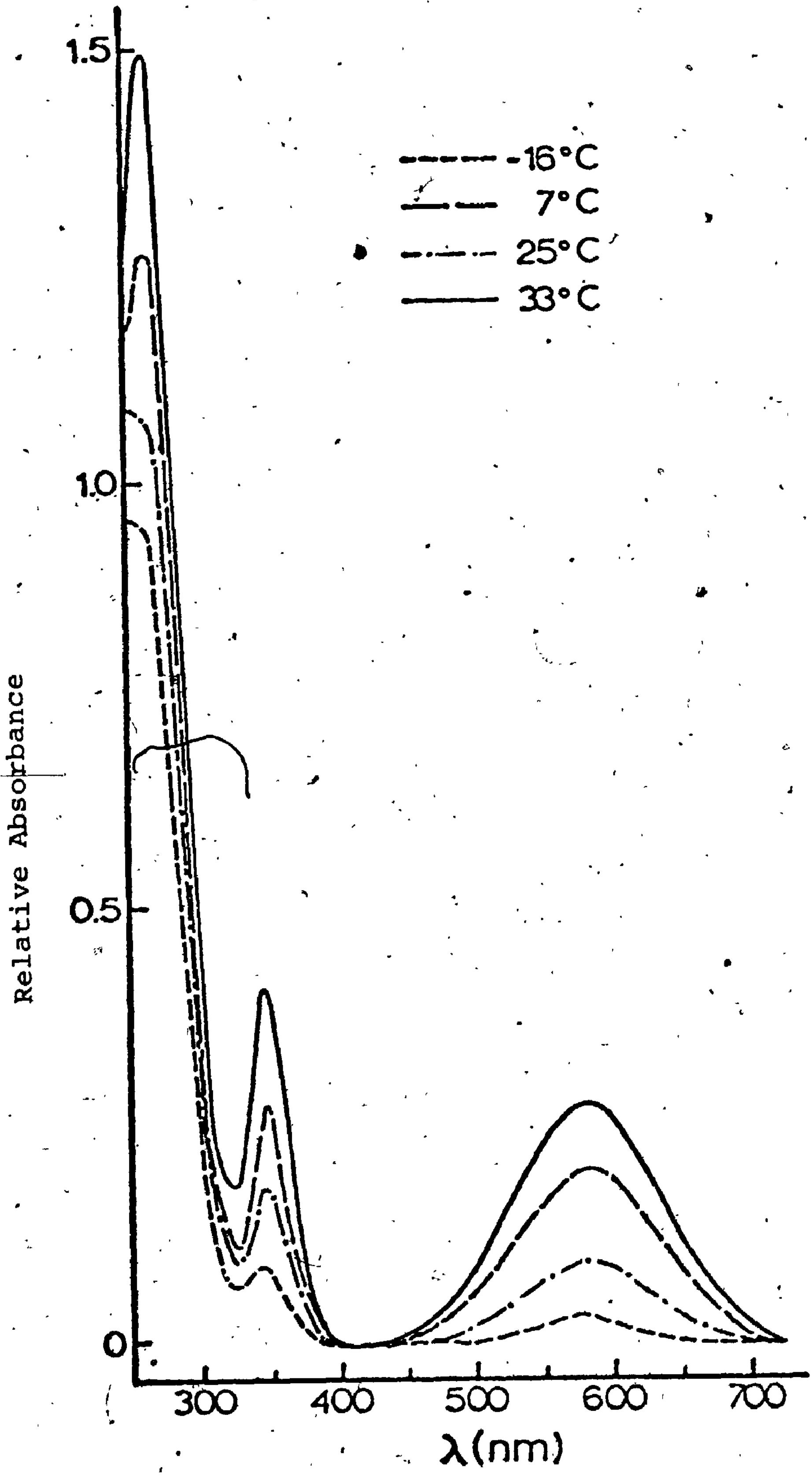


Figure 14. Temperature effect on the uv absorption of 59 in methylene chloride.

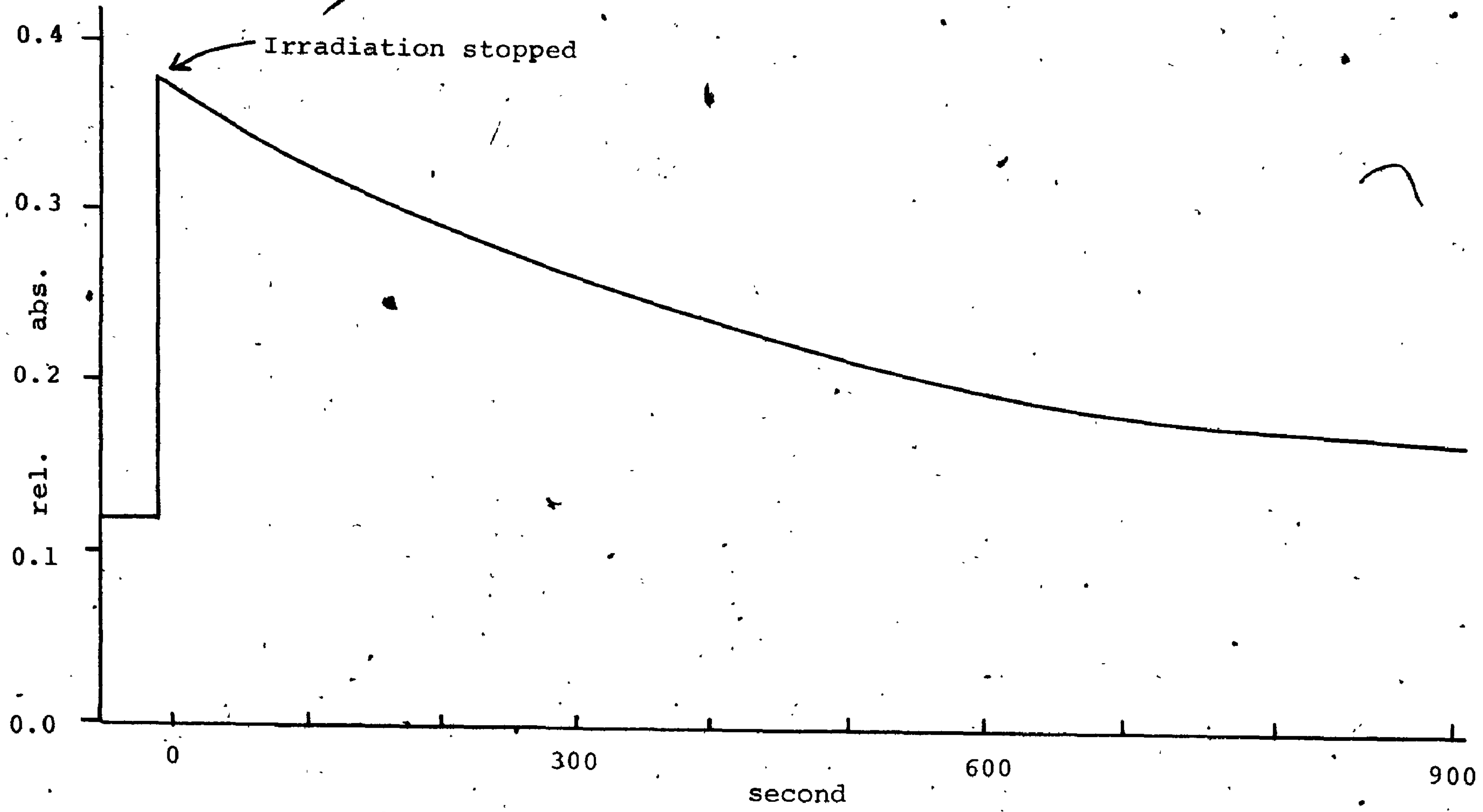


Figure 15. The effect of light on the equilibrium of 59 (dimer→monomer).

of the monomer was obtained by the relationship:

$$\% \text{ of monomer} = \frac{\varepsilon}{\varepsilon_o}$$

where ε_o is the molar absorption extinction at zero concentration. The concentrations of the monomer and dimer were obtained after calculation of the weight of each component:

$$W_m = \text{percent of monomer} \times W_o$$

$$W_d = W_o - W_m$$

where W_o, W_m and W_d are the weight of the total, monomer and dimer respectively. The equilibrium constant, K_c, is defined as

$$K_c = \frac{[A]^2}{[A_2]} \tag{6}$$

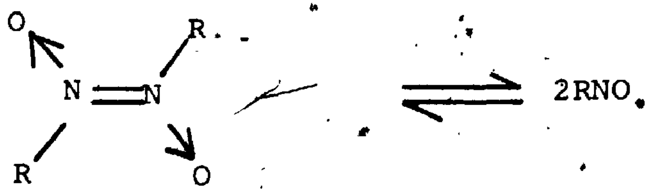
$$\Delta G = -RT\ln K_c \tag{7}$$

for an equilibrium

$$A_2 \rightleftharpoons 2A$$

where A_2 and A denote dimer and monomer. The concentration used in these studies was about 3.4 mg (±0.05 mg) in 50 ml (±0.5 ml) of solvent. Samples were equilibrated at a particular temperature (temperature readings were better than ±.2°C); the absorbances of the sample at different temperatures were measured. The error in absorbance is highly dependent on the nature of the adducts. Owing to the low degree of dissociation of 59 (especially at low temperature), the error in absorbance for 59 is about 5%. In the case of 60 the error is around 1%. The values obtained for the equilibrium constants K_c and free energy (ΔG) are given in Tables 11-14. A plot of $\ln K_c$ against the reciprocal of the absolute temperature gave a good straight line (see Figs. 16-19). From the slope of the plot the standard values of the equilibrium enthalpy, ΔH^o, for the process $A_2 \rightleftharpoons 2A$ together with the entropy change, ΔS^o, were computed by the least and squares methods. The results are shown in Table 15.

The ΔH^o of 59a $\rightleftharpoons$ 59 which is about 2 Kcal/mole smaller than that of 60a $\rightleftharpoons$ 60, is probably due to the steric bulk of the eight methyl groups causing crowding in the dimer. The same effect has been demonstrated by Stowell (99) in the nitrosoalkane dimer equilibria. It was shown that the ΔH^o of nitroso-tert-butane equilibrium is 9 Kcal/mole smaller than that for the nitrosocyclohexane. This was explained by the steric interaction in the dimer. The importance of the steric factor in controlling the equilibrium position in aromatic nitroso compounds has also been shown (90).



76 R = cyclohexyl

77 R = t-Butyl

TABLE 11

Equilibrium Constant and Free Energy of 59 in Benzene at Various Temperatures at a Concentration of 3.49 mg/50 ml of Solvent

Temperature (K^{O})	Equil. Const. (mole/liter)	ΔG° in Cal./mole
289.0	4.43×10^{-7}	8436
293.5	7.05×10^{-7}	8321
308.0	2.54×10^{-6}	7950
313.0	3.82×10^{-6}	7821
319.0	6.06×10^{-6}	7668
324.0	9.40×10^{-6}	7540
331.6	1.46×10^{-5}	7360

TABLE 12

Equilibrium Constant and Free Energy of 59 in Chloroform at Various Temperatures at a Concentration of 3.38 mg/50 ml of Solvent

Temperature (K^{O})	Equil. Const. (mole/liter)	ΔG in cal./mole
249.2	2.86×10^{-7}	7498
254.4	5.11×10^{-7}	7415
259.8	7.30×10^{-7}	7328
269.4	1.64×10^{-6}	7173
273.8	2.42×10^{-6}	7102
279.2	3.60×10^{-6}	7015
289.0	7.49×10^{-6}	6885
291.8	8.39×10^{-6}	6812
299.0	9.15×10^{-6}	6696
307.4	2.38×10^{-5}	6561
318.6	4.93×10^{-5}	6381
323.4	6.53×10^{-5}	6304

TABLE 13

Equilibrium Constant and Free Energy of 60 in Benzene at Various Temperatures at a Concentration of 3.43 mg/50 ml of Solvent

Temperature (K^{O})	Equil. Const. (mole/liter)	ΔG in cal./mole
282.2	8.38×10^{-5}	5368
286.6	1.19×10^{-4}	5168
293.8	2.09×10^{-4}	5007
293.4	1.97×10^{-4}	5012
297.8	2.73×10^{-4}	4883
304.2	4.42×10^{-4}	4684
311.4	7.43×10^{-4}	4460
315.2	9.87×10^{-4}	4341
321.4	1.54×10^{-3}	4149
326.6	2.20×10^{-3}	3987
333.3	3.04×10^{-3}	3778

TABLE 14

Equilibrium Constant and Free Energy of 60 in Chloroform at Various Temperatures at a Concentration of 3.31 mg/50 ml of Solvent

Temperature (K^{o})	Equil. Const. (mole/liter)	ΔG in cal./mole
245.8	2.65×10^{-4}	4052
256.2	5.68×10^{-4}	3825
264.4	1.06×10^{-3}	3647
271.4	1.52×10^{-3}	3494
277.6	2.34×10^{-3}	3359
285.4	3.48×10^{-3}	3189
292.0	5.94×10^{-3}	3045

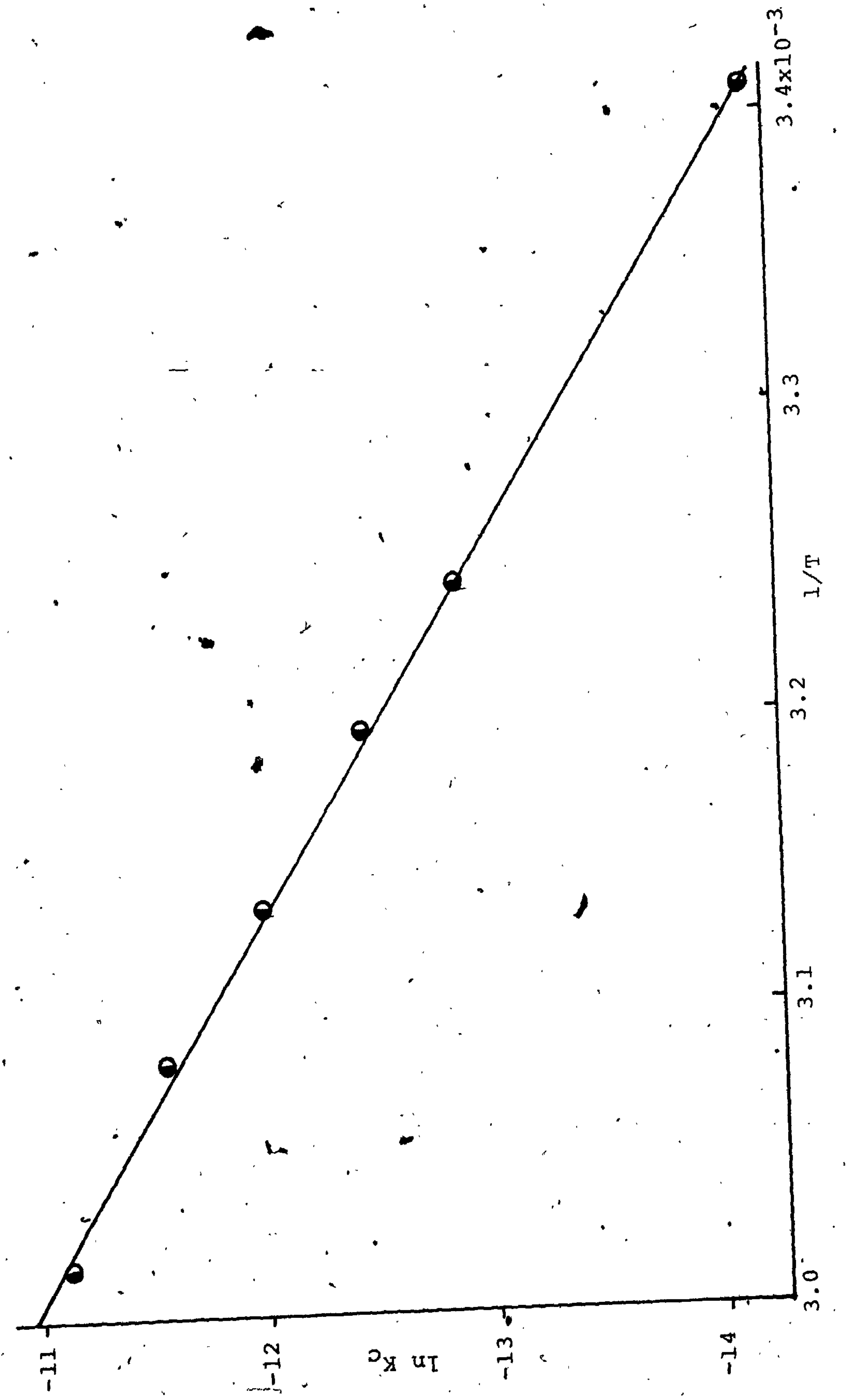


Figure 16. Plot of ln K_c of 59 in benzene as a function of the reciprocal absolute temperature, T.

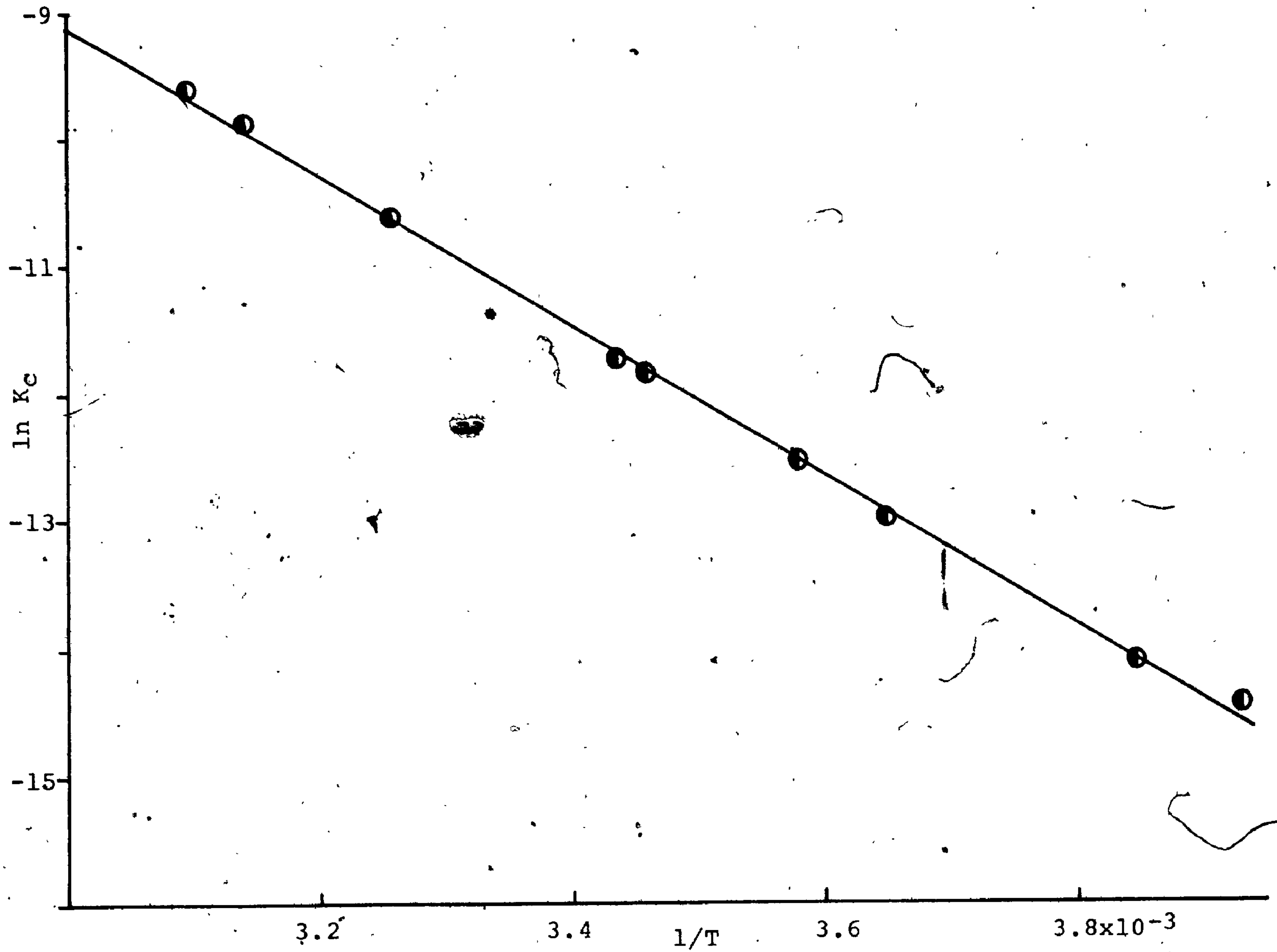
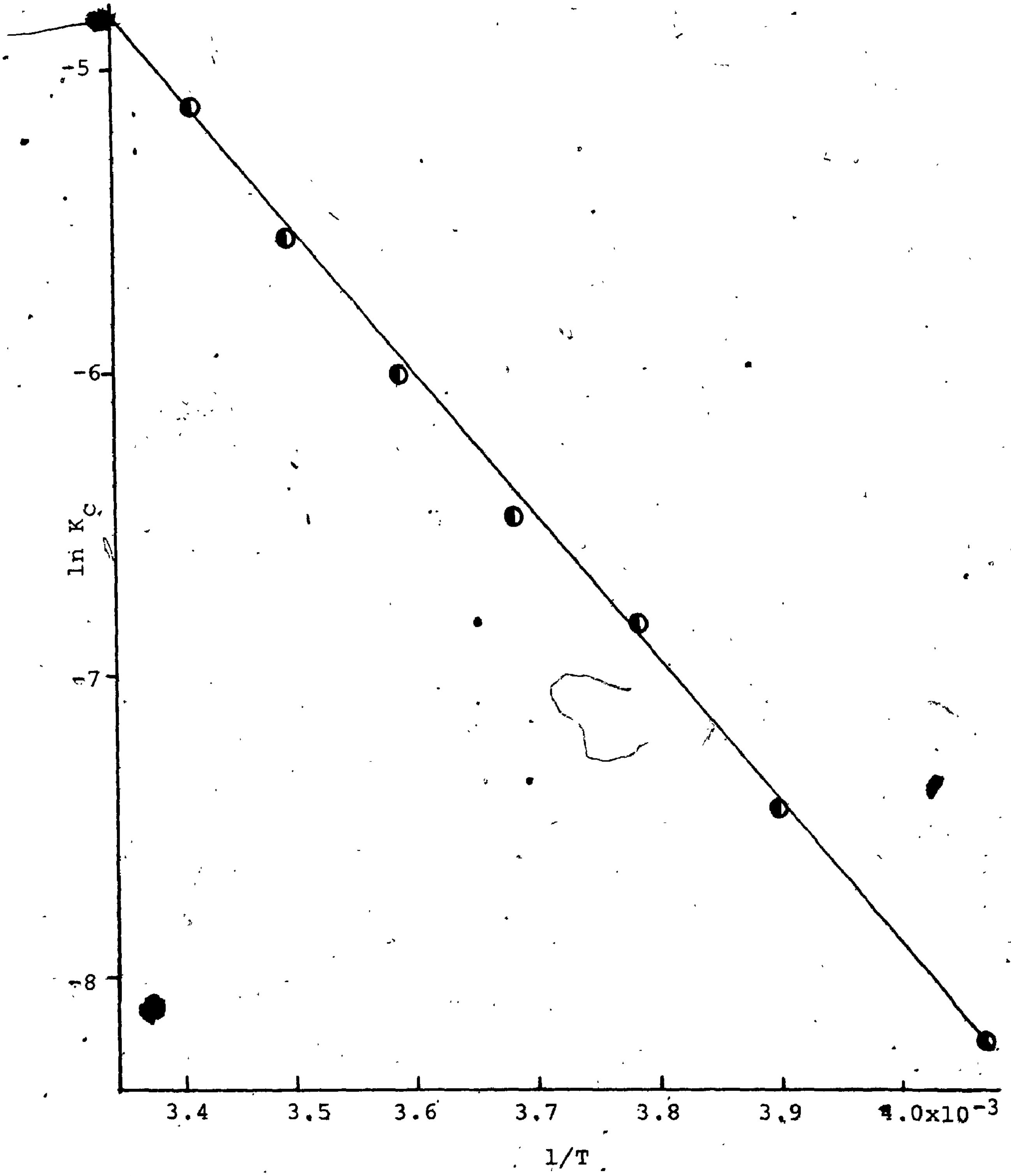


Figure 17. Plot of ln K_c of 59 in chloroform as a function of the reciprocal absolute temperature, T.

Figure 18. Plot of $\ln K_c$ of 60 in chloroform as a function of the reciprocal absolute temperature, T.



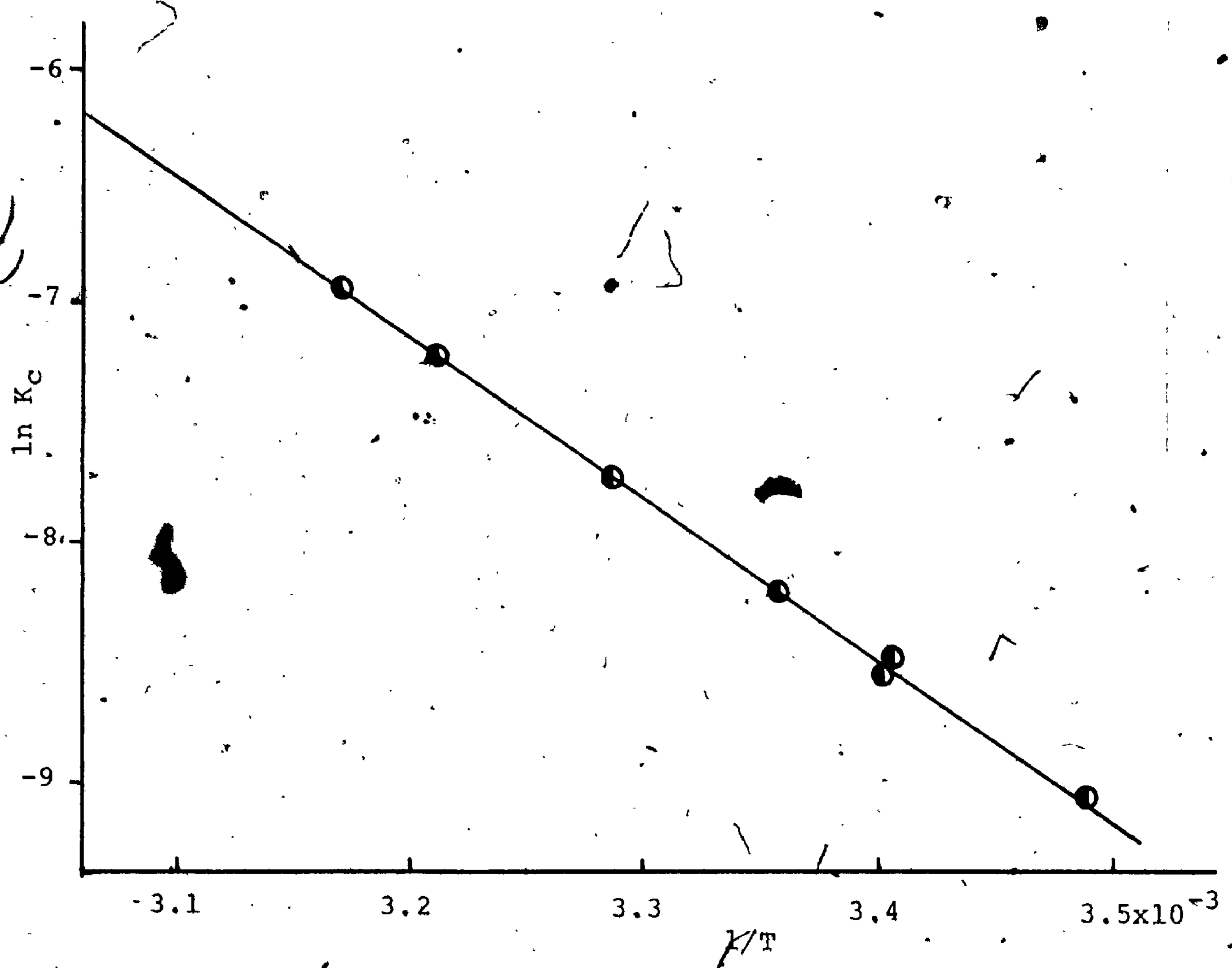


Figure 19. Plot of ln K_c of 60 in benzene as a function of the reciprocal absolute temperature, T.

TABLE 15

ΔH^o and ΔS^o for 59 and 60

System	Cyclopentene adduct 59		Tetramethylethylene adduct 60	
	dimer ⇌ monomer		dimer ⇌ monomer	
Solvent	C_6H_6	$CHCl_3$	C_6H_6	$CHCl_3$
ΔH^o (Kcal/mole)	15.8±1.0	11.5±0.4	14.1±0.3	9.4±0.2
ΔS^o (e.u.)	25.6±2.0	16.1±1.2	31.1±0.8	21.8±0.8

2.6 Summary

Two α,β-unsaturated thioketones which are part of an orthoquinoid system have been successfully synthesised by the photochemical addition of 4,5-benzo-1,2-dithiole-3-thione to cyclopentene and tetramethylethylene. These thiones are in thermal equilibrium with the corresponding dimers formed by a 4+4 addition. The structure of the monomers have been assigned while the stereochemistry of the dimer has not been conclusively proven. Some thermodynamic parameters for the dissociation of the dimers were obtained. The difference between the parameters obtained for these two adducts was explained by the steric factor.

EXPERIMENTAL

CHEMICALS

Cyclopentene and tetramethylethylene were refluxed over zinc dust for 1 hour, then distilled through a Vigreux column. Acetylene dicarboxylic dimethyl ester was distilled under reduced pressure. Benzene for thermodynamic studies was purified in the same way as that for irradiation (see Part 1). Chloroform (Fisher, spectroanalysed) for the thermodynamic measurement was distilled through a 50 cm Vigreux column. Only a middle fraction was used. Ether (Mallinkrodt), methylene chloride (Fisher), n-hexane (Fisher) and acetonitrile (Fisher) were used without further purification.

Preparation of 4,5-Benzo-1,2-dithiole-3-thione 58

The 1,2-dithiole-3-thione, 58, was prepared according to the method of Lozach et al (100). o-Benzoic sulfimide (35 gm) (Aldrich) and phosphorus pentasulfide (35 gm) were ground together. The mixture was heated to 140° in an oil bath. After all the mixture had turned an orange-red, it was heated to 160° for 10 minutes and was then allowed to cool. It was dissolved in 50% aqueous alcohol solution (500 ml) and the alcoholic solution was extracted with three 100 ml portions of benzene. The benzene extract was dried over anhydrous potassium carbonate and the solvent was removed. The residue was chromatographed on silica gel (500 gm) using petroleum (60-80°)-benzene (2:1) as eluent. The orange-red solid isolated was recrystallized from ethanol to give 58 (7 gm), m.p. 93-4°; nmr ($CDCl_3$) 7.25-7.60 (m, 1H), 7.60-7.83 (m, 2H), 8.17 (m, 1H); uv (cyclohexane) $\lambda_{max.}$ 450, 430, 324, 320, 319, 283, 274, 245, 225 nm (ε= 4730, 4400, 3230, 3170, 3320, 8200, 8150, 6770, 6250); mass spectrum m/e 184.

Preparation of 2-Benzyl-N-phenylsuccinimide

2-Benzyl-N-phenylsuccinimide was prepared according to Arcoria and coworkers (101). Hence 2-benzylsuccinic acid (0.4 gm), which was prepared according to Moffett (102), Weizmann (103), and Cohen (104), and aniline (0.18 gm) were heated at 180° to give the imide (79% yield) m.p. 128-30°; ir ($CHCl_3$) 1778, 1714 cm^{-1}; nmr ($CDCl_3$) 2.60-3.40 (m, 5H), 7.0-7.6 (m, 10HO.

Calcd. for $C_{17}H_{15}NO_2$: 265.1102. Found: 265.1090.

Preparation of N-n-Propyl-maleimide

N-n-Propyl-maleimide was prepared according to Mehta et al. (105). Thus, n-propylamine (6 gm) and maleic anhydride (13 gm) gave 12 gm N-n-proyl maleamic acid (m.p. 97-99°) which was cyclized in acetic anhydride to give N-n-propylmaleimide (10.2 gm); m.p. 79-80°; nmr (CCl_4) 0.82 (t, J=3, 3H), 2.50 (m, 2H), 3.40 (t, J=3, 2H), 6.95

(s, 2H); mass spectrum m/e 139.

Stability of 4,5-Benzo-1,2-dithiole-3-thione in the Presence of Olefin

A. With Cyclopentene

A solution of 4,5-benzo-1,2-dithiole-3-thione (2.8 mg/ml) and cyclopentene 100 mg/ml in ether was kept in the dark at room temperature. The absorbance (700-470 nm) was followed up to 4.5 hours. The data obtained is as follows:

Time (hour)	Relative Absorbance at 585 nm	Relative Absorbance at 530 nm	Relative Absorbance at 490 nm
0	0	0.24	0.52
1	0	0.24	0.52
1.5	0	0.24	0.52
4.5	0	0.24	0.50

B. With Tetramethylethylene

A solution of 4,5-benzo-1,2-dithiole-3-thione (5 mg/ml) and tetramethylethylene 100 mg/ml in ether was kept in the dark at room temperature. The absorbance (700-470 nm) was followed. The result obtained is as followed:

Time	585 nm	520 nm	490 nm
0	0.01	0.56	0.86
2.5 hrs.	0.02	0.55	0.85
20 min. (room light)	0.035	0.09	0.12
80 min. (room light)	0.04	0.08	0.11

At the end of 12 hours in room light, the solution became deep blue.

Irradiation of 58 and Cyclopentene

A mixture of 58 (99 mg), cyclopentene (1 ml) and ether (30 ml) was irradiated with a 450 watt Hanovia medium pressure lamp until the solution turned deep blue which usually took 2 hours. After the solvent had evaporated, the solid residue was chromatographed on silica gel (9 gm) with petroleum (60-80°)-benzene (2:3) as eluent to give 59 which was obtained as a white solid after it was recrystallized from a mixture of methylene chloride and methanol, in 80% yield (112 mg), m.p. 158-60° (dec.); nmr (CDCl$_3$) 1.93 (m, 6H, the methylene protons of the cyclopentyl ring), 3.95 (m, 1.5H, -S-CH-CH-S-), 4.40 (m, 0.5H, -S-CH-CH-S-), 6.83 (m, 2H, the aromatic protons), 7.20 (m, 1H, the aromatic protons), 7.52 (m, 1H, the aromatic proton); uv (benzene) c=5.24x10^{-3} mole/liter, $\lambda_{max.}$=585, 351 nm (ε=24.8, 139), (acetonitrile) c=6.61x10^{-4} mole/liter, $\lambda_{max.}$ 580, 346 nm (ε=348, 620), (methylene chloride) c=5.02x10^{-3}, $\lambda_{max.}$ 585, 347, 260 nm (ε=97, 245, 136, 3590); mass spectrum m/e (%), 284 (1.7), 252 (1.0), 216 (9.3), 184 (100), 120 (51), 76 (30.3), 68 (58.2) and 67 (77.9).

Molecular weight determination of 59: Method (1) - The molecular weight of 59 was determined in benzene by means of a freezing point lowering method. The molecular weight was found to be 496±10 at a concentration of 2.04

and 3.01 mg/ml of solvent. The value required for the dimer, 59a, is 504. Method (2) - The molecular weight of 59 was found to be concentration dependent (it was determined in chloroform using a Hewlett and Packard 301 Vapor Pressure Osmometer and benzil as calibrant). The value (conc.) were: 428±20 (4.9×10^{-3} mole/liter), 471±20 (6.4×10^{-3} mole/liter), 495±25 (7.4×10^{-3} mole/liter) and 532±30 (1.7×10^{-2} mole/liter).

Thermal Decomposition of 59

A solution of 59 (20 mg) in carbon tetrachloride (5 ml) was refluxed for 12 hours. Only one spot appeared on tlc. When the solvent was evaporated and the residue was recrystallized from hexane, compound 58 was obtained in quantitative yield.

The thermal decomposition was also carried out in a sealed tube without solvent at 130° for four hours. Decomposition was complete but tlc showed about seven spots in addition to that from compound 58. No further investigations were made.

Desulfurization of 59a

A mixture of 59a (1.08 gm), active Raney nickel (10 gm) and benzene (15 ml) was heated to 40° for 20 hours. After this time starting material was still present. The reaction temperature was raised to 60° and the reaction was completed after 4 hours. It was worked up in the usual way. The residue was separated from preparative tlc using petroleum ether (60-80^{o})-benzene (20:3) as eluent. Less than 1 mg of material was isolated from the band with the largest Rf value and no investigation was made on this compound. The second compound was dibenzyl in 4% yield; m.p. and mixed m.p. 49-50^{o}; nmr (CCl_4) 2.90 (s, 4H), 7.04 (s, 10H), mass spectrum m/e (%) 182 (54) and 91 (100). The third compound was benzyl alcohol in 13.5% yield. The ir and nmr spectra of this product and that of an authentic sample were identical.

Trapping 59 by N-Phenylmaleimide

A solution of 59 (39 mg) and N-phenylmaleimide (29 mg) in benzene (10 ml) was stirred at room temperature for four hours in the dark. The 1:1 adduct 61 was separated by preparative tlc using chloroform-benzene (1:4) as eluent and was obtained in 80% (53 mg) yield. It was recrystallized from ethyl acetate to give white crystals, m.p. 93-95^{o}, ir ($CHCl_3$) 1770, 1710 cm^{-1}; nmr ($CDCl_3$) 1.5-2.4 (m, 6H, the methylene protons of the cyclopentyl ring), 4.1-4.4 (m, 2H, -S-CH-CH-S-), 4.93 (s, 2H, -S-CH(CO-)-CH(CO-)-C-), 6.80-8.13 (m, 9H, the aromatic protons); when 53 mg Eu(fod)$_3$ was added, the singlet at 4.93 shifted to lower field and became a pair of doublets (J=9Hz), each doublet was integrated to be 1 proton; uv (MeOH) $\lambda_{max.}$ 283 nm (s) (ε= 300), mass spectrum m/e 425.

Anal. calcd. for $C_{22}H_{19}NO_2S_3$: C, 62.11; H, 4.50; N, 3.29. Found: C, 62.11: H, 4.56; N, 3.30.

Desulfurization of 61 by Raney Nickel

A mixture of 61 (300 mg), Raney nickel (3 gm) and benzene (10 ml) was refluxed for 24 hours. When the solvent was evaporated, a solid was obtained. It was recrystallized from ethanol-water (1:1) to give 2-benzyl-N-phenylsuccinimide (142 mg, 77% yield) m.p. and mixed m.p. 128-30°. The ir, nmr and mass spectra of the product and those of an authentic sample were identical.

Trapping 59 with Acetylene Dicarboxylic Acid Dimethyl Ester

A solution of 59 (100 mg) and acetylene dicarboxylic acid dimethyl ester (100 mg) in benzene (10 ml) was stirred in the dark for 20 hours. The resulting mixture was separated by a preparative tlc using benzene as eluent. A gummy solid, 62, was obtained in 75% (120 mg) yield. It seemed that it might contain more than one compound which could not be separated using tlc. Attempts to sublime this solid at 0.1 mm Hg at 100° resulted in decomposition. The gummy solid had a m.p. 39-40°; ir ($CHCl_3$) 1721 cm^{-1}; nmr ($CDCl_3$) 1.6-2.2 (m, 6H, the methylene protons of the cyclopentylene protons of the cyclopentyl ring), 3.78 (s, 3H, $-COOCH_3$) 3.80 (s, 3H, $-COOCH_3$) 4.0-4.5 (m, 2H, -S-CH-CH-S-), 7.20-8.20 (m, 4H, the aromatic protons); uv ($CHCl_2$) $\lambda_{max.}$ 318, 253 nm (ε=3900, 8400); mass spectrum m/e 388. 62 (95 mg) was desulfurized by Raney nickel to give an oil which was distilled at 125-32°/mm Hg, giving dimethyl benzylsuccinate in 25% (20 mg) yield. The ir and mass spectra of this product and those of an authentic sample were identical.

Irradiation of 58 and Tetramethylethylene

The irradiation was similar to the irradiation of 58 and cyclopentene. The reaction product (from 90 mg) was crystallized from a methylene chloride-methanol mixture to give pale blue crystals, 135 mg, of 60 (90% yield) m.p. 136-8° (dec.), nmr (220 Hz) (CD_2Cl_2) (at -50°) 1.20 (s, 3H, the methyl protons), 1.33 (s, 3H, the methyl protons), 1.59 (s, 3H, the methyl protons), 1.80 (s, 3H, the methyl protons), 6.94 (1H, the phenyl proton), 7.02 (1H, the phenyl proton), 7.67 (the phenyl proton), 7.90 (1H, the phenyl proton); uv (benzene) $C=2.59 \times 10^{-4}$ mole/liter, $\lambda_{max.}$=585 nm, (ε=2270), (chloroform) $C=2.4 \times 10^{-4}$ mole/liter; nmr (^{13}C) (CD_2Cl_2) 148.6 (s), 139.40 (d), 134.19 (s), 129.52 (d), 128.67 (d), 128.07 (s) (these are the 6 aromatic carbons), 77.60 (s, -S-C-S-), 66.23 (s, $-S-\underline{C}-C_3$), 66.12 (s, $S-\underline{C}-C_3$), 28.32 (q), 26.93 (q), 23.48 (q) , 23.31 (q), (these four quartets are the methyl carbons).

Anal. calcd. for $C_{13}H_{16}S_3$: 268.0409. Found: 268.0405 (Anal. calcd. C, 58.20; H, 6.01; S, 35.79. Found: C, 58.33; H, 6.19; S, 34.88).

Molecular weight of 60: The molecular weight of 60 was measured at 5.8 mg/ml at 38° by Vapour Pressure Osmometry and was found to be 496. The calculated percentage of monomer present at this concentration using this method was 7.4% whereas a uv absorbance method led to an estimate of 9.7%.

Trapping 60 with N-Phenyl-maleimide

A solution of 60 (500 mg) and N-phenyl-maleimide (400 mg) in benzene (50 ml) was stirred in the dark at room temperature for 24 hours. A light yellow solution was obtained. The solid obtained after the removal of solvent was recrystallised from ethyl acetate to give the 1:1 adduct 65 (700 mg, 85% yield); m.p. 242-5°; ir ($CHCl_3$) 1775, 1710 cm^{-1}; nmr ($CDCl_3$) 1.36 (s, 3H, $-C-CH_3$), 1.46 (s, 3H, $-C-CH_3$), 1.58 (s, 3[illegible]; $-C-CH_3$), 1.70 (s, 3H, $-C-CH_3$), 4.405 (s, 1H, -CH-CON-), 4.415 (s, 1H, -CH-CON-), 6.75-8.3 (m, 9H, the aromatic protons). After 28 mg Eu(fod)$_3$ had been added, the signals at 4.41 disappeared completely while two new doublets at 4.83 (d, J=9 Hz, 1H) and 5.9 (d, J=9 Hz, 1H) appeared. Uv (CH_2Cl_2) $\lambda_{max.}$ 286 nm (ε=2600); mass spectrum m/e 441.

Anal. calcd. for $C_{23}H_{23}NO_2S_3$: C, 62.58; H, 5.25; N, 3.17; S, 21.75. Found: C, 63.28; H, 5.55; N, 3.20; S, 21.55.

Attempted Desulfurisation of 65 by an Old Raney Nickel

A mixture of 65 (163[illegible]g) and a four-year old sample of Raney nickel (stored in absolute alcohol) in absolute alcohol (20 ml) was refluxed for 22 hours. A solid was obtained upon the removal of solvent and this solid was separated using preparative tlc to give two products. The first one consisted of white solids of 66 (119 mg, 73% yield); m.p. 225-7°; ir ($CHCl_3$) 1775, 1710 cm^{-1}; nmr ($CDCl_3$) 1.46 (s, 3H, $-C-CH_3$), 1.55 (s, 3H, $-C-CH_3$), 1.60 (s, 3H, $-C-CH_3$), 1.66 (s, 3H, $-C-CH_3$), 3.34 (d, J=19 Hz, 1H, -CH-CON-), 4.11 (d, J=19 Hz, 1H, -CH-CON-), 7.06-7.7 (m, 9H, the aromatic protons); uv (CH_2Cl_2) $\lambda_{max.}$ 298 nm (ε=2500); mass spectrum m/e 441.

Anal. Calcd. for $C_{23}H_{23}NO_2S_3$: C, 62.58; H, 5.25; N, 3.17; S, 21.75. Found: C, 62.62; H, 5.13; N, 3.27; S, 21.72.

The second product was the starting material 60; m.p. 242-4°.

The adduct 65 (500 mg) was eventually desulfurised, under the same conditions but with freshly prepared Raney nickel (12 gm) to give 2-benzyl-N-phenyl-succinimide (230 mg); m.p. and mixed m.p. 128-30°. The ir and nmr spectra of the product obtained and those of an authentic sample were identical.

Trapping 60 with N-n-Propyl-maleimide

A solution of 60 (100 mg) and N-n-propyl-maleimide (50 mg) in benzene (30 ml) was allowed to stand in the dark at room temperature for 30 minutes. The solvent was removed and the residue was separated using preparative tlc with benzene as eluent. The 1:1 adduct 64 was obtained in 79% yield (128 mg). It had a m.p. 213-4°; ir ($CHCl_3$) 1724 cm^{-1}; nmr ($CDCl_3$), 0.4 (t, J=4, 3H, $-N-CH_2CH_2C\underline{H}_3$), 0.9-1.3 (m, 2H, $-N-CH_2C\underline{H}_2-$), 1.26 (s, 3H, $-C-CH_3$), 1.46 (s, 3H, $-C-CH_3$), 1.53 (s, 3H, $-C-CH_3$), 1.70 (s, 3H, $-C-CH_3$), 3.20 (t, J=4, 2H, $-N-CH_2-$), 4.20 (s, 2H, -CH(CO-)-CH(CO-)-), 7.20-8.20 (m, 4H, the aromatic protons); mass spectrum m/e 407.

Anal. calcd. for $C_{20}H_{25}NO_2S_3$: C, 58.96; H, 6.18; N, 3.44 S, 23.56. Found: C, 58.96; H, 6.09; N, 3.41; S, 23.79.

Trapping 60 with Acetylene Dicarboxylic Acid Dimethyl Ester

A solution of 60 (100 mg) and acetylene dicarboxylic acid dimethyl ester (0.5 ml) in benzene (10 ml) was stirred at room temperature in the dark for 12 hours. Separation was achieved on a preparative tlc to gave the 1:1 adduct 63 in 67% yield (95 mg). This was recrystallised from methanol to give white crystals, m.p. 94-7°; ir ($CHCl_3$) 1721 cm^{-1}; nmr ($CDCl_3$) 1.40 (s, 6H, the methyl protons), 1.54 (s, 6H, the methyl protons), 3.94 (s, 3H, $-COOCH_3$), 3.96 (s, 3H, $-COOCH_3$), 7.5-8.5 (m, 4H, the aromatic protons). The variable temperature nmr of 63 was done in carbon disulfide in a temperature range from +30 to -110°. It was found that the frequency separation of the resolved signals at low temperature was 160±15 Hz. The results are shown in Fig. 7.

Anal. calcd. for $C_{19}H_{22}O_4S_3$: C, 55.61; H, 5.40; S, 23.39.

Found: C, 56.10; H, 5.70; S, 22.88.

63 (145 mg) was desulfurised to give dimethyl 2-succinate in 15% yield (14 mg). The ir and mass spectra of the product and those of an authentic specimen were identical.

Molar Extinction Coefficient of 59 and 60

The spectrophotometric measurement was carried out with a Gilford Spectrophotometer 240 equipped with a double set of thermospacers through which water from a constant temperature bath was circulated. Matched 1.0 and 10.0 cm quartz cell were used and the temperature was maintained at 24.5±0.2°. Optical densities were determined at 585 nm, the wavelength of maximum absorption. Optical densities were reproducible to within ±0.5%. The molar extinction coefficient, ε_m, was determined by linear extrapolation of ε vs ε^2,c plots (90, 91) (where c is the concentration of total 59 or 60, all figured as monomers) to zero concentration. The resulting values of ε_m were then used in the calculation of equilibrium constants. The data for 59 in chloroform is given in Table 7 and Fig. 10. The data for 60 in benzene and chloroform are given in Tables 8-9 and Figs. 11-12 respectively.

The uv absorption spectrum of 59 was measured on the Cary-14 instrument using a spectrophotometer cell which could be thermostated. The Haake model KT-62 served as a constant temperature circulator. The absorption spectrum of 59a was measured in ether at -15° ($c=8.4c10^{-5}$ mole/liter) and is shown in Fig. 8.

The Uv Absorption Spectra of 59 in Different Solvent Mixture

The measurements were carried out on the Cary-14 in solvent mixtures of n-hexane/methylene chloride ($c=3.6x10^{-3}$) at room temperature. These are shown in Fig. 13.

Thermodynamic Measurements of 59 and 60

Thermodynamic measurements were carried out by means of uv techniques. Uv absorbances at 585 nm were determined by the Cary-14 spectrophotometer using a spectrophotometer cell which could be thermostated. The Kryothermat Haake model KT-62 was used as a constant temperature circulator. The temperature reading of the spectrophotometer cell was measured by means of an iron-constantan thermocouple using an ice-water bath as a reference. A digital voltmeter, Dana 5330 model, was used to measure the differences in voltages which could be converted into temperature readings. The uv absorption spectrum was taken after constant temperature had been attained, equilibration usually requiring at least one hour. The thermodynamic parameters were determined in benzene and chloroform at 7 to 12 different temperatures. The data obtained are shown in Table 15 and Fig. 16-19.

Temperature Effect on the Uv Absorption Spectrum of 59

The same setup was used as for the thermodynamic measurement. A solution of 59 in methylene chloride (c= 9.8×10^{-5} mole/liter) was measured at 4 different temperatures between -16 and +33°. Results are shown in Fig. 14.

Effect of Light on the 59a $\rightleftharpoons$ 59 Equilibrium

The absorbance of the solution of 59 in benzene (2×10^{-1} mole/liter) was measured at 585 nm at 25°. The solution was then irradiated with a 450 watt Hanovia medium pressure mercury arc lamp for 5 minutes. The absorbance at 585 nm was measured over a period of 15 minutes after the irradiation had stopped. The absorbance increased from 0.060 to 0.235 during the irradiation and returned to about 0.09 at the end of the measurement. This is shown in Fig. 15.

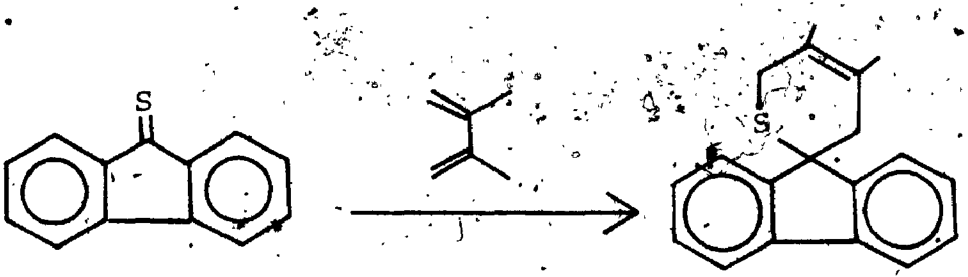
PART 3: THE CYCLOADDITION OF THIOKETONE TO α,β-UNSATURATED THIOKETONES

CHAPTER 1

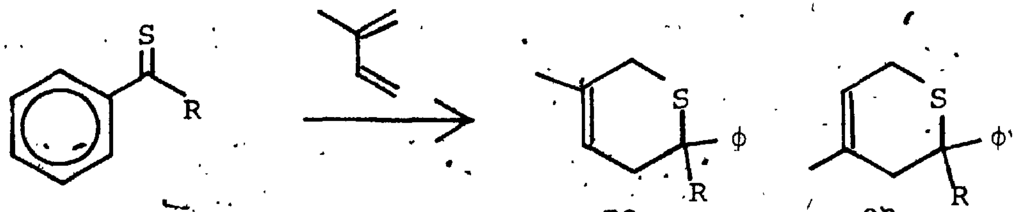
INTRODUCTION

In the study of the structure of the monomers derived from cyclopentene and tetramethylethylene with 4,5-benzo-1,2-dithiole-3-thione, we employed trapping reactions with standard dienophiles to form a Diels-Alder type of adduct (see Part 2). Alicyclic thioketones were also used since it was thought, at one time, that they would give adducts resembling the structure of dimer via a Diels-Alder reaction. Later on, it was shown that the dimers were 4+4 adducts instead of 4+2 adducts. However, it was noted that the addition between thiones and the monomer, 59, (an α,β-unsaturated thione) was proven to be irrelevant to the structure elucidation of the dimer, and we thought it might be worthwhile to investigate the reaction in more detail. Surprisingly, the mutual addition of an α,β-unsaturated thione to a thione function has not been reported in the literature.

The use of thioketones and α,β-unsaturated thioketones as potential dienophiles and dienes in a Diels-Alder reaction was not studied until recently. The earliest work reported in this field was the addition of perfluorothioketones to dienes (106). At about the same time, aromatic thioketones were also shown to be good dienophiles. Schonberg and Koning (107) mixed thiofluorenone with 2,3-dimethyl-1,3-butadiene and obtained the spiro cycloadduct 78. It was demonstrated by Tsuchihashi and coworkers (108) that both thiobenzophenone and thioacetophenone reacted smoothly with 2-methyl-1,3-butadiene in the dark to give the bicyclic adduct 79 and 80 in good yield.



78



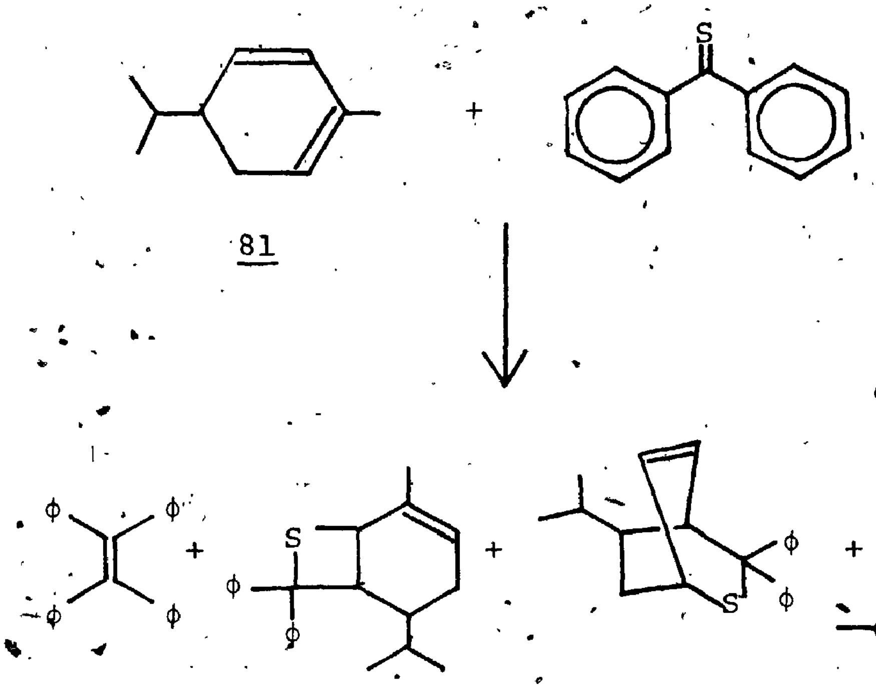
R = ϕ or CH_3

79

80

Sugiyama and coworkers (109) also found that thiobenzophenone could undergo both 1,2 and 1,4 photochemical addition with diene, 81, to give products 82, 83 and 84. Recently, Cantrell (110) showed that thiobenzophenone added photochemically to cyclooctatetraene solely at the 1,4 position. In these cases, a radical reaction is assumed.

Examples of α,β-unsaturated thioketones serving as the diene in a Diels-Alder reaction are scarce. Nasielski's



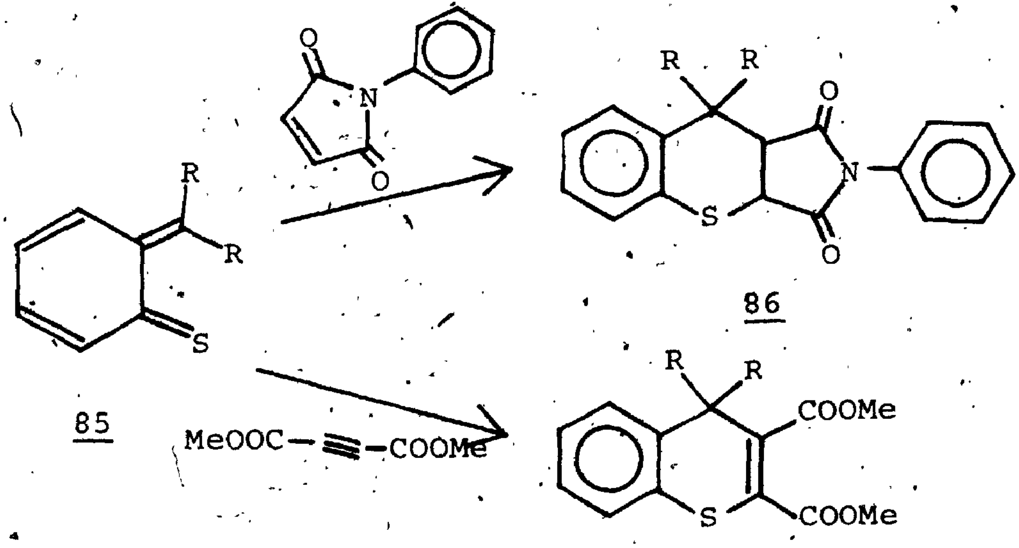
81

82

83

84

(73) observation as well as results from our laboratory (see Part 2) have demonstrated the addition of the thioortho quinoid 85 with N-substituted maleimide and acetylene dicarboxylic acid dimethyl ester to give adducts 86 and 87, respectively.

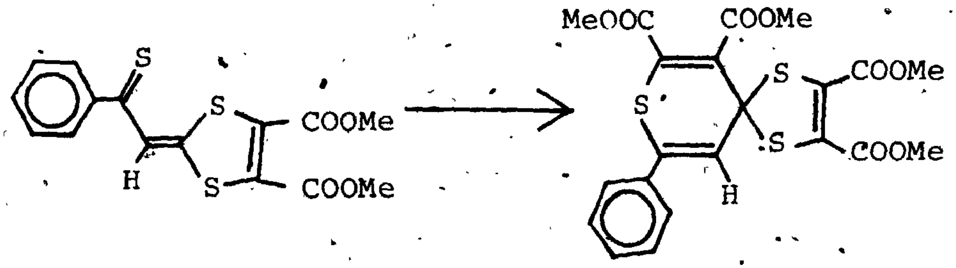


85

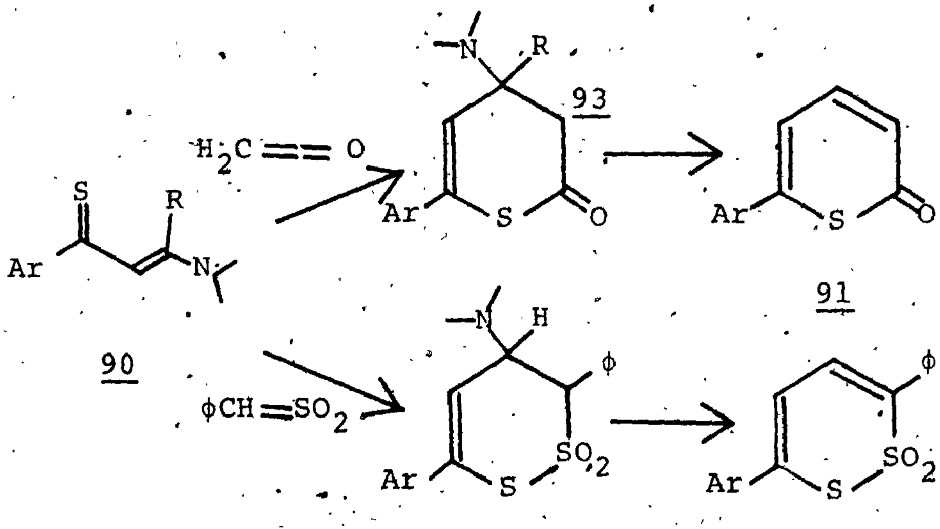
86

87

Acyclic α,β-unsaturated thioketones also undergo similar reaction with dienophiles. The addition of acetylene dicarboxylic acid dimethyl ester to 88 resulting in 89 has been reported by Leaver and coworkers (111). Quiniou and his collaborators (112, 113) succeeded in reacting ketene and sulphenes to amino-substituted α,β-unsaturated thioketone 90 to give 93 and 94 which were deaminated to 91 and 92.



88 89



90 91 94 92

In the present work, the formation of 1,3-dithianes from aliphatic thioketones and α,β-unsaturated thioketones were investigated and the results are described in the following section.

CHAPTER 2

RESULTS AND DISCUSSION

2.1 The Diels-Alder Cycloaddition between α,β-Unsaturated Thiones and Thiones

A. The Cycloaddition of Thioketones to 59

The thioketones chosen in this study were 2-adamantane-thione, 2-thionorcamphor, cyclohexanethione and thiocamphor. The pure adducts (95a, 95b, 96a, 97a and 97b) of the first three compounds with 59 were prepared by mixing 59 with the thioketones in a molar ratio of 1:1.1 in benzene. The solution were kept in the dark at room temperature for 24 hours. Isolation was achieved by two successive preparative tlc. In the first tlc, the products were separated as one fraction from the reaction mixture. The fraction obtained was further separated into 2 compounds by another tlc eluting at least 4 times with cyclohexane. The yields, mass and nmr spectral data of the adducts are listed in Table 16. Their proof of structure will be dealt with in the following section.

In the case of 2-thionorcamphor, only one adduct was isolated from the reaction. The second fraction was an oily material which could not be induced to crystallise and probably contained stereoisomers. This point was confirmed by the nmr spectral data of this oily material which showed

TABLE 16

The Nmr, Molecular Ion and Chemical Yields of Adducts from Thiones and α,β-Unsaturated Thiones

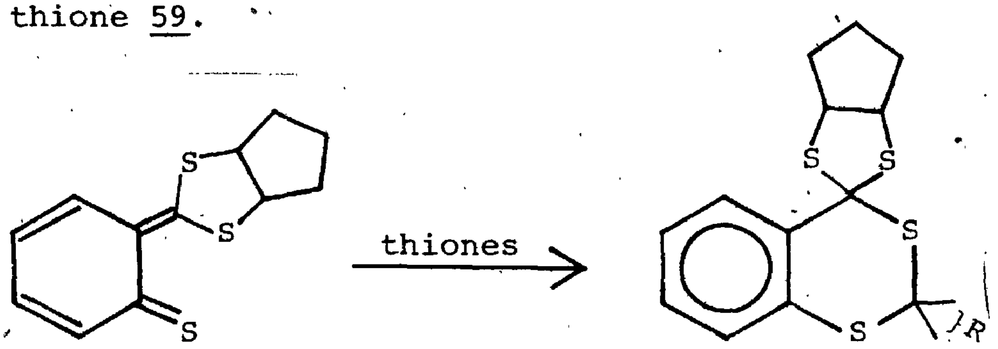
adducts	% of yield	mol. ion (m/e)	chemical shift (δ)
95a	51	418	1.6-2.7 (m, 20H, the protons on the adamantyl skeleton and the methylene protons on the cyclopentyl ring), 4.43 (m, 2H, -SCH-CH-S-), 7.1-8.2 (m, 4H, the aromatic protons).
95b	22	418	1.6-2.7 (m, 20H, the protons on the adamantyl skeleton and the methylene protons on the cyclopentyl ring), 4.03 (m, 2H, -S-CH-CH-S-), 7.1-8.2 (m, 4H, the aromatic protons).
96a	63	378	1.4-2.3 (m, 15H, the protons on the norcamphyl skeleton and the methylene protons on the cyclopentyl ring), 4.40 (m, 2H, -S-CH-CH-S-), 7.1-8.3 (m, 4H, the aromatic protons).
97a	64	466	1.5-2.2 (m, 16H, the protons on the cyclohexyl skeleton and the methylene protons on the cyclopentyl ring), 4.40 (m, 2H, -S-CH-CH-S-). 7.1-8.2 (m, 4H, the aromatic protons).

TABLE 16 (cont'd)

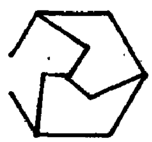
adducts	% of yield	mol. ion (m/e)	chemical shift (δ)
97b	25	366	1.4-2.2 (m, 16H, the protons on the cyclohexyl skeleton and the methylene protons on the cyclopentyl ring), 4.02 (m, 2H, -S-CH-CH-S-) 7.1-8.2 (m, 4H, the aromatic protons).
98	88	382	1.36 (s, 6H, the methyl protons), 1.56 (s, 6H, the methyl protons), 1.6-2.0 (m, 10H, the protons on the cyclohexyl skeleton), 6.98-8.00 (m, 4H, the aromatic protons).
100a	18	--	1.6-2.8 (m, 20H, the protons on the adamantyl skeleton and the methylene protons on the cyclopentyl ring), 4.50 (m, 2H, -S-CH-CH-S-) 6.29 (s, 1H, =CH-S-), 7.2-7.5 (m, 5H, the aromatic protons).

more than one signal in the 4.0-4.4 ppm region. This is the region at which the hydrogens α- to the sulfur atoms absorb. Since two absorptions were observed at 4.0 and 4.4 ppm, this oily material was not a single compound. The mixture of isomers could not be separated by preparative tlc.

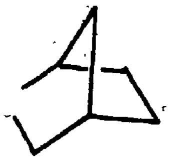
The rate of cycloaddition was slowest in the case of thiocamphor. Three days passed before the purple color of the thione disappeared. Unfortunately, the adduct decomposed as the solvent was being removed at 40° at reduced pressure. The resulting red sublimate was shown to be thiocamphor while the residue was the α,β-unsaturated thione 59.



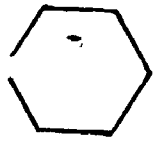
95a,b R =



96a R =

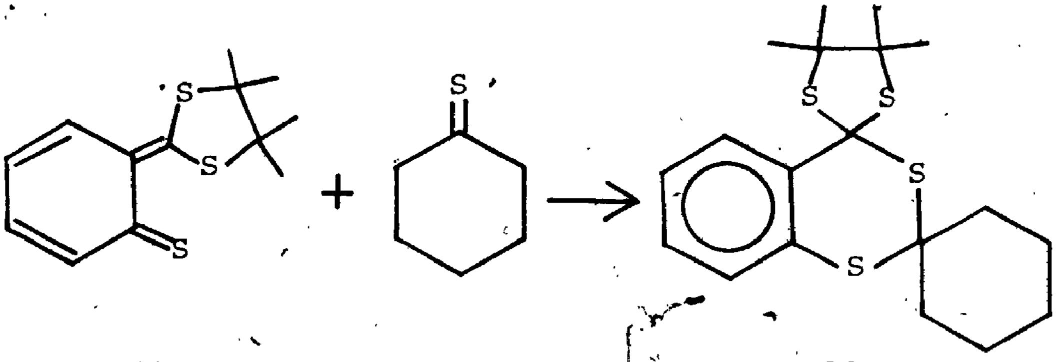


97a,b R =



B. Cycloaddition of Thioketones with 60

The thiones in this study were the same ones used with the α,β-unsaturated thione 60. Only cyclohexanethione reacted to give an adduct, 98, which was stable enough to be isolated. Repeated tlc showed that the adduct was a single compound.



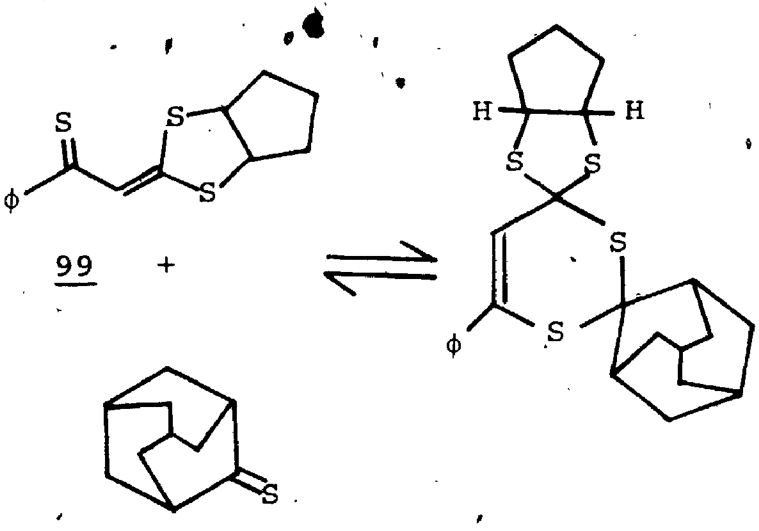
60

98

In the case of adamantanethione and 2-thionorcamphor, the products which were formed after 3 days decomposed to the starting thiones during removal of the solvent at room temperature. With thiocamphor, no cycloaddition reaction occurred, as judged by the persistence of the purple color of the thiones even after keeping the reaction mixture for 4 days in the dark.

C. The addition of 99 to adamantanethione

The reaction between the α,β-unsaturated thioketone, 99, with adamantanethione gave a mixture of 1:1 adducts 100a,b, in 25% yield. The nmr spectrum (see Table 16) of the mixture showed 14 protons at 1.6-2.3 ppm and 6 protons



99 +

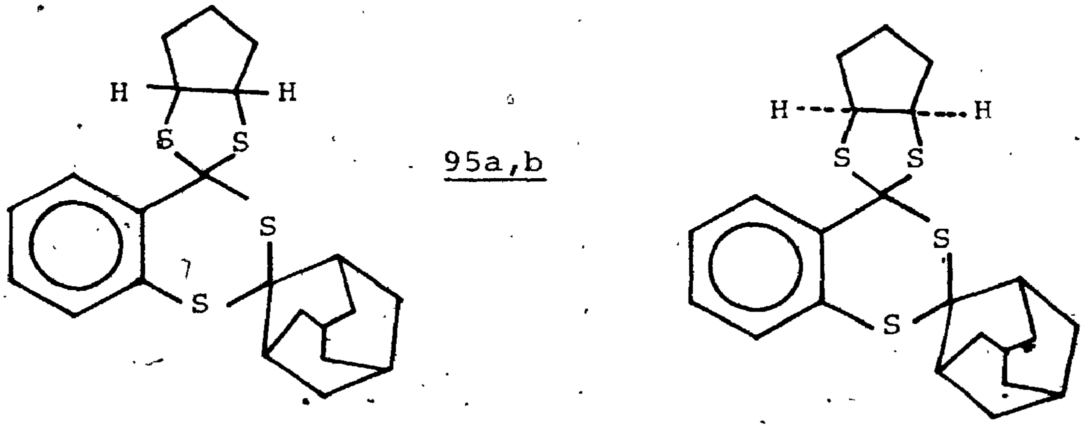
100a,b

at 2.4-2.7 ppm which account for the protons of the adamantyl and cyclopentyl skeletons, a multiplet of 2 protons at 4.5 ppm, 2 singlets of 1 vinyl proton at 6.27 and 6.29 ppm in a ratio of 1:3 and 5 aromatic protons. It was concluded that these two products were isomers similar to those of the adducts obtained from 59 and thioketones. This was based on the fact that the sum of the peaks at 6.27 and 6.29 ppm integrated to exactly one proton while the peak for the methine protons α to the sulfur atoms integrated to 2.

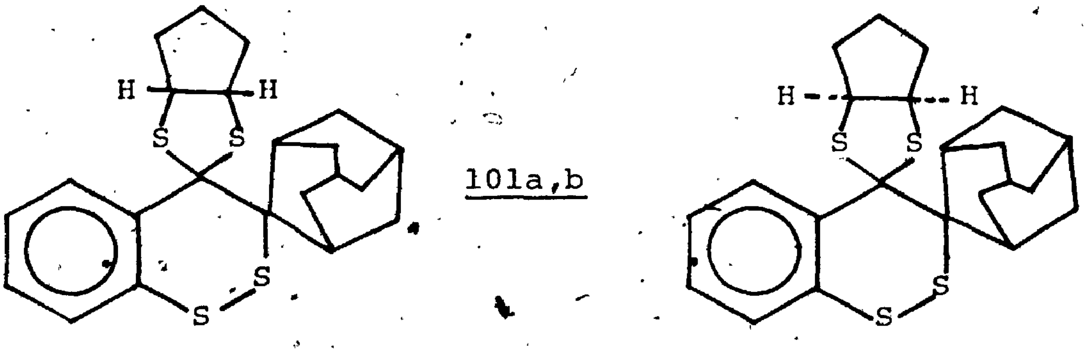
Owing to their instabilities (they decomposed quite readily in solution as well as on tlc plate), only the major product was isolated. Its nmr spectrum is shown in Table 16.

2.2 The Structure Determination of the Adducts

The structures of the adducts were deduced from their spectral data as well as from chemical transformation on adducts 95a and 95b. The adducts 95 were chosen for study because they were comparatively stable. With the structures of adducts 95a and 95b determined, the structures of the other adducts could be inferred by analogy because all the adducts had very similar nmr spectra and because their mass spectra* indicated that they were all 1:1 adducts (see Table 16). The nmr data for 95a and 95b were consistent with the view that these two compounds were either geometrical isomers 95a,b or 101a,b or structural isomers 95 and 101.



95a,b



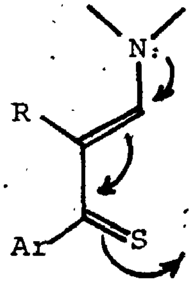
101a,b

---

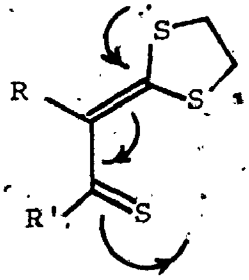
*100 did not give any molecular ion.

The possibility that these compounds were structural isomers was eliminated by the mass spectral fragmentation pattern of the two adducts (e.g. 95a and 95b). The fragmentation patterns of these two isomers were identical and this result is not expected for isomers differing in gross structures. It was also shown that the α,β-unsaturated thione, 60, reacted with cyclohexanethione to give only one product. In this case, only one geometrical isomer is possible whereas there are still two possibilities for structural isomers.

The orientation of this Diels-Alder reaction may be rationalised by a consideration of the direction of the polarity of the thione and the α,β-unsaturated thione. For a thiocarbonyl group, the polarisation is quite similar to that of a carbonyl group (114). Thus the carbon atom of the C=S group in a thioketone is electrophilic in character. On the other hand, the polarisation direction of the α,β-unsaturated thioketone (represented as 102) studied here is



90



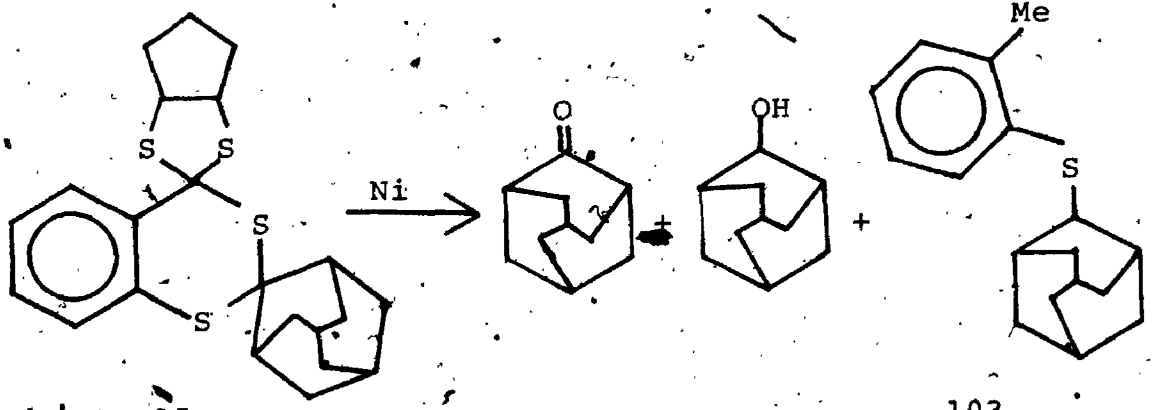
102

analogous to that of a β-amino-α,β-unsaturated thioketone 90, the lone pair electrons of the sulfur atoms in 102 being equivalent to the electrons of the amino group in 90. The polarisation of 90 in a Diels-Alder reaction has been shown by Quiniou et al (112, 113) as the direction of the arrows in structure 90 which is an expected polarisation postulated for a Diels-Alder reaction (115). On the basis of these arguments, it may be concluded that the adduct has a 1,3-dithiane rather than a disulfide structure, 101.

Unfortunately, it is a known fact that substituents in the dienophile or diene may change the course of addition. It has been shown that the orientation of the addition of 9-substituted anthracenes is dependent upon the nature of these substituents (116-119). Valenta and his coworkers have also shown that the percentage of the two possible isomers derived from the addition of olefins to p-quinones may be altered when catalyst is introduced (120). With this complication, the previous assignment of the mode of addition becomes uncertain.

The distinction between the two structure types was made on the basis of chemical transformations. The adduct 95 was found to be stable to the action of lithium aluminium hydride reduction in refluxing 1,4-dioxane for 4 days. Normally, under these conditions a disulfide would have been reduced to the corresponding thiol (121). This suggested that the disulfide structure was incorrect. A positive structure proof was achieved by Raney nickel reduction and by the hydrolysis of the 1,3-dithiane linkage by mercuric oxide. The Raney nickel (W_3) reduction of 95 gave 2-adamantanone and 2-adamantanol in 17 and 21% yield respectively. These two products were identified by comparison of melting points and spectral data with those of authentic samples.

In addition to adamantanone and 2-adamantanol, a small amount of o-tolyl-2-adamantyl sulfide, 103, was also obtained in about 1% yield. The structure of 103 was not rigorously proven. The identity of 103 with o-tolyl-2-adamantyl sulfide was suggested by a comparison of the nmr and mass spectral data as well as the Rf value with those of an authentic sample which was prepared by heating 2-bromoadamantane with o-methyl-thiophenol in the presence of potassium hydroxide. 103 showed an molecular ion at m/e= 258. The nmr spectrum, apart from the peaks for the aromatic and adamantyl protons, showed a singlet at 2.4 ppm and a multiplet at 3.4 ppm. The former peak could be accounted as the methyl protons of the tolyl group and that of the latter was the proton α- to the sulfur atom. These

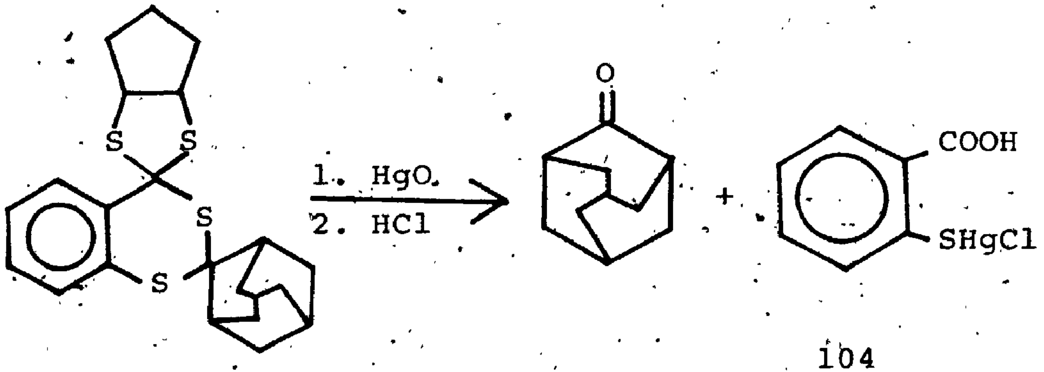


95 103

two peaks were superimposable on the equivalent peaks of an authentic sample.

The formation of 103 was unusual. However, it has been shown that a sulfur atom attached to an aromatic ring is more resistant towards desulfurisation than a sulfur atom attached to an aliphatic carbon atom (see Part 1). Since 103 was obtained impure and in very low yield, a proper identification was not possible and an alternative proof of structure was sought.

When 95 was stirred with mercuric oxide in the presence of boron trifluoride at $0^{\circ}C$, two compounds were formed. The first compound obtained by extraction with ether was adamantanone in 50% yield. It was identified by a comparison of its melting point as well as its 2,4-dinitrophenylhydrazone with those of authentic specimens. The second, highly insoluble and acidic, compound was o-mercaptobenzoic acid which was isolated as the mercaptide chloride 104 in 50% yield.



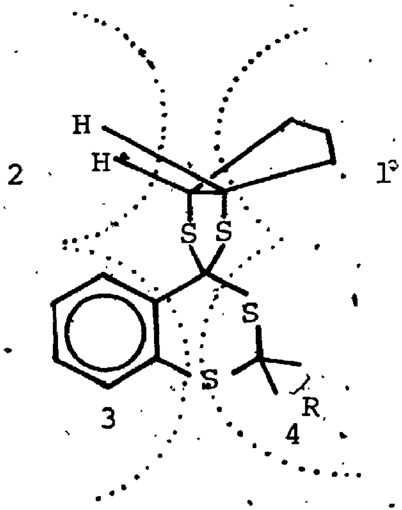
104

The structure of the mercaptide chloride 104 was established from its physical data and ir spectrum. The ir spectrum of 104 showed bands at 3400 and 1680 cm^{-1}, indicating the presence of an aromatic acid (122); a sharp band for a four contiguous aromatic hydrogens out-of-plane bending at 745 cm^{-1} (123) was also seen. The absence of an absorption at a region 1610-1550 cm^{-1} excluded the possibility of an anion of a carboxylic group in the molecule (124). The structure of 104 was confirmed by comparison of the Rf value and m.p. with those of an authentic sample synthesised by a different route using o-mercaptobenzoic acid and mercuric chloride (125). The ir spectra of the two sample were superimposable.

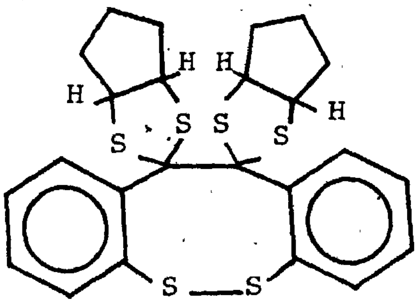
The formation of the o-mercaptobenzoic acid derivative from the hydrolysis of 95 may be viewed in the following way. The two 1,3-dithiane linkages in 95 were hydrolysed in a manner typical of a 1,3-dithiane to give the thiolacid derivative (-COS-) subsequently hydrolysed in the presence of hydrochloric acid to give the carboxylic acid derivative, viz 104. The alternative structure would not give the products obtained and, moreover, mercuric compounds do not cleave a disulfide bond (126). An alternative rationalisation could be that the adduct decomposed to 59 and adamantanethione and that the hydrolysis products were derived from these. The adduct is however thermally stable under these condition except for the isomerisation (see below), and we have shown that the isomerisation does not involve dissociation. Hence we concluded that the hydrolysis results are valid evidence for the presence of a 1,3-dithiane.

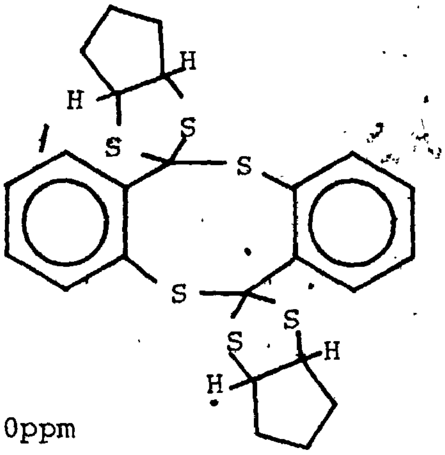
2.3 The Stereochemistry of the Isomers

It has been pointed out that the adducts obtained from the Diels-Alder reaction with 59 were pairs of isomers. In this, the cyclopentyl adduct series, the four groups attached to the 1,3-dithiolane ring were different and so syn and anti isomer are possible: namely, the methylene protons of the cyclopentyl ring; the two methine hydrogens; the phenyl ring; and the sulfide group. These are represented as groups 1,2,3 and 4 in the following representation. Two isomers are possible. With adduct 96, 4 isomers are possible since there is an additional centre of asymmetry.



The dimeric form of 59 showed the methine protons absorption at 3.95 and 4.40 ppm (see Part 2). This observation was rationalised since there were two different stereo environments for the methine protons: syn or anti to the nearby phenyl ring. This is exactly the same situation as obtained in the cycloadduct of the cyclopentyl series. On the other hand, the two geometrical isomers of 100 did not show different absorptions for the two sets of methines in the two isomers both being at 4.5 ppm: i.e. the chemical shift of the methine protons in 100 was the same no matter on which side of the molecule the protons might be. The upfield shift of the methine protons in one isomer of 95 (97) must be due, therefore, to the aromatic ring and can only occur in the syn isomer. Thus the anti isomer was assigned to the a-series (δ=4.4 ppm) and the syn to the b-series (δ= 4.0 ppm).



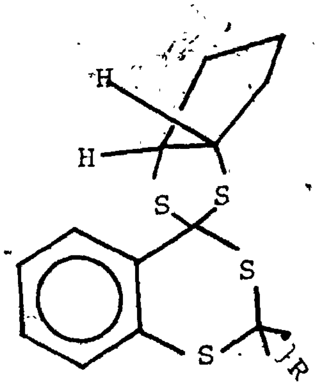


Dimer of 59

δ=3.95 and 4.40ppm

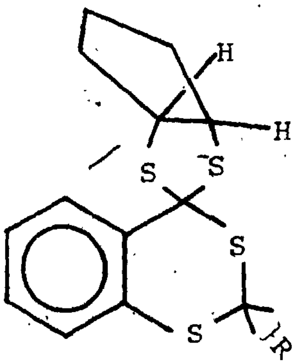
(3 isomers possible)

(3 isomers possible)



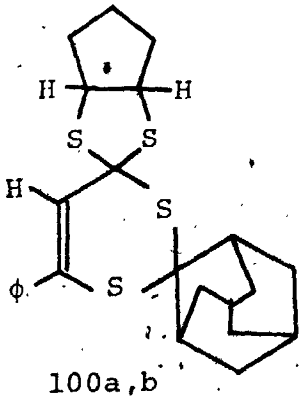
95b (97b)

δ=4.0 ppm



95a (96a, 97a)

δ=4.4 ppm



100a,b

δ=4.5 ppm

Fig. 20 Assignment of isomers with chemical shifts of the methine protons shown

CHAPTER 3

ISOMERISATION OF THE GEOMETRICAL ISOMERS

3.1 Isomerisation of 95 in Deuterated Chloroform

It was found that the nmr spectrum of a pure adduct derived from the α,β-unsaturated thioketone 59 changed with time. A freshly prepared solution of adduct 95a in deuterated chloroform gave only methine proton absorption at δ=4.4 ppm. When the spectrum of the same solution was taken 12 hours later, it showed a new absorption peak at 4.0 ppm in addition to the one at 4.4 ppm. This observation was accounted for by the isomerisation of 95a to 95b since both 95a and 95b were isolated from this solution.

It was desired to study the isomerisation in more detail by recording the change with time. Pure adducts 95a and 95b (about 0.1 M in deuterated chloroform) were used as starting materials. The isomerisation was monitored at 32° by the increase in the methine protons absorption due to the newly formed isomer and the decrease in the absorption due to the original isomer. The change was followed until no more change was seen (see Fig. 21, 22). The ratio of the two isomers at different periods of time was measured by integration of the two peaks at 4.0 and 4.4 ppm and the results are listed in Tables 17 and 18. It was shown that the ratio of the two isomers after 40 hours was ~1 in both

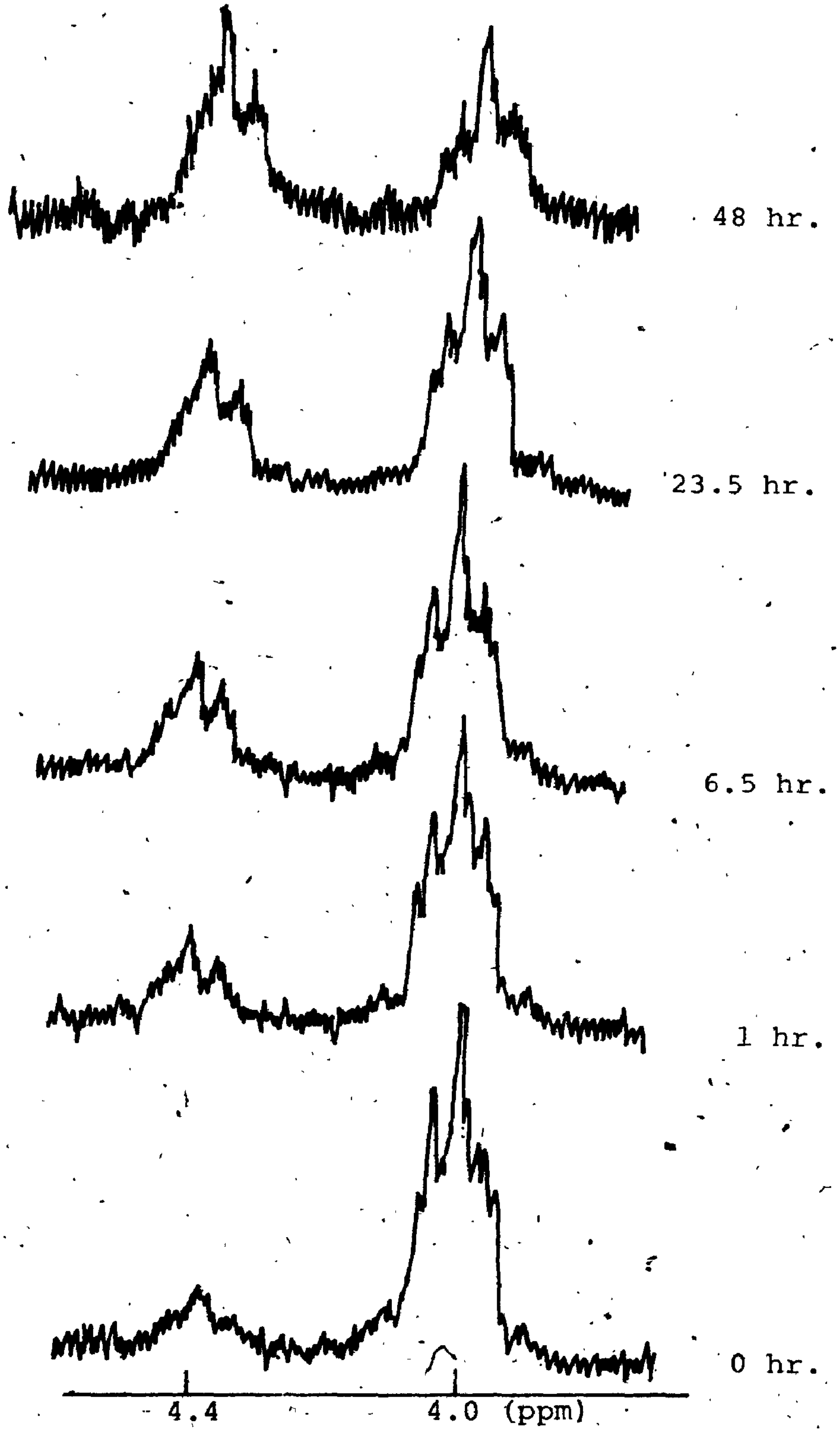


Figure 21. Time dependent nmr spectra of 95b in $CDCl_3$.

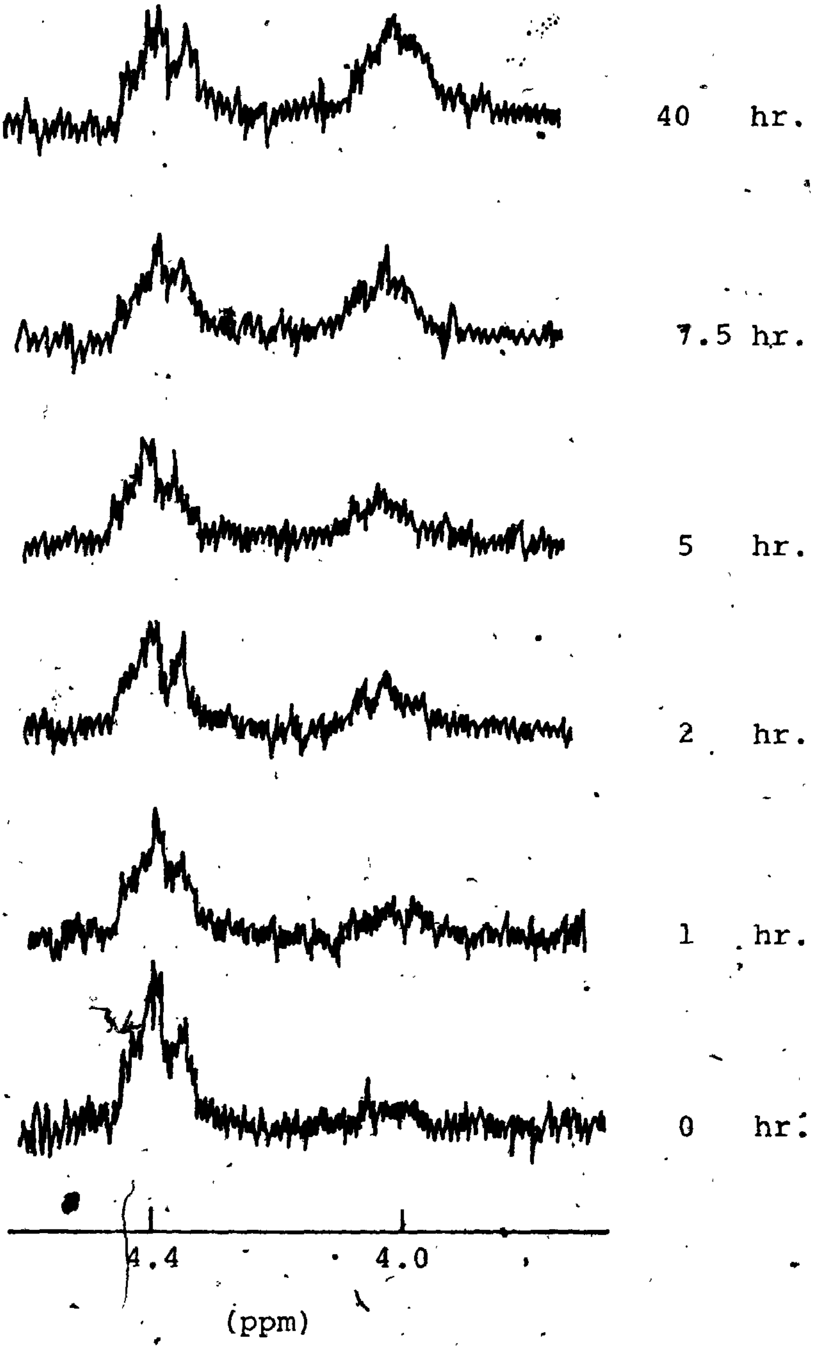


Figure 22. Time dependent nmr spectra of <u>95a</u> in $CDCl_3$.

TABLE 17

Isomerization of 95a to 95b in Deuterated Chloroform

Time (min.)	$\frac{[\underline{95a}]}{[\underline{95a}]+[\underline{95b}]}$
20	0.89
80	0.75
155	0.66
265	0.62
395	0.60
1400	0.51
2800	0.50

TABLE 18

Isomerisation of 95b to 95a in Deuterated Chloroform

Time (min.)	$\frac{[95b]}{[95b]+[95a]}$
20	0.88
155	0.81
265	0.73
395	0.69
1400	0.52
2800	0.50

cases*.

3.2 Isomerisation of 95 in Benzene

The same isomerisation of 95a to 95b could also be achieved in benzene at 80° (see Fig. 23). The results are shown in table 19. It was noted that isomerisation occurred at a much slower rate and required a higher temperature.

3.3 Solvent Effect on the Isomerisation of 96

The isomerisation of 96a to the other isomer was followed in carbon tetrachloride as well as in a mixture of methylene chloride-d_2-acetonitrile-d_3 in the ratio of 2:1 at 40°C. It was found that isomerisation took place with 20% conversion after 48 hours. Under the same conditions, 96a did not undergo isomerisation in carbon tetrachloride after 4 days. This finding indicated that the isomerisation was solvent dependent. Since a more polar solvent favored the isomerisation, it suggested that the intermediate was polar in character.

3.4 Acid Catalysed isomerisation of 97a to 97b

The large difference in the rate of isomerisation of

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*This value was different from that obtained in benzene during the preparation of 95. Here the ratio was about 3. However, as will be seen later, the adduct formation was kinetically controlled and the equilibration was very slow. The ratio of 1:1 for the two isomers reflected stability.

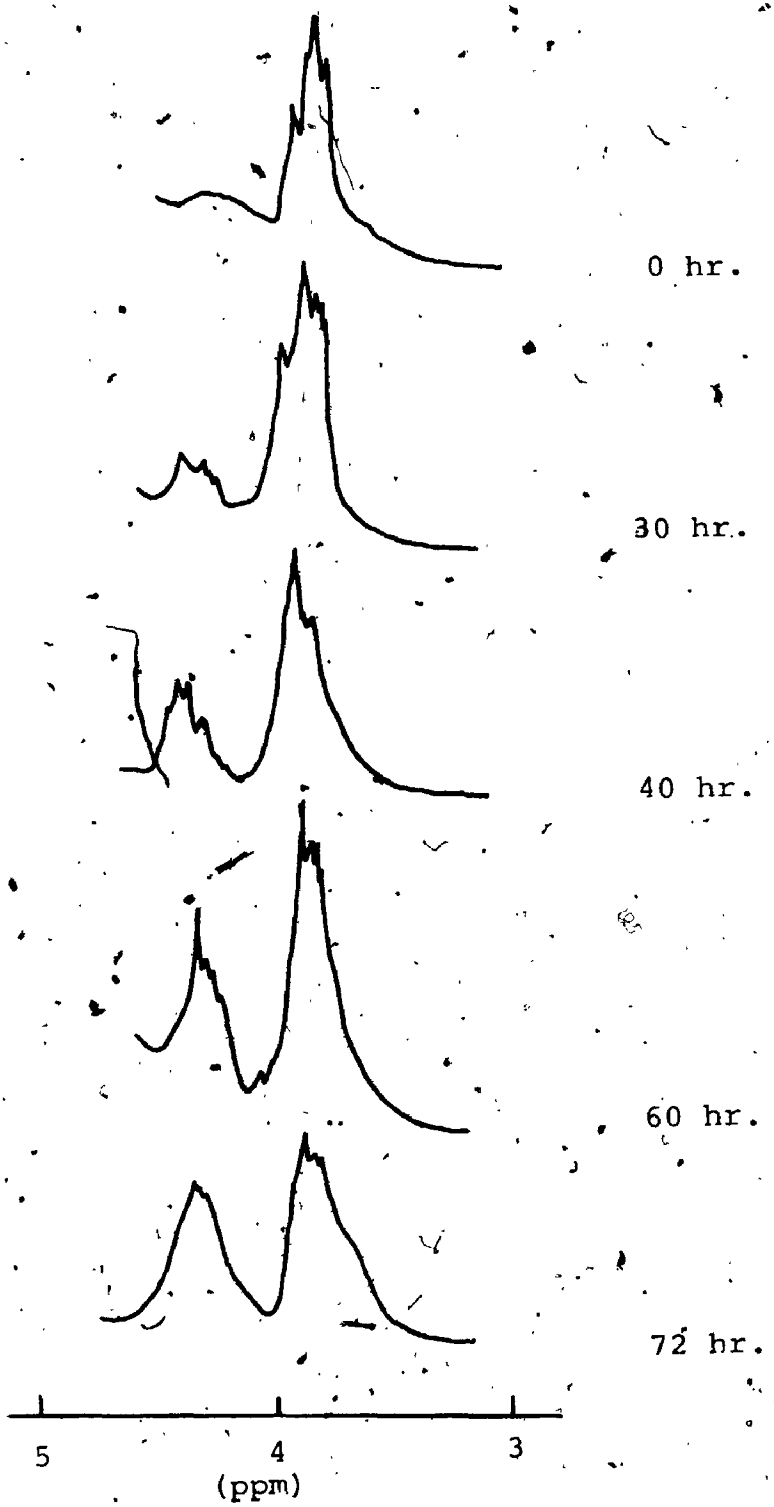

Figure 23. Time dependent nmr of 95b in benzene

TABLE 19

Isomerisation of 95b to 95a in Benzene at 80°C

Time (hour)	$\frac{[95b]}{[95a]+[95b]}$
0.133	0.95
2	0.94
24	0.80
30	0.75
40	0.60
60	0.55
72	0.55

95 in benzene and chloroform suggested that a trace of acid, frequently present in the latter solvent, might have been responsible. To verify this point, a carbon tetrachloride solution of adducts 97a and 97b in a ratio of 4:1* was prepared and acidified with dry hydrogen chloride gas just prior to the nmr measurement. The study was carried out at 32°C and the change in the ratio of the two isomers was measured in the usual way (see Fig. 24). The results are shown in Table 20. The change in the ratio of the two isomers with time is shown in Fig. 25. In the absence of hydrogen chloride, the isomerisation did not occur. The results showed clearly that isomerisation was indeed acid catalysed.

The mechanism of the interconversion could be postulated as being (A), a retrogression of the adduct to the two starting thiones, which could then recombine to give either isomer, or (B), a breaking of one C-S bond of the thioorthoester group, and subsequent recombination to give either isomers after bond rotation.

Since the adduct formation was thermally reversible, it was thought that the isomerisation might be a dissociation process. In this mechanism, represented by Scheme 8, breakage of two bonds is required to form the starting materials. The resulting thiones, which might be kept in a

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*It was difficult to obtained a pure sample and it was not absolutely necessary for this study. The ratio was determined by integrating the two methine protons' peaks.

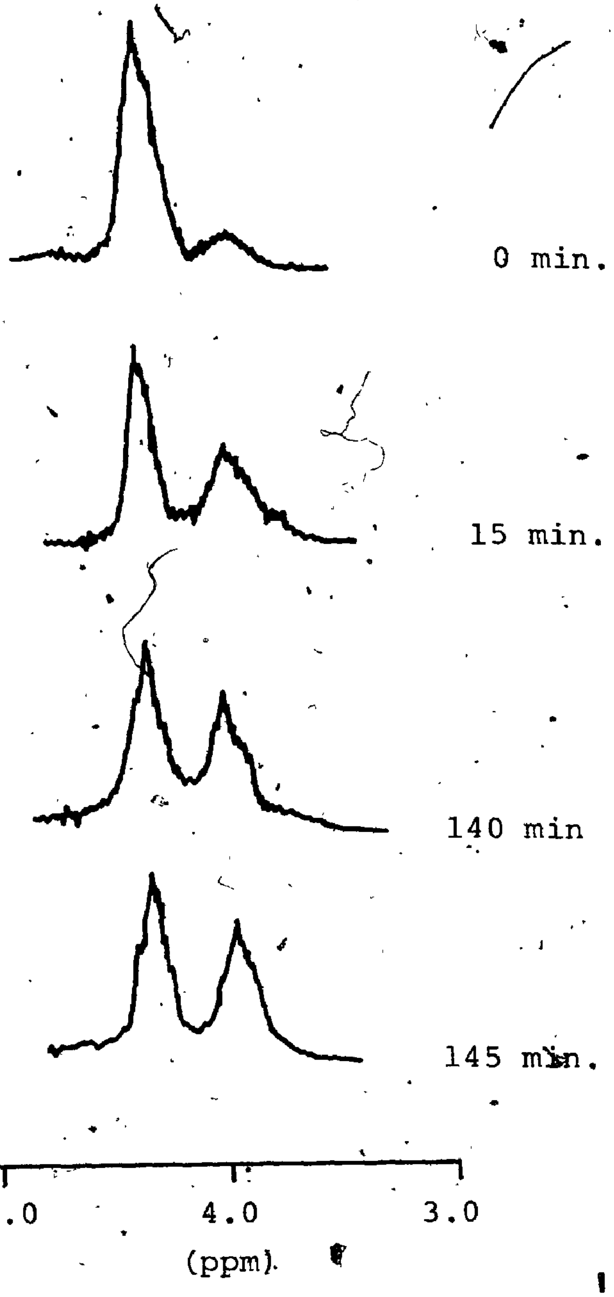


Figure 24. The isomerisation of 97a in HCl/ CCl_4.

TABLE 20

Acid Catalysed Isomerisation of 97a to 97b in Carbon Tetrachloride

Time (min.)	$\frac{[\underline{97a}]}{[\underline{97a}]+[\underline{97b}]}$
0.	0.800
15	0.660
40	0.615
140	0.590
270	0.585
600	0.580
1400	0.570
3480	0.570

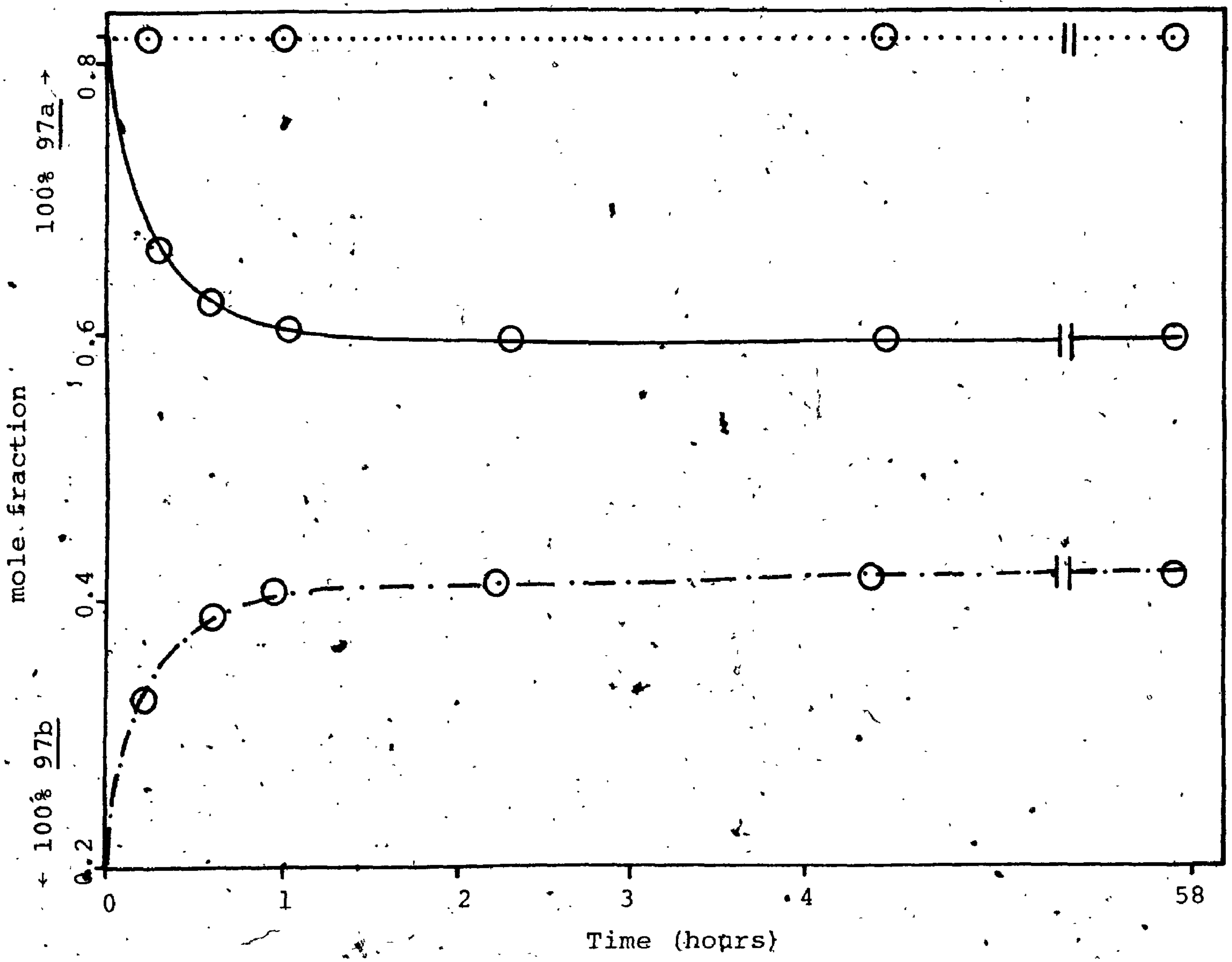
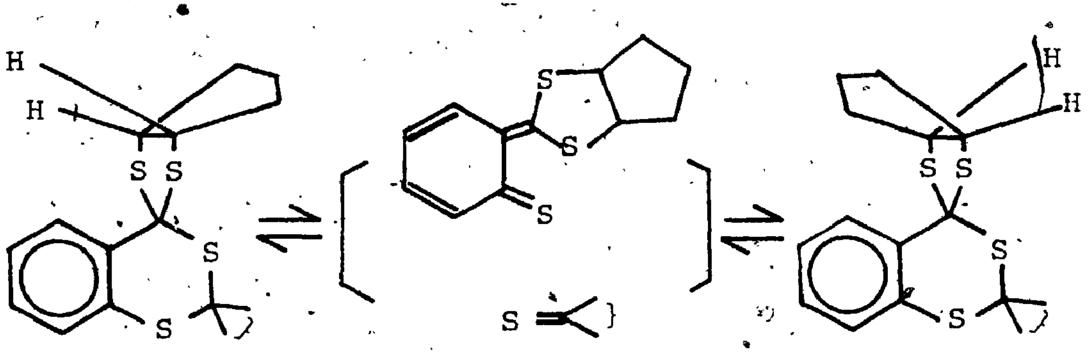


Figure 25. The isomerisation of 97a in CCl_4; ········ 97a in CCl_4; ——— 97a in CCl_4/HCl; —·—· 97b in CCl_4/HCl.

solvent cage, may recombine rapidly to form both isomers. The mechanism resembles that for the interconversion of the

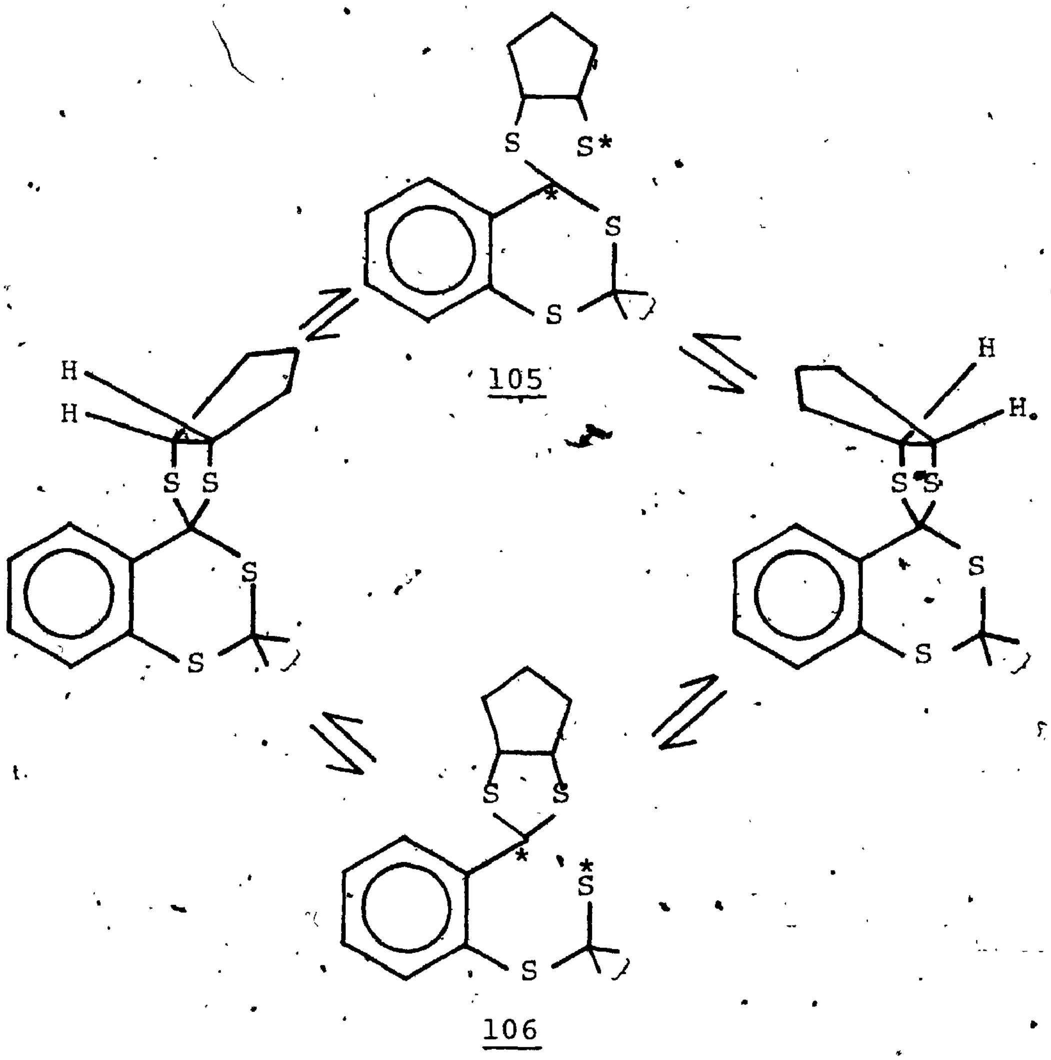


Scheme 8

endo to exo isomer in the Diels-Alder reaction involving cyclopentadiene and N-phenyl-maleimide. This reaction mechanism has been discussed in detail by Berson and his coworkers (127).

The isomersation of the adduct could be achieved, in principle, by only breaking one of the thioorthoester bonds. This is shown in Scheme 9. The breaking of one of the C-S bonds leads to an intermediate 105 or 106. The re-formation of the C-S bond may occur after bond rotation to give either isomer.

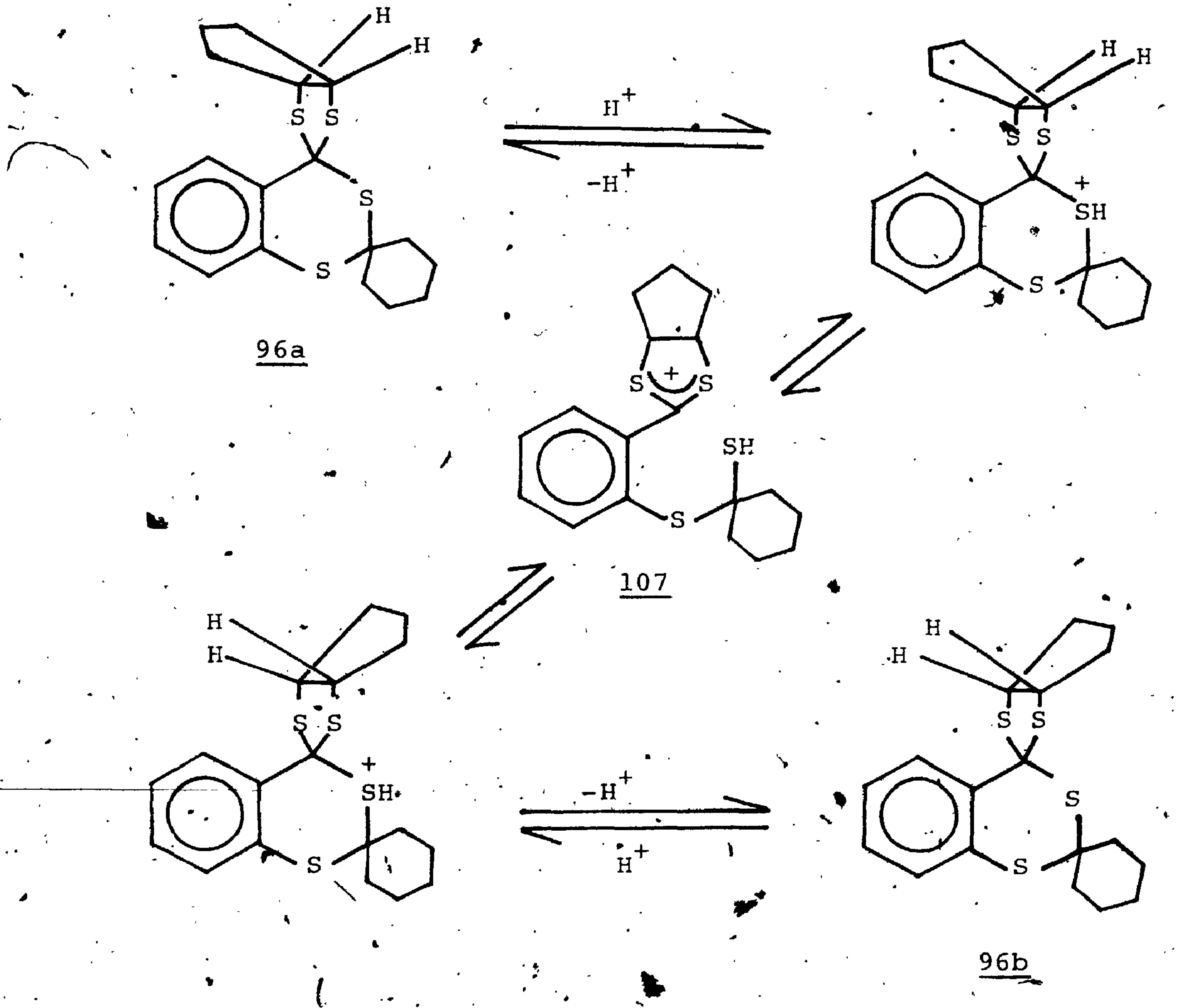
A distinction between the two possibilities was made as follows. The isomerisation of 96 in benzene at 80° was carried out in the presence of thionorcamphor-$\alpha\alpha d_2$. The adduct which was isolated contained no deuterium, as determined by mass spectrometry, and hence it could be



Scheme 9

concluded there had been no exchange between the labelled and unlabelled thionorcamphor. Similarly, isomerisation of 96a in the presence of the powerful dienophile, N-phenyl maleimide, both in benzene and chloroform solution, did not lead to the formation of 61.

The observed results involving the isomerisation are consistent with the one-bond-breaking mechanism. Since the isomerisation is acid catalysed, it may be concluded that the isomerisation involves an ionic intermediate and not a radical. It has been pointed out that an alkyl thio group in a compound having more than one S-alkyl group attached to the same carbon atom, a thioorthoester for instance, can act as both an electron donor and an acceptor. In the presence of acid, the thioorthoester may react with a proton to form a sulfonium ion, 107, in which bond rotation may occur and lead to isomerisation (see Scheme 10).



Scheme 10

Since the isomerisation is acid catalysed, it should not occur in benzene. The actually observed slow isomerisation in benzene may be attributed to the presence of a trace amount of acid on the glass ware.

EXPERIMENTAL

CHEMICAL

Norcamphor (Pfaltz and Bauer), camphor (Eastman) and adamantanone (Aldrich) were used without purification. Cyclohexanone was distilled once. All the deuterated solvents (acetonitrile-d_3, methylene dichloride-d_2, chloroform-d_1 and methanol-d_1) were supplied by Merck Sharp and Dohme and were used as received. Boron trifluoride etherate was purified according to Fieser (128).

Preparation of 5-Phenyl-1,2-dithiole-3-thione

The title thione was prepared according to Klingsberg (24). Ethyl cinnamate (30 ml) was heated to the boil in a 500 ml wide mouth Erlenmeyer flask and sulfur (9 gm) was added to the boiling liquid. The sulfur dissolved readily and the mixture was boiled gently for 1 hour, cooled, diluted with 12 ml of ethanol, chilled thoroughly, and filtered. The resulting light brown solid was recrystallised from ethanol to give 5-phenyl-1,2-dithiole-3-thione, m.p. 114-6° (Lit. 114-7°) (24).

A solution of 5-phenyl-1,2-dithiole-3-one (12 gm) and phosphorus pentasulfide (18 gm) in pyridine (120 ml) was refluxed for 4 hours, cooled partially, diluted with 150 ml of water, chilled and filtered. The brown crude product was recrystallised from n-hexane to give orange crystals of thione in 70% yield (9.0 gm), m.p. 125-7^{o} (Lit. 125-7^{o}); nmr (CDCl$_3$) 7.4 (s, 1H), 7.4-7.8 (m, 5H); mass spectrum m/e 210.

Preparation of 2-Thiobenzoylmethylene-1,3-dithiolane, 99

The dithiolane was prepared according to the method of Okazaki and coworkers (17). A solution of 5-phenyl-1,2-dithiole-3-thione (150 mg) and cyclopentene (1 ml) in benzene (20 ml) was saturated with nitrogen and irradiated in a Rayonet reactor at 254 nm for 4 hours. The solvent was evaporated and the residue was subjected to preparative tlc using benzene as eluent. A green band was collected to give 100 mg 99 (55% yield). This was recrystallised from a solvent mixture of methanol-methylene chloride to give dark green crystals m.p. 123-4^{o} (Lit. 122-3^{o}); nmr (CDCl$_3$) 2.20 (m, 6H), 4.04-4.5 (m, 2H), 7.3-7.8 (m, 5H), 7.9 (s, 1H); mass spectrum m/e 278.

Preparation of Adamantanethione and Thionorcamphor

Adamantanethione was prepared according to the method of Greidanus (129). A solution of adamantanone (2.5 gm) and phosphorus pentasulfide (0.9 gm) in dry pyridine (15 ml) was stirred at 90^{o} for 12 hours. The reaction mixture was taken up in 50 ml petroleum ether (40-60) and was washed with two 50 ml portions of 2N hydrochloric acid followed by two 50 ml portion of water. The organic phase was dried over magnesium sulfate and was then stripped of solvent on a rotary evaporator. The residue thus obtained was chromatographed on silica gel (40 gm) using petroleum ether (30-60) as eluent. The orange-red fractions were collected to give 1.5 gm of adamantanethione (50%) after removal of solvent and sublimation of the resulting solid (70°/0.5 mm Hg).

Thionorcamphor was prepared in the same manner as that for the preparation of adamandanethione. The final product was distilled at 55-60°/0.02 mm Hg in 38% yield, mass spectrum m/e 126.

Calcd. for $C_7H_{10}S$: 126.0503. Found: 126.0509.

Preparation of Cyclohexanethione

Cyclohexanethione was prepared according to Sen (130). A solution of cyclohexanone (10 gm) in absolute alcohol (20 ml) was treated with a current of dry hydrogen chloride and dry hydrogen sulfide. The solution slowly changed to deep red after 20 minutes. The emulsion was treated with ice-cold water and extracted with ether. The etheral solution was washed with water and sodium bicarbonate solution, and was dried over sodium sulfate. After the removal of the solvent the red thione was distilled at 40-4°/15 mm Hg (Lit. 46°/15 mm Hg). The yield was about 0.5 gm.

Preparation of Thiocamphor

Thiocamphor was prepared according to Sen (131). A solution of camphor in absolute alcohol (20 ml) was treated with dry hydrogen chloride and hydrogen sulfide for 1 hour. It was extracted with ether and washed with a sodium bicarbonate solution, then water and was dried. The ether was evaporated and the residue was chromatographed to gave 2.6 gm thiocamphor, m.p. 144-5° (Lit. 145-6°).

Preparation of 2-Adamantanol

2-Adamantanol was prepared by the reduction of adamantanone in the presence of lithium aluminum hydride. It was recrystallised from methanol to give white crystals, m.p. 260-2°, nmr ($CDCl_3$) an exchangeable proton at 3.85, mass spectrum m/e 152.

Preparation of Thiosalicyclic Acid Mercuric Chloride, 104

The chloride was prepared according to Sachs and Bless (125). To a solution of thiosalicyclic acid (154 mg) in absolute alcohol (10 ml) mercuric chloride (275 mg) was added. The white precipitate, 104, (420 mg, 99% yield) was collected and washed 3 times with alcohol. It had a melting point 270° (sublimed); ir (KBr) 3400 (b), 1680 (s), 1470, 1422, 1300, 1270 and 745 cm^{-1}.

Preparation of Deuterated Thio-norcamphor

Sodium metal (0.5 gm) was added to a solution of methanol-d_1 (10 gm) and was stirred until all the metal had disappeared. Norcamphor (1 gm) was added to the solution which was then refluxed for 24 hours. Deuterated water (2 ml) was then added and the mixture was extracted with ether. The etheral layer was dried. The residue, after the removal of solvent, was converted to the corresponding thioketone by reacting it with phosphorus pentasulfide to give deuterated thionorcamphor (0.51 gm). The deuterium content was determined mass spectrometrically. The ratio of the non-: mono-: dideuterated thioketone was 1.1:1.0:1.9.

The Reaction of Thioketones and α,β-Unsaturated Thioketones, 59, 60 and 99

A typical example was the addition of adamantanethione to 59.

A solution of 59 (420 mg; 1.67 m. mole) and adamantanethione (320 mg; 2.0 m. mole) in benzene (20 ml) was kept in the dark at room temperature for 24 hours. The solvent was evaporated and the residue was separated using preparative tlc with petroleum (60-80)-methylene chloride (1:1) as eluent. The adduct thus obtained usually contained two isomers which could be further separated by another preparative tlc using cyclohexane as eluent (4 cycles) to give 2 products.

The compound (with a larger Rf value), 95a, was obtained as a white solid (280 mg; 51% yield). It was recrystallised from ethyl acetate with a resulting m.p. 188-9°; nmr (freshly prepared) ($CDCl_3$) see Table 16; uv

(CH_2Cl_2) $\lambda_{max.}$ 298 (s) nm (ε=1500); mass spectrum 418, 252, 184, 166, 91 and 67.

Anal. calcd. for $C_{22}H_{26}S_4$: C, 63.15; H, 6.26; S, 30.59.
Found: C, 63.10; H, 6.18; S, 30.33.

The slower compound (with a smaller Rf value), 95b, was also obtained as a white solid in 22% yield (109 mg). It was recrystallized from ethyl acetate with a resulting m.p. 145-6°, nmr (freshly prepared) ($CDCl_3$) see Table 16; $\lambda_{max.}$ 275 nm (ε=2500); mass spectrum m/e 418, 252, 184, 166, 91 and 67.

Anal. calcd. for $C_{22}H_{26}S_4$: C, 63.15; H, 6.26; S, 30.59.
Found: C, 63.64; H, 6.41; S, 30.19.

Raney Nickel Desulfurization of 95

A mixture of 95 (200 mg) and active Raney nickel (5 gm) in alcohol (20 ml) was refluxed for 16 hours. It was found that under these condition, no isomerization had occurred. The reaction product was distilled (sublimed) at 150°/0.1 mm Hg. The sublimate was separated into 3 compounds by preparative tlc using a mixture of ether-methylene chloride (1:20) as eluent.

The first compound (highest Rf value) which is a low melting solid was obtained impure (1 mg). Nmr (CCl_4) 1.6-2.2, 2.4 (s), 3.4 and 7.0; mass sp[illegible]rum: m/e (%) 258 (10%), 135 (100) 134 (45), 91 (60).

The second compound was adamantanone in 17% yield m.p. 259-60°. The mixed melting point showed no depression.

The nmr and ir spectra of this product and that of an authentic sample were identical.

The third compound was 2-adamantanol in 21% yield m.p. and mixed point 260-3°. The nmr and mass spectra of this product and that of an authentic sample were identical.

Reaction between 59 and Thionorcamphor

The faster compound 96a, was obtained in 63.5% (132 mg from 120 mg of 59) yield. It was crystallized from ethyl acetate to give white crystals, m.p. 143-5°; nmr ($CDCl_3$) (freshly prepared) see Table 16. When the solution was left overnight, a new peak at 4.02 appeared while the peak at 4.40 decreased in intensity. The ratio of these two peaks (4.4/4.0) was about 1/3; uv (CH_2Cl_2) $\lambda_{max.}$ 300 (s) nm (ε=1200); mass spectrum m/e 378, 252, 184, 126 and 67. Anal. calcd. for $C_{19}H_{22}S_4$: C, 60.31; H, 5.86. Found: C, 60.41; H, 6.10.

The slower compound was an oil in 20% (42 mg) yield which could not be induced to crystallise. Nmr spectrum of the oil showed absorption at 4.0 ppm and 4.4 ppm. It might have contained two or more isomers. No further efforts were made to separate these isomers.

Reaction between 59 and Cyclohexanethione

The faster compound, 97a, was obtained in 64% yield (79 mg from 92 mg of 59) m.p. 106-8°; nmr (freshly prepared) ($CDCl_3$) see Table 16; uv (CH_2Cl_2) $\lambda_{max.}$ 296 (s) nm (ε=2750);

mass spectrum m/e (%) 366 (9), 332 (2), 252 (20), 184 (100), 120 (35), 114 (25) and 67 (35).

Anal. calcd. for $C_{18}H_{22}S_4$: C, 59.01; H, 6.05; S, 34.94.
Found: C, 59.45; H, 5.74; S, 35.08.

The slower compound, 97b, was obtained in 25% yield (31 mg), melting point, 143-5°; nmr (freshly prepared) see Table 16; uv (CH_2Cl_2) $\lambda_{max.}$ 270 (s) nm (ε=4000); mass spectrum m/e (%) 366 (10), 332 (2), 252 (25), 184 (100), 120 (35), 114 (23) and 67 (35).

Anal. calcd. for $C_{18}H_{22}S_4$: C, 59.01; H, 6.05; S, 34.94.
Found: c, 59.21; H, 6.01; S, 35.02.

Reaction between 59 and Thiocamphor

Three days passed before the blue color of 59 disappeared. When the solvent was being removed by a rotary evaporation at about 35°, some orange solid sublimed which might be thiocamphor. The residue gave a blue solution when methylene chloride was added and tlc showed the return of 59. No attempt was made to isolate a product from the residue.

Reaction between 60 and Cyclohexanethione

This gave the 1:1 adduct 98 in 88% yield (250 mg from 200 mg of 60). Tlc showed the presence of only one compound which was crystallized from ethyl acetate to give needle-like crystals, m.p. 142-4°; nmr (CCl_4) see Table 16.

Uv (CH_2Cl_2) $\lambda_{max.}$ 270 (s) nm (ε=2000); mass spectrum m/e 382, 392, 268 and 184.

Anal. calcd. for $C_{19}H_{26}S_4$: C, 59.67; H, 6.85; S, 33.47. Found: C, 60.20; H, 7.01; S, 33.08.

Reaction of 60 with Adamantanethione, Thionorcamphor and Thiocamphor

With adamantanethione and thionorcamphor, the reactions took 3 days to achieve completion as judged by the disappearance of the blue color of 60. On evaporation of the solvent at 35°, reversion to the starting materials occurred. With thiocamphor, there was no reaction.

Reaction between 99 and Adamantanethione

This gave two isomers 100a and 100b in about 25% yield (10 mg from 28 mg of 99). The nmr spectrum showed the presence of the 2 isomers in a ratio of 3:1 (100a:100b) (two singlets at 6.27 and 6.29 in chloroform). One of the isomers (100a) was separated using preparative tlc whereupon the compound decomposed partially. It was crystallised from ethyl acetate to give a white solid, the 1:1 adduct, m.p. 136-8°; nmr (CCl_4) 1.6-2.1 (m, 14H), 2.4-2.8 (m, 6H), 4.5 (m, 2H), 6.29 (s, 1H), 7.2-7.5 (m, 5H); uv (CH_2Cl_2) $\lambda_{max.}$ 298 nm (ε=300); mass spectrum m/e (%) 278 (6), 210 (80), 166 (100), 145 (60), 91 (45), 77 (20) and 67 (25).

Anal. calcd. for $C_{24}H_{28}S_4$: C, 64.85; H, 6.35. Found: C, 64.99, H, 6.35.

When a solution of 100a was kept overnight in methylene chloride the solution turned green, the uv absorption spectrum of this solution being identical with that of 99. Compound 99 did not react with thiocamphor or thionorcamphor.

Hydrolysis of 95 with Mercuric Oxide

A cooled solution ($0^{o}C$) of 95 (20 mg) in tetrahydrofuran (5 ml) was added to a stirred solution of red mercuric oxide (2 mole equivalent), boron trifluoride etherate, (2 mole equivalent) in 15% aqueous tetrahydrofuran (15 ml). After 30 minutes, diethyl ether was added and the precipitate was filtered.

The filtrate was washed to neutrality with saturated sodium carbonate and sodium chloride solutions. It was dried and the solvent was removed. The residue, which showed only one spot on tlc, was sublimed to give adamantanone with a m.p. 258-9°, in 50% yield (3 mg). The sublimate gave a 2,4-dinitrophenylhydrazone derivative which had a m.p. and mixed m.p. 219-220° [Lit. 221-221.5°(132)].

The precipitate obtained originally from the reaction was collected and was stirred with concentrated hydrochloric acid for 3 hours at room temperature. The white solid (10 mg) was collected and washed with water, This compound was soluble in a potassium carbonate solution. It had a same Rf value as that of thiosalicyclic acid mercaptide chloride. The value was 0.67 on an Eastman 6060 silica gel chromagram sheet using a mixture of isopropanol, triethylamine, water (2:1:1) as developer. The melting point determined in a sealed capilary tube was 270° (sublimed). Ir (KBr) 3400 (b), 1680 (vs), 1470, 1422, 1300, 1270 and 745 cm^{-1}.

Attempted reduction of 95 by lithium aluminium hydride

A solution of 95 (20 mg) in dioxane (1 ml) was added to a solution of lithium aluminium hydride (10 mg) in dioxane (10 ml), and the mixture was stirred at 80° for 4 days. Tlc showed that no reaction had occurred.

Isomerisation of 95a and 95b

(1) A solution of 95a (12 mg) in deuterated chloroform (0.3 ml) was introduced into an nmr tube. The nmr spectrum was taken at intervals. At the end of 48 hours, it was found that both isomers 95a and 95b were present in a 1:1 ratio. The results are shown in Table 17, and Fig. 21.

(2) The isomerization of 95b to 95a in deuterated chloroform was carried out in the same way as above. The result are shown in Table 18 and Fig. 22.

(3) Isomerization of 95b to 95a in benzene was carried out in a sealed nmr tube at 80°. The results are shown in Table 19 and Fig. 23.

Isomerisation of 96 at 40°

The nmr spectra of 96 were measured in carbon tetrachloride and a mixture of deuterated methylene chloride-acetonitrile (2:1) respectively. In the latter solvent, the isomerisation was detected after 12 hours. A 20% conversion was estimated after 48 hours. It was found that isomerisation did not occur in carbon tetrachloride after 4 days.

Acid Catalysed Isomerisation of 97a

Two small bubbles of dry hydrogen chloride were passed into a solution of 97a in carbon tetrachloride. The nmr spectrum was taken at intervals. The results are shown in Table 20 and Fig. 24, 25.

Exchange Experiments

1. With Deuterated Thionorcamphor

A solution of 96a (12 mg) and deuterated thionorcamphor (10 mg) in benzene (2 ml) was sealed under nitrogen in a glass tube and was kept at 80° for 4 days. It was found previously that under these conditions the thionorcamphor was stable and that isomerisation could be achieved. The reaction mixture which contained only the two starting materials was separated by a preparative tlc and the band corresponded to 96 was collected. The mass spectrum of this product showed that the ratio of peaks m, m+1, m+2 was 100:24:17. The ratio for the non-deuterated 96 was

100:24:21. The minimum amount of exchange should be at least 4 percent in order to be detected by this method. The nmr of this product showed absorption at both 4.0 and 4.4 ppm.

2. With N-Phenylmaleimide

(a) A solution of 96 (10 mg) and N-phenylmaleimide (15 mg) in chloroform (1 ml) was kept in the dark at room temperature for 3 days. Tlc showed that there was no trace of the adduct derived from N-phenylmaleimide.

(b) A solution of 96 (10 mg) and N-phenylmaleimide (15 mg) in benzene (1 ml) was kept in a sealed tube at 80° for 3 days. Tlc showed no trace of the adduct 63.

APPENDIX 1

Equilibrium "Constant" of 59 at Different Concentrations in Different Possible Equilibrium Processes (Chloroform) at 24.5°C

Concentration (mg/50 ml)	Type of Equilibrium Process		
	$A \rightleftharpoons A$	$A_3 \rightleftharpoons 3A$	$2A_3 \rightleftharpoons 3A_2$
3.38	0.133	1.25×10^{-14}	6.23×10^{-7}
2.08	0.178	8.35×10^{-15}	9.07×10^{-7}
0.406	0.433	1.13×10^{-15}	1.95×10^{-6}
0.161	0.788	4.20×10^{-16}	3.95×10^{-6}
0.027	2.69	3.06×10^{-17}	1.26×10^{-5}
0.00108	6.20	7.47×10^{-21}	3.21×10^{-6}
0.000065	64.0	2.59×10^{-23}	2.35×10^{-5}

APPENDIX 2

Equilibrium 'Constant' of 60 at Different Concentrations with Different Equilibrium Processes (in Benzene) at 24.5°C

Concentration (mg/50 ml)	Type of Equilibrium Process		
	$A \rightleftharpoons A$	$A_3 \rightleftharpoons 3A$	$2A_3 \rightleftharpoons 3A_2$
3.43	0.82	3.34×10^{-8}	8.94×10^{-5}
2.05	1.16	2.35×10^{-8}	1.22×10^{-4}
1.23	1.64	1.6×10^{-8}	1.72×10^{-4}
0.369	4.5	7.06×10^{-9}	5.44×10^{-4}
0.074	16.0	1.33×10^{-9}	1.57×10^{-3}

REFERENCES

1. A. Schonberg and A. Stephenson, Ber., 66B 567 (1933).
2. A. Schonberg and A. Mostafa, J. Chem. Soc., 275 (1943).
3. E.T. Kaiser and T.F. Wulfers, J. Am. Chem. Soc., 86 1897 (1964).
4. A. Ohno, Int. J. Sulfur Chem. B, 6 184 (1971); and references therein.
5. P. de Mayo, Acc. Chem. Res., 4 41 (1971).
6. P.E. Eaton, Acc. Chem. Res., 1 50 (1968).
7. D. Blackwell, Ph.D. Thesis, University of Western Ontario, 1975.
8. R. Suau, Personal communication.
9. N. Ishibe, M. Sunami and M. Odani, Tetrahedron 29 2005 (1973).
10. J.L. Fourrey, P. Jouin and J. Moron, Tetrahedron Letters, 3229 (1973).
11. A.A. Nicholson, Israeli J. Chem., 10 341 (1972).
12. A. Ohno, Y. Ohnishi and G. Tsuchihashi, Tetrahedron Letters, 283 (1969).
13. C.C. Liao and P. de Mayo, Chem. Comm., 1525 (1972).
14. R. Lapouyade and P. de Mayo, Can. J. Chem., 50 4068 (1972).
15. C. Th. Pedersen and J. Møller, Acta. Chem. Scand. 26

250 (1972).

16. J.C. Sheehan, R.M. Wilson and A.W. Oxford, J. Am. Chem. Soc., 93 7222 (1971).

17. R. Okazaki, F. Ishii, K. Ozawa and N. Inamoto, Chem. Lett. 9 (1972).

18. E.K. Fields, J. Am. Chem. Soc., 77 4255 (1955).

19. M. Saquet and A. Thuiller, Bull. Chim. Soc. Fr., 1582 (1966).

20. A. Lüttringhaus and W. Cleve, Liebigs Ann. Chem., 575 112 (1952).

21. R. Mayer, P. Rosmus and J. Fabian, J. of Chromato., 15 153 (1964).

22. N. Lozach, Record Chem. Progress, 20 23 (1959).

23. R.A.W. Johnstone and S.D.Ward, Tetrahedron 25 5485 (1969).

24. E. Klingsberg, J. Am. Chem. Soc., 83 2934 (1961).

25. Q.N. Portor, Austral. J. Chem., 20 103 (1967).

26. H. Budzikiewicz, C. Djerassi and D.H. Williams, 'Mass Spectrometry of Organic Compounds', Holden-Day, San Francisco, California, (1967) p. 631.

27. D.M.S., 'UV Atlas of Organic Compounds', Plenum Press, New York, Vol. 5, H5/T1.

28. R.W. Fessenden and J.S. Waugh, J. Chem. Phys., 31 996 (1959).

29. C. Pascual, J. Meier and W. Simon, Helv. Chim. Acta., 49 164 (1966).

30. H. Oediger and K. Eiter, Liebigs Ann. Chem., 682 58

(1965).

31. T. Lesiak, Roczniki Chem., 39 589 (1965).

32. Y. Minoura, J. Chem. Soc. Japan, 73 244 (1952).

33. R. Lapouyade, private communication.

34. A.G. Schultz and M.B. DeTar, J. Am. Chem. Soc., 96 296 (1974).

35. A.G. Schultz, personal communication.

36. D. Cagniant, C. Charaux and P. Cagniant, Bull. Chim. Soc. Fr., 3644 (1966).

37. B.P. Roques, S. Combrisson, R. Oberlin and J. Barbet, Tetrahedron Letters, 1641 (1974).

38. S. O'Brien and D.C.C. Smith, J. Chem. Soc., 2907 (1963).

39. H.S. Desai, D.S. Rao and B.D. Tilak, Chem. and Ind., 464 (1957).

40. W. Carruthers, A.G. Douglas and J. Hill, J. Chem. Soc., 704 (1962).

41. F. Momicchioli and A. Rastelli, J. Chem. Soc. B, 1353 (1970).

42. C.C. Liao, Ph.D. Thesis, The University of Western Ontario, 1972.

43. C.S. Barnes and J.L. Occolowitz, Austral. J. Chem., 16 219 (1963).

44. J.E. Blackwood, C.L. Cladys, K.L. Loening, A.E. Petrarca and J.E. Rush, J. Am. Chem. Soc., 90 509 (1968).

45. Saltiel and H.C. Curtis, J. Am. Chem. Soc., 93 2056 (1971).

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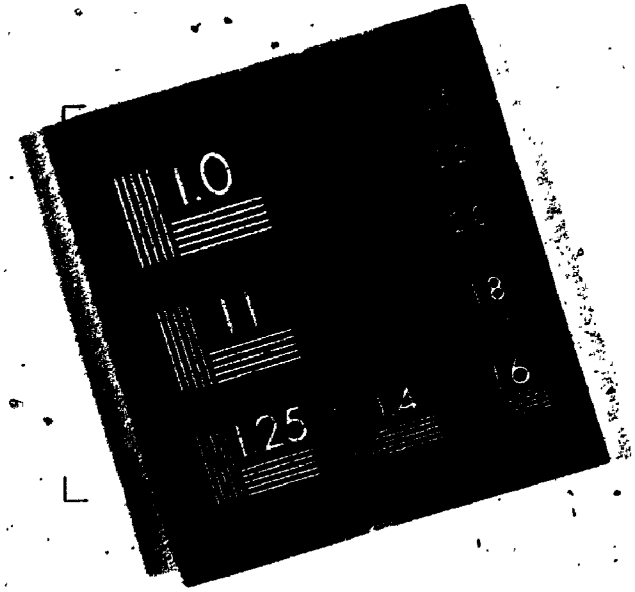

ARC - 374

46. E.J. Baum and R.O.C. Norman, J. Chem. Soc., 749 (1968).

47. J. Saltiel, H.C. Curtis, L. Metts, J.W. Miley, J. Winterle and M. Wrighton, J. Am. Chem. Soc., 92 410 (1970).

48. J.W. Cook, J. Chem. Soc., 456 (1932).

49. W.S. Rapson and W.F. Short, J. Chem. Soc., 128 (1933).

50. M. Saquet & A. Thuillier, Bull. Soc. Chim. Fr., 1582 (1966).

51. J. Schmitt and A. Lespanol, Bull. Soc. Chim. Fr., 459 (1950).

52. M.M. Martin and G.J. Gleicher, J. Am. Chem. Soc., 86 233 (1964).

53. K. Yamamoto and F. Hirata, Chem. Abst., 60 p. 460.

54. Yu A. Fialkov, D.N. Kpzachuk and L.M. Yagupolskii, Zh. Obsh. Klim., 2085 (1970) (Eng. Ed.)

55. J.P. Freeman, J. Org. Chem., 22 1608 (1957).

56. M.S. Shvartsberg, M.I. Bardamova & I.L. Kotlyrevisk, Zh. Obsh. Klim., 440 (1960).

57. R.N. McDonald and T.W. Campbell, J. Org. Chem., 24 1969 (1959).

58. K. Hirayama, Handbook of Ultraviolet and Visible Absorption Spectra of Organic Compound, Pleunm Publishing Corporation, New York, 1967.

59. J.E. Mackenzie, J. Chem. Soc., 69 987 (1896).

60. G.J. Gleicher, D.D. Newkirk and J.C. Arnold, J. Am. Chem. Soc., 95 2526 (1973) and references therein.

61. M.P. Cava and A.A. Deana, J. Am. Chem. Soc., 81 4266 (1959).

62. R.K. Smalley and H. Suschitzky, Tetrahedron Letters, 3465 (1966).

63. O.L. Chapman and C.L. McIntosh, Chem. Comm., 383 (1971).

64. K. Salishury, Tetrahedron Letters, 737 (1971).

65. M.P. Cava and R.L. Shirley, J. Am. Chem. Soc., 82 654 (1960).

66. C.M. Bowes, D.F. Montecalvo and F. Sondheimer, Tetrahedron Letters, 3181 (1973).

67. M.S. Ao and E.M. Burgess, J. Am. Chem. Soc., 93 5298 (1971).

68. R.S. Becker and J.M. Michl, J. Am. Chem. Soc., 88 5931 (1966).

69. R.S. Becker and J. Kolc, J. Phys. Chem., 49 2092 (1968).

70. J. Kolc and R.S. Becker, J. Am. Chem. Soc., 91 6513 (1969).

71. B.S. Lukjanow, M.I. Knjazschanski, J.W. Rewinski, L.E. Niworozschkin and W.I. Minkin, Tetrahedron Letters, 2007 (1973).

72. J. Nasielski and G. Jacqmin, Tetrahedron, 597 (1972).

73. G. Jacqmin, J. Nasielski, G. Billy and M. Remy, Tetrahedron Letters, 3655 (1973).

74. A.A. Nicholson, Ph.D. Thesis, The University of Western Ontario, 1972.

75. A.H. Lawrence, Ph.D. Thesis, The University of Western Ontario, 1974.

76. W. Küster and P. de Mayo, J. Am. Chem. Soc., 96 3502 (1974).

77. P. de Mayo and H.Y. Ng, Tetrahedron Letters, 1561 (1973).

78. R. Okazaki, K. Okawa and N. Inamoto, Chem. Comm., 843 (1971).

79. R. Forster and C.A. Fyfe, Spectrochim, Acta., 21 1785 (1965).

80. T. Matsuo, Kogyo Kagaku Zasshi, 68 1422 (1965); CA 64 4478d.

81. H.O. House, H. Babad, R.B. Toothill & A.W. Noltes, J. Org. Chem. 27 4141 (1962).

82. H.S. Gutowsky and C.H. Hohn, J. Chem. Phys., 25 1228 (1956).

83. I.C. Calder and P.J. Garratt, J. Chem. Soc. (B) 660 (1967).

84. P. Ahern, T. Navratil and K. Vaughan, Tetrahedron Letters, 4547 (1973) and references therein.

85. O.L. Chapman and C.L. McIntosh, J. Am. Soc., 92 7001 (1970).

86. A.O. Pedersen, S.O. Lawesson, P.D. Klemmensen and J. Kolc, Tetrahedron 26 1157 (1970).

87. W.J. Bailey and R.A. Raylouny, J. Org. Chem., 27 3476 (1962).

88. C.G. Krespan, J. Am. Chem. Soc., 83 3434 (1961).

89. V.V. Keussler and W. Lüttle, Z. Elektrochem., 63 614 (1959).

90. R.R. Holmes, J. Org. Chem., 29 3076 (1964).

91. P. Metzner and J. Vialle, Bull. Soc. Chim Fr., 3138 (1972).

92. M.J. Janssen, Rec. Trav. Chim., 79 464 (1960).

93. K.J. Rosehgren, Acta, Chem. Scand., 16 2284 (1962).

94. D.S.L. Blackwell, C.C. Liao, R.O. Loutfy, P. de Mayo, S. Paszyc, Mol. Photochem., 4 171 (1972).

95. H. Behringer and R. Wiedendman, Tetrahedron Letters, 3705 (1965).

96. R.S. Becker and J. Kolc, J. Phys. Chem., 72 997 (1968).

97. A.I. Scott, Interprepation of the Ultraviolet Spectra of Natural Products, Pergamon Press, Oxford, 1964.

98. C.C. Price & S. Oae, Sulfur Bonding, The Ronald Press Company, New York, 1962.

99. J.C. Stowell, J. Org. Chem. 3055 (1971).

100. L. Legrand, Y. Mollier and N. Lozac'h, Bull. Soc. Chim. Fr., 327 (1953).

101. A. Arcoria, H. Lumbroso and R. Passerini, Bull. Soc. Chim. Fr., 754 (1959).

102. R.B. Moffett, Org. Syn. Coll., IV pg.291.

103. A. Weizmann, J. Org. Chem., 8 285 (1943).

104. S.G. Cohen and A. Milovanovic, J. Am. Chem. Soc., 90 3495 (1968).

105. N.B. Mehta, A.R. Phillips, F. Fu. Lui and R.E. Brooks,

J. Org. Chem., 25 1012 (1960).

106. W.J. Middleton, J. Org. Chem., 30 1390 (1965).

107. A. Schonberg and B. Koning, Tetradegron Letters, 3361 (1965).

108. A. Ohno, Y. Ohnishi and G. Tsuchihashi, Tetrahedron, 25 871 (1969).

109. K. Yamada, M. Yoshioka and N. Sugigama, J. Org. Chem., 33 1240 (1968).

110. T.S. Cantrell, ibid, 39 853 (1974).

111. D.B.J. Easton, D. Leaver and T.J. Rawlings, J. Chem. Soc. Perkin 1, 41 (1972).

112. J.C. Meslin & H. Quiniou, Bull Chim. Soc. Fr., 2517 (1972).

113. M. Bard, J.C. Meslin and H. Quiniou, J.C.S. Chem. Comm., 672 (1973).

114. N. Lozac'h, Rec. Chem. Prog., 20 23 (1959).

115. S.B. Needleman and M.C. Chang Kuo, Chem. Rev., 62 405 (1962).

116. J.S. Meek, P.A. Monrol and C.J. Bouboulis, J. Org. Chem., 28 2572 (1963).

117. J.S. Meek, B.T. Boon and S.J. Cristol, J.Am. Chem. Soc., 74 761 (1952).

118. K. Alder and K. Heimbach, Chem. Ber., 86 1313 (1953).

119. J.S. Meek, D.R. Wilgus and J.R. Dann, J. Am. Chem. Soc., 82 2566 (1960).

120. R.A. Dickinson, R. Kubela, G.A. MacAlpine, E. Stojanac & Z. Valenta, Can. J. Chem. 50 2377 (1973).

121. R.C. Arnold, A.P. Lien and R.M. Alm., J. Am. Chem. Soc., 72 731 (1950).

122. L.J. Bellamy, The Infrared Spectra of Complex Molecules, John Willy and son, 1966, p. 162.

123. K. Nakanishi, Infrared Absorption Spectroscopy, Holden-day Inc., San Francisco, 1962, p. 26.

124. K. Nakanishi, ibid, p. 44.

125. G. Sachs and H. Bless, Ber., 58 1493 (1925).

126. E.E. Reid, Organic Chemistry of Divalent sulfur, Vol. III.

127. J.A. Berson, R.D. Reynolds and W.M. Jones, J. Am. Chem. Soc., 78 6409 (1956).

128. L.F. Fieser and M. Fieser, Reagents for organic synthesis, John Wiley and Sons, New York, 1967.

129. J.W. Greidanus, Can. J. Chem. Soc., 48 3530 (1970).

130. D.C. Sen, J. Ind. Chem. Soc., 13 268 (1936).

131. D.C. Sen, ibid, 12 647 (1935).

132. P. von Schleyer and R.D. Nicholas, J. Am. Chem. Soc., 182 (1961).