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Observations on Photochemically and Thermally Induced Rearrangements and Fragmentations in 2,5-Dihydrothiophene Derivatives

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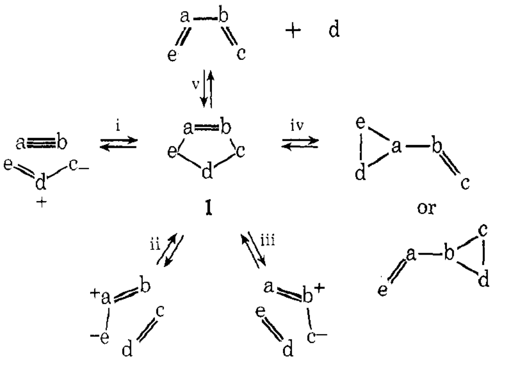
By means of the addition of thiocarbonyl ylides to dimethyl acetylenedicarboxylate, a series of 2,5-dialkyl-substituted 2,5-dihydrothiophenes (**4**) was prepared. These compounds were also oxidized to the respective sulfoxides (**20**) and sulfones (**19**). The compounds 4 undergo ring contraction on irradiation, producing vinyl episulfides. These on desulfurization afford dienes. The sulfoxides **20** provide the same dienes on either irradiation or thermolysis. The only exception is the 2,2,5,5-tetramethyl derivative (**20b**), which gives a complex mixture of products on thermolysis. The sulfones **19** also yield dienes on either irradiation or thermolysis. The stereochemistry of all these reactions has been determined. In complete accord with earlier work, the sulfone thermolyses are completely stereospecific and follow expectations from orbital symmetry considerations. All other reactions studied exhibit lessened stereoselectivity and this is construed as evidence for the intervention of biradical intermediates. In the photochemical reactions of 4 both cisoid and transoid forms of the allylic portion of the biradical formed on cleavage of a carbon-sulfur bond are involved. Related mechanisms are thought to be involved in the photochemical reactions of **19** and **20**. Arguments are advanced that the thermolysis of **19** and **20** involve different mechanisms because the reaction coordinate for the latter reaction cannot be symmetrical; this forces the reaction into a nonconcerted pathway.

Imagine a generalized five-membered heterocycle **1** derivable in principle through a 1,3-dipolar cycloaddition.[1] Routes i–iii (eq 1) all have adequate precedent. Nearly unanimously these reactions involve 1,3-dipole and dipolarophile in their *ground states. Excited states* of **1** could conceivably fragment through one of these pathways. This seems not to be common, however.[2] Although the detailed explanations differ widely from compound to compound, a rationale might be that excited states of **1** must attain a sterically unfavorable antarafacial-suprafacial geometry to fulfill orbital symmetry demands for fragmentations through paths i–iii.[3]



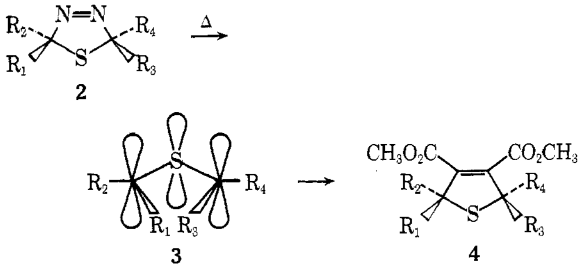
(1)

The number of examples is limited, but path iv, a vinyl cyclopropane-like rearrangement,[4] and path v appear to be possible for both ground and excited states. Photochemical examples are restricted chiefly to fragmentations of **1**.[5-7] In these cases orbital symmetry considerations place less stringent steric requirements on the required transition states.

More complete descriptions of the extent to which orbital symmetry factors control these types of reactions, especially those involving excited states, should be forthcoming from stereochemical studies. Such investigations require in practice systems in which carbon atoms with their unique stereochemical properties are present at points at which bonds are made or broken. The common philosophy is that if a given reaction leads to only one of several possible geometrical isomers, all of which are accessible through stereochemically acceptable transition states, and if the isomer formed is that predicted by orbital symmetry factors, this can be considered *ipso facto* as evidence for orbital symmetry control.[3] We offer here the descriptive aspects of the photo- and thermochemistry of 2,5-dihydrothiophenes **4** and their sulfoxide and sulfone derivatives.[8,9] This is a limited study of only one compound type. We hope nevertheless that the results obtained are not only interesting in their own right but lend also some insight into the broader problems hinted at in eq 1.

Results

A. Thermochemistry and Photochemistry of 4. The genesis of compounds **4** lies in the thermally induced ste-

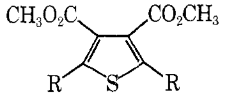


(2)

a, $R_1 = R_4 = t\text{-}C(CH_3)_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
e, $R_1 = R_4 = C_2H_5$; $R_2 = R_3 = H$
f, $R_1 = R_3 = C_2H_5$; $R_2 = R_4 = H$

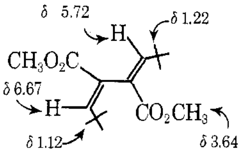
reospecific addition of thiocarbonyl ylides **3** to dimethyl acetylenedicarboxylate (eq 2).[9]

No significant thermochemistry of cycloadducts **4** is observed up to 500° save that **4d** and **4f** dehydrogenate, affording thiophenes **5a** and **5b**, respectively.



5a, R = CH_3
b, R = C_2H_5

In contrast, these compounds proved to be very photolabile. The reaction of **4a** serves as an example. On irradiation in degassed solution using a high-pressure mercury lamp, **4a** provided two products in a ratio of about 4:1 as determined by gas–liquid partition chromatography (glpc) using copper columns. A small amount of a third compound was also observed. These three products were isolated and were identified as dienes **6** (*Z,E,* major product), **7** (*E,E,* minor product), and **8** (*Z,Z,* trace product).



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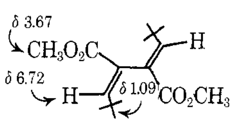

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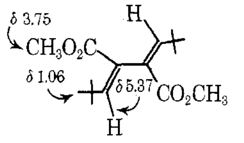
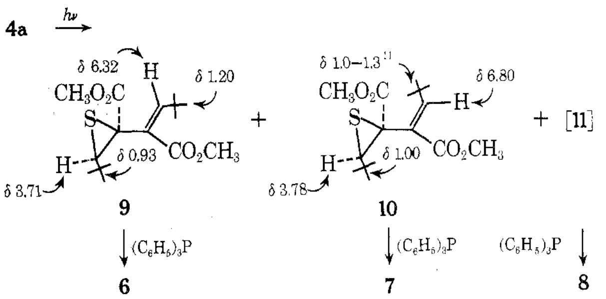


8

No ambiguity exists in stereochemical assignment of **6** owing to the nonequivalence of the vinyl and *tert*-butyl protons in the pmr spectrum (CCl_4). Assignment of the various protons can be made with confidence, for carboalkoxy groups exert a stronger deshielding effect than either vinyl or alkyl groups on cis-oriented vinylic protons.[10] These same shielding arguments allow assignment of *E,E* and *Z,Z* configurations to **7** and **8**, respectively.

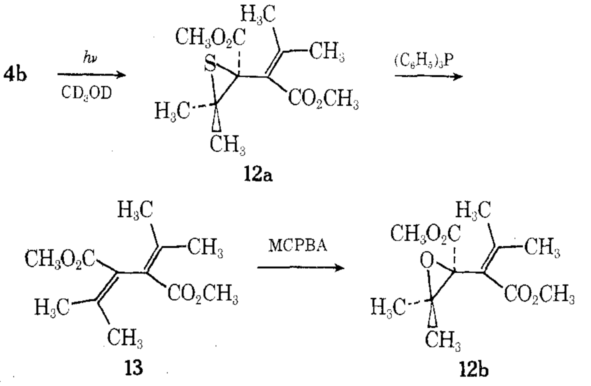
Monitoring of the reaction of **4a** using either pmr spectroscopy or glpc on glass columns showed that **6–8** *are not* primary photochemical products. Two unstable compounds, **9** and **10**, in the same ratio as **6** and **7** were seen in the glpc traces (a precursor to **8** was never detected, perhaps because of its low concentration). On glpc with copper columns, or on standing at room temperature, **6** and **7** were formed. By careful preparative glpc small samples of **9** and **10** (contaminated with about 20% of **6** and **7**, respectively) were isolated. Mass spectrometry (glpc coupled directly to mass spectrometer) established that **9** and **10** had the same molecular composition ($C_{16}H_{26}O_4S$) as starting material. Osmometric measurements demonstrated that the compounds were monomeric. The infrared spectra showed carbonyl absorptions at 1720 (sh) and 1739 cm^{-1} whereas **6** and **7** have a single carbonyl absorption at 1720 cm^{-1}. On treatment with triphenylphosphine **9** and **10** were converted quantitatively to **6** and **7**, respectively. On the basis of the above coupled with the pmr absorptions (eq 3) **9** and **10** must be assigned vinyl episulfide (thiirane) structures.

In **10** the episulfide linkage is perforce at a potentially *E* double bond. In **9**, however, the episulfide linkage could be at either potentially *E* or *Z* double bond positions. The former assignment is made since the vinylic proton is shifted upfield relative to **10**, indicating a change in configuration about the double bond; also, the chemical shifts of the methine protons in both **9** and **10** are similar, indicating the same configuration about the episulfide ring. A vinyl episulfide **11** is thought to be a precursor of trace product **8**, but the amount was too small to allow detection. Conversions are quantitative providing that the solutions are well degassed; otherwise some oxidation to a thiophene occurs.



(3)

Evidence was also accumulated for the presence of vinyl episulfide intermediates in the photochemically induced reactions of **4b–f**. This is described in the Experimental Section. Compound **12a** was observed by nmr spectroscopy as the product of irradiation of **4b**. This was converted to diene **13**. Treatment of **13** with *m*-chloroperbenzoic acid (eq 4) led to vinyl epoxide **12b** with pmr spectral characteristics closely resembling those of **12a**, which was too unstable to be isolated.



(4)

Test reactions demonstrated that desulfurization of the intermediate vinyl episulfides with triphenylphosphine occurred with retention of configuration. The same was true if the vinyl episulfides were desulfurized by contact with a metal injector port in the glpc. For stereochemical investigations one or the other of these techniques was used and the resulting diene isomers were examined. To establish stereospecificities the diene ratios were determined at various levels of conversion and extrapolated back to zero time. Up to about 20% conversion there was no significant deviation in the ratios. For cis isomers **4d** and **4f** fewer checks were made owing to a shortage of material; these isomers could be purified only by tedious preparative glpc. Both compounds contained about 5% thiophene arising from frustratingly facile dehydrogenation during isolation.

The results of the stereochemical investigations are compiled in Table I. The stereochemistries of the dienes were assigned on the basis of the shielding arguments developed previously. Cis,trans pair **4c,d** proved most tractable to work with and data obtained for these two compounds are most accurate. Trans isomers **4c** and **4e** underwent during irradiation isomerization to cis isomers **4d** and **4f**, respectively. This is illustrated in eq 5 for **4c**. The amount of trans–cis isomerization was 25–35% that of ring contraction. Accurate determinations of the exact amount of isomerization were difficult because of the error in ex-

Table I
Stereochemistry of Dienes Obtained on Desulfurization of Primary Photoproducts from 2,5-Dihydrothiphenes 4

Compd	Diene[a] (yield, %)		
	Z,E	*E,E*	*Z,Z*
4a	**5** (65)	**6** (31)	**7** (4)
4c[b]	**14** (50)	**15** (50)	**16** (1)
4d	**14** (30)	**15** (60)	**16** (10)
4e[b]	**17** (96)	**18** (4)	*c*
4f	**17** (50)	**18** (50)	*c*

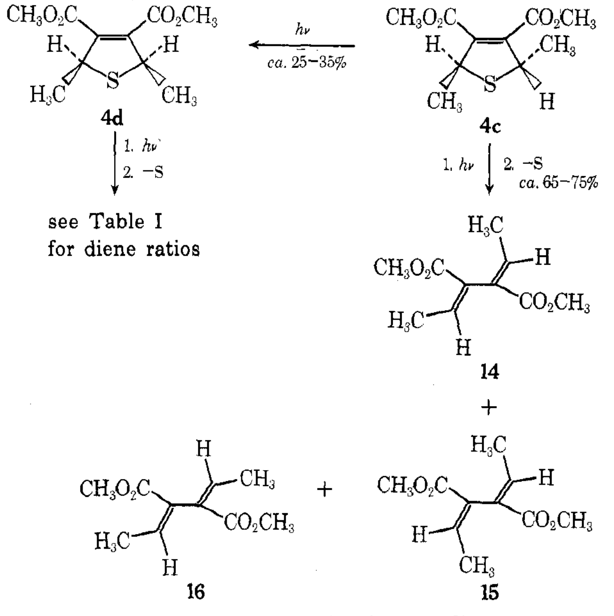
[a] Yields account quantitatively for consumed starting material. [b] Undergoes isomerization; see text. [c] Not detected.

Table II
Results of Photochemical Experiments[a] with 19

Compd	Diene[b] (yield, %) *Z,E*	*E,E*	*Z,Z*	Other
19a	**5** (72)	**6** (10)	**7** (18)	
19b				**12** (100)
19c	**14** (58)	**15** (29)	**16** (13)	
19d	**14** (64)	**15** (36)	**16** (0)	

[a] Reactions run in CD_3OD at room temperature with analysis by nmr; essentially the same product distribution is obtained using diethyl ether. [b] All consumed material accounted for as diene.

trapolation back to zero time. This mechanistically significant process is within experimental error irreversible; no trace of cis to trans isomerization of the dihydrothiophenes was ever observed.



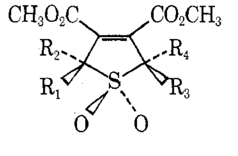
(5)

Some quenching and sensitization studies were carried out with **4b**. This isomer was most suitable for study because oxidation to a thiophene derivative is impossible. This problem complicated investigation of 2,5-dialkyl derivatives. Benzophenone (E_T 69.3 kcal/mol) and acetophenone (E_T 73.6 kcal/mol) both sensitized ring contraction; phenanthrene (E_T 64 kcal/mol) had no effect. This brackets the triplet level of **4b** between 64 and 68 kcal/mol, a conclusion that would agree also with a weak, structureless phosphorescence emission observed from **4b** with a maximum at 540 nm (66 kcal/mol).[12] Somewhat surprisingly, the ring contraction of **4b** brought about with 300-nm excitation was only weakly quenched by 1,3-pentadiene. A maximum of 20% retardation was observed with 2.5×10^{-2} *M* **4b** 0.1 *M* in diene (highest concentration used).

Table III
Results of the Thermolysis of 19a–d

Compd	Diene (yield, %) *Z,E*	*E,E*	*Z,Z,*	Other
19a	**5** (100)	**6** (0)	**7** (0)	
19b				**12** (100)
19c	**14** (100)	**15** (0)	**16** (0)	
19d	**14** (0)	**15** (0)	**6** (100)	

B. Photochemistry and Thermochemistry of 2,5-Dihydrothiophene *S*-Dioxide Derivatives. The sulfones **19a–d** were prepared by oxidation of **4a–d** with 2 equiv of *m*-chloroperbenzoic acid. On irradiation they cleanly lost sulfur dioxide, yielding dienes. No other products were detectable. The relative thermal instability of the sulfones made glpc analysis impossible; reactions were monitored in a quartz nmr tube using a high-pressure mercury lamp as light source. The results of this investigation are assembled in Table II. About 20% conversions were necessary to obtain nmr spectra that could be integrated well. The dienes did not isomerize appreciably during the irradiation times used. No cis–trans or trans–cis isomerization was detected with **19c,d.**



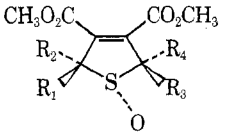
19a, $R_1 = R_4 = t\text{-}C(CH_3)_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

Attempts to run reactions at lower temperatures in the hope of trapping ring contraction products failed; in all solvents used the starting material precipitated at nmr concentrations. A vinyl sulfone would be expected to be thermally unstable.[13]

Loss of sulfur dioxide from **19b** was sensitized by both acetophenone and benzophenone but not by phenanthrene. At 300 nm loss of sulfur dioxide was somewhat inhibited by 1,3-pentadiene. A concentration of 0.1 *M* halves the rate of sulfur dioxide loss (2.5×10^{-2} *M* in **19b**).

As expected, thermolysis of **19a–d** also led cleanly to dienes. In preparative runs yields were >80% and near quantitative in small-scale experiments. The reactions are at least 99.9% stereospecific when pyrolyses were carried out at 250° in a glass-lined injector port of a glpc apparatus. The results are assembled in Table III.

C. Photochemistry and Thermochemistry of 2,5-Dihydrothiophene *S*-Oxides. The sulfoxides **20a–d** were prepared by careful oxidation of **3a–d** with 1 equiv of *m*-chloroperbenzoic acid. The S–O linkage in **20d** (single diastereomer) is tentatively placed anti to the methyl groups on the basis of shielding data (Experimental Section).[14,15]



20a, $R_1 = R_4 = t\text{-}C(CH_3)_3$; $R_2 = R_3 = H$
b, $R_1 = R_2 = R_3 = R_4 = CH_3$
c, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
d, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

On irradiation clean conversion to dienes occurred with no detectable production of side products. Using the same

Table IV
Results of Photochemical Experiments with Sulfoxides 20

	Diene (yield, %)			
Compd	Z,E	E,E	Z,Z	Other
20a	**5** (57)	**6** (25)	**7** (18)	
20b				**12** (100)
20c	**14** (79)	**15** (21)	**16** (0)	
20d	**14** (52)	**15** (37)	**16** (11)	

Table V
Results of Thermolyses of Sulfoxides 20

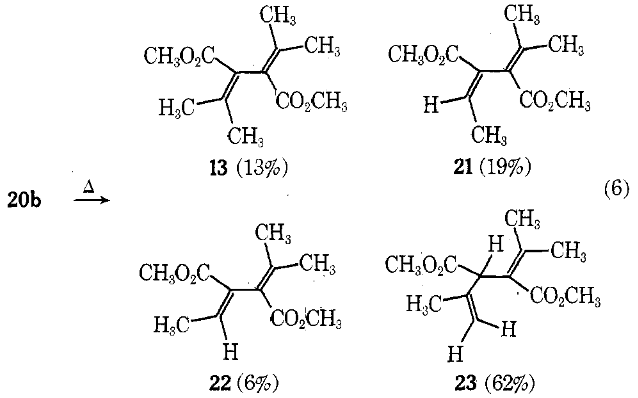
	Diene (yield, %)		
Compd	Z,E	E,E	Z,Z
20a	**5** (75)	**6** (12)	**7** (13)
20c	**14** (95)	**15** (2.5)	**16** (25)
20d	**14** (6)	**15** (10)	**16** (84)

techniques employed for sulfones **19**, the stereospecificities of these reactions were determined; the results are compiled in Table IV. Irradiations were carried out in perdeuteriomethanol. Attempts to identify unstable intermediates, *i.e.*, vinyl episulfoxides, were again frustrated as with sulfones 19 by the insolubility of the compounds in acceptable solvents at low temperatures. At room temperature no indications of any intermediates were obtained. No isomerization of starting material was found.

Smooth conversion to dienes also occurred on thermolysis. Pyrolyses were carried out preparatively at 350–400° in a short pyrolysis tube leading to >80% overall yields of dienes. Experiments with **20a,c,d** wherein pyrolysis was carried out in a glass-lined injector port at *ca.* 250° led only to dienes and no detectable side products. The stereochemical results are compiled in Table V.

Attempts to trap sulfur monoxide, presumably produced in thermal reactions, were frustrated by the relatively high temperatures needed for pyrolysis of **20**. Some experiments with 3,4-diphenylbutadiene as trapping agent were carried out, but any addition product, if formed, would almost certainly be pyrolyzed again at the temperatures employed.[16] Appropriate conditions could not be devised for the trapping of sulfur monoxide that might have been produced in photochemical reactions.

The pyrolysis of **20b** led to a completely different product distribution than that observed in any other reactions. When pyrolyzed under the conditions used for the other isomers, **20b** gave in *ca.* 70% overall yield the products shown in eq 6, where the percentages (in parentheses) refer to isomer ratios. The four products were identified from analytical and spectroscopic data as described in the Experimental Section.

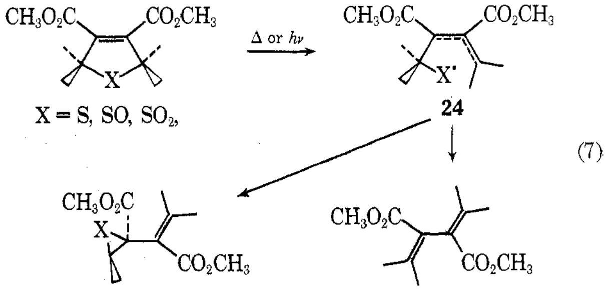


(6)

Discussion

A. General Points. All the reactions here described, be they thermally or photochemically induced, lead ultimately to loss of the sulfur unit with retention of the carbon skeleton. The pyrolytic results with **20b** provide the only (partial) exception. Of the possibilities with precedent outlined in eq 1 (and others are conceivable), paths iv and/or v are followed. No hint was ever obtained of the operation of paths i–iii to any detectable extent. In the case of **4**, path i would be a reversal of the route employed for synthesis (eq 2).

Only the thermolyses of the sulfones **19** are distinguished by complete stereospecificity. This agrees in all respects with earlier experiments on closely related systems.[6] We believe that the present results can be divided into two sharply different categories. The sulfone thermolyses stand apart, representing, as maintained by Lemal[6b] and Mock,[6a] concerted $[4_s + 2_s]$ reactions in which orbital symmetry considerations dictate a disrotatory motion of the alkyl groups at the 2,5 positions. Steric effects influence stereochemistry only in cis isomer **19d** by directing the reactions into the disrotatory mode that rotates the alkyl groups outward leading to *Z,Z* diene **16**. In our opinion all the other reactions reported here are best interpreted as involving initial fragmentation of a carbon–sulfur bond leading to biradicals **24** that may either undergo ring contraction or lose immediately the sulfur segment (eq 7).[17] Only one of several possible conformations of **24** is indicated. The stereochemistry of the products is determined by conformational factors in **24**. The pictorial representation **24** does not communicate differences in internal energy that likely exist between intermediates formed from thermal and photochemical pathways; we intend no more than to represent rupture of a σ bond induced by light or heat. Indeed, we make a sweeping generalization in lumping photochemical and thermal reactions together; this ignores myriad details of exactly how the biradicals **24** behave dependent on their mode of generation.



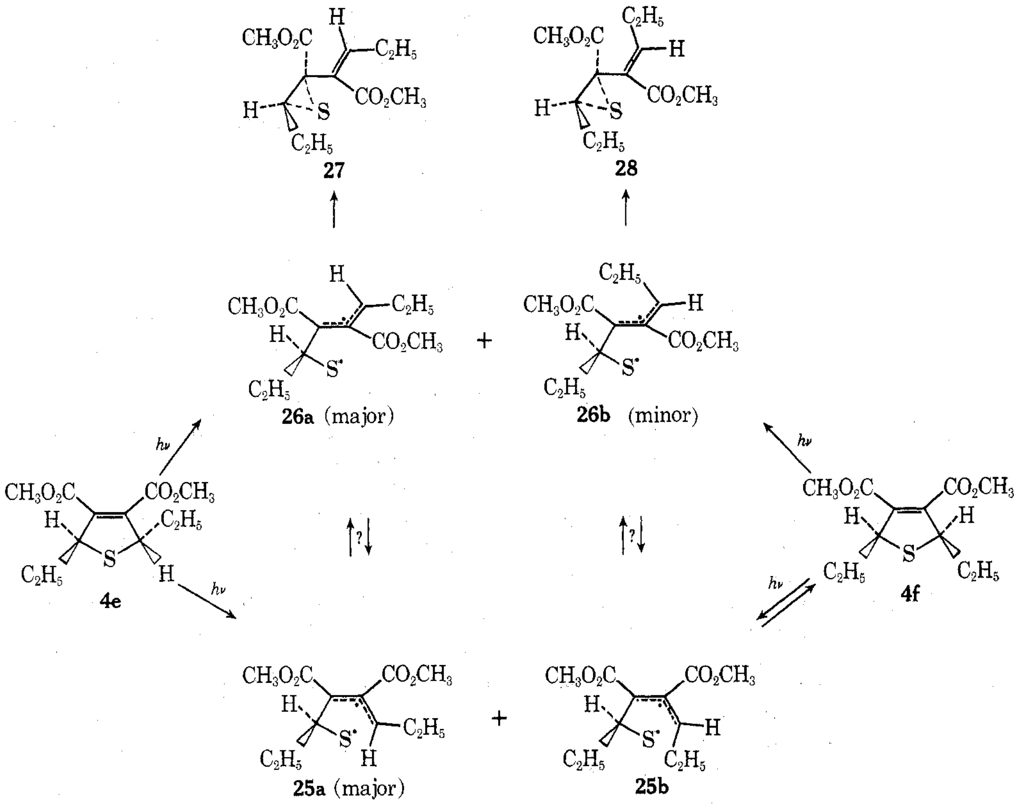
(7)

Evidence for biradical intermediates can be found as discussed in the following sections. Some guesses concerning their geometry can be made.

The stereochemical results could be explained in terms of pericyclic reactions invoking either combinations of $[{}_{\sigma}2 + {}_{\pi}2]$ reactions or nonlinear chelotropic eliminations.[3,17] We are less convinced by such an approach for reasons that will become clear in the subsequent discussion. However, although the point is well-nigh impossible to prove, orbital symmetry might well play a decisive role, particularly in the photochemical reactions, by imposing on fragmentation pathways i–iii (especially i) of eq 1 a sterically difficulty accessible antarafacial–suprafacial geometry in the transition state.

B. Photochemical Reactions. Some details of the photochemical reactions of **4**, **19**, and **20** will now be considered.

The most complete information comes from the 2,5-dihydrothiophenes **4**. Here intermediates, vinyl episulfides, were intercepted. The available data indicate that some factor or factors control the stereochemistry of the episulfide linkage fairly rigorously. The alkyl groups and the carboalkoxy groups are oriented trans, *i.e.*, a poten-

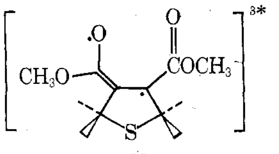


(8)

tially *E* double bond (on desulfurization) is generated. Stereochemical control is less at the vinylic carbon but from the trans isomers chiefly *Z* double bonds are formed. There is little tendency for either a cis or a trans isomer to yield a *Z,Z* diene on desulfurization (Table I).

The strongest evidence in favor of biradical intermediates is the observed trans to cis isomerization of **4c** to **4d** and **4e** to **4f**. This must involve cleavage and recombination of a carbon–sulfur bond. This process competes well with ring contraction. It is reasonable that isomerization and ring contraction are both manifestations of the behavior of a common precursor.

A rationalization of the photochemical results illustrated with **4e** and **4f** is given in eq 8. The most important aspect of this fairly complicated scheme is the postulation of the cisoid and transoid biradicals, **25a,b** and **26a,b**. In the formalism introduced by Zimmerman[18] one representation of an excited triplet state of **4** is **29**. The sulfur atom is positioned for β-elimination as a thiyl radical; this coupled with a turning of the methylene group produces cisoid **25a** and **25b**. This type of β-elimination process has much precedent in radical chemistry[19a] and also in some known photochemical reactions.[19b] However, the excited triplet states of dialkyl maleates, in common with other simpler olefins, should twist about the double bond.[20] This motion in excited **29** coupled with breaking of the



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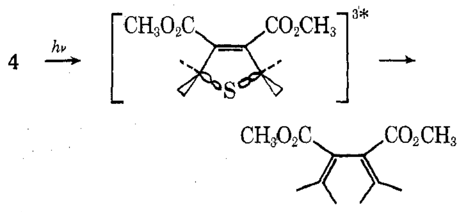
carbon–sulfur bond leads to transoid biradicals **26a,b**. Inspection of molecular models leads to the conclusion that this twisting motion occurs with the least steric interference by holding substituents on the carbon atom originally bonded to sulfur "outside," leading ultimately to **26a** in preference to **26b**. Ring closure arranging the alkyl and carbomethoxy groups trans on the episulfide ring produces the observed major products.[21,22]

The most reasonable fate of **25a,b** is recoupling to form **4**; this process seems to form exclusively cis isomer (with the exception of 2,5-di-*tert*-butyl-substituted **4a**, which shows no trace of isomerization). We do not have any reasonable explanation for this selectivity.

It is interesting that the dihydrothiophenes show no detectable tendency to make use of the route of eq 9. The



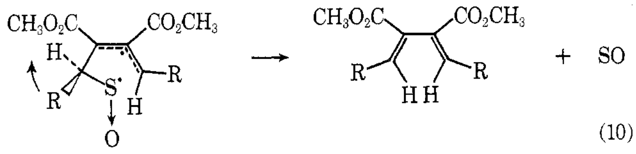
(9)

reactions originate from the triplet state, and reaction leading to diene and triplet sulfur, a species well characterized in the photolysis of carbonyl sulfide,[23] should be possible through an "allowed" $[4_s + 2_a]$ reaction.

The photolyses of sulfones **19** and sulfoxides **20** likely involve similar mechanisms. Ring-contracted intermediates analogous to those isolated in the photoreactions of **4** were not identified. Vinyl episulfoxide or episulfone intermediates should be very unstable, however.[13] A ring-contraction step is not mandatory; loss of the sulfur oxide from the biradical intermediates in the manner indicated in eq 7 (only one possible conformer shown) is a reasonable alternative.

C. Thermal Reactions. The sulfoxide pyrolyses, with the exception of **20b**, afford diene with a fairly high tendency toward disrotatory participation of this component. However, in no case do the stereospecificities match those observed with sulfones **19**. Lemal and Chao[16a,b] have demonstrated both 1,4-addition of sulfur monoxide to 2,4-hexadienes and thermal elimination from the respective 2,5-dihydrothiophene *S*-oxides. Reasonable stereospecificity was observed in the addition reaction but relatively little in the elimination reaction. A mechanism involving biradicals was suggested to account for the experimental results.

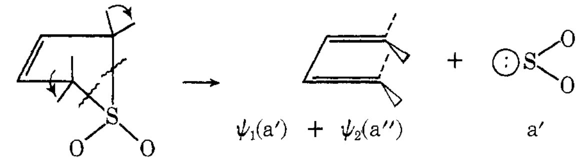
On a energetic basis one might anticipate a changeover in mechanism from sulfones **19** to sulfoxides **20**. The dienes formed are identical but there is a drastic difference in the sulfur oxides being eliminated. Oxidation of sulfur monoxide to sulfur dioxide by molecular oxygen is 61 kcal/mol exothermic.[24] Sulfur monoxide is a ground-state triplet with a singlet state lying 18 kcal/mol higher.[25] If spin conservation holds the energetically even less favorable singlet would have to be formed. Avoidance of this difficulty by cleavage of the sulfoxide–carbon bond (bond dissociation energy *ca.* 50 kcal/mol)[26] with subsequent fragmentation of the biradical **30** is reasonable (eq 10). The predominance of diene product formed from a disrotatory motion of the 2,5-carbon atoms in **20** is readily understandable if rupture of the sulfur–carbon bond is accompanied by an outward rotation of the bulky alkyl substituent, placing it cis to the carboalkoxy group. Thereafter outward rotation of the sulfur unit in cisoid biradical **30** (a strong driving force for formation of a transoid biradical as in the photochemical experiments is lacking) concomitant with its departure would produce the observed major diene product.



(10)

30

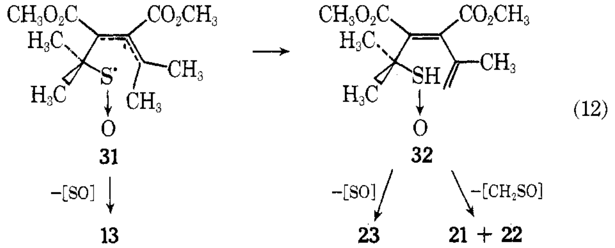
Possible support for initial rupture of a sulfur–carbon bond in the thermal reactions of **20** is provided by Pearson's[27] approach to the analysis of orbital symmetry effects. For a concerted $[4_s + 2_s]$ cycloelimination of sulfur monoxide to occur, a disrotatory motion of the 2,5 substituent is required. This means that a σ plane perpendicular to the five-membered ring is maintained. In the Pearson analysis a reaction can be concerted and subject to orbital symmetry requirements only if the total reaction coordinate is symmetrical. In 2,5-dihydrothiophene sulfones this condition is met in a thermal reaction (eq 11), since in the C_s point group applicable for a disrotatory movement of the carbon atoms the breaking σ bonds have a′ and a″ symmetry and the π orbital has a′ symmetry; in butadienes the filled MO's are a′ and a″ and the filled lone pair in sulfur dioxide is a′. The reaction coordinate can be totally symmetrical. This is, of course, exactly the conclusion reached by Woodward and Hoffmann,[3] who describe this as a linear chelotropic reaction.



(11)

This situation changes for the same type of concerted reaction involving loss of sulfur monoxide; the highest occupied MO in sulfur monoxide is antibonding and lies in the length of the molecule.[28] It has a″ symmetry, forcing the total reaction coordinate to be not symmetrical; the reaction would be forbidden. This analysis is exceedingly simple minded. Detailed examination of the electronic structure of sulfur monoxide coupled with an analysis of the reaction along the lines developed by Kearns[29] indicates that a concerted path is probably available.[30] The experimental evidence would suggest, however, that the molecules investigated here choose nevertheless to avoid concerted decomposition.

One interpretation of the complicated reaction seen with **20b** is that an intermediate biradical **31** partitions itself between "normal" reaction leading to **13** and intramolecular hydrogen abstraction producing sulfenic acid **32**. The latter serves as precursor of the "anomalous" products **21–23** (eq 12). Although a cyclic pathway, well known in simpler sulfoxides,[31] provides access to **32**, the formation of **13** through this route is difficult to explain.



(12)

Experimental Section

Melting points and boiling points are not corrected. Gas chromatography was done on F & M Models 700 and 810 apparatus; for preparative work an F & M 775 was used. Nmr spectra were obtained on a Varian A-60 or XL-100 apparatus. Phosphorescence measurements were made using on Aminco-Bowman spectrofluorimeter. Most of the compounds used in this study have been described in ref 9. The properties of the dienes isolated from the various photochemical and thermal reactions are compiled in Table VI.

Preparation of *trans*- and *cis*-2,5-dimethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene (4c and 4d) was carried out by a modification of the procedure described in ref 9. A mixture of hydrogen sulfide (15 g, 0.44 mol) and freshly distilled acetaldehyde (39 g, 0.89 mol) was vigorously stirred at −90°. To this mixture was added over 30 min hydrazine hydrate (20 g, 0.40 mol). After 2 hr of stirring a white precipitate had formed. The solution was warmed to *ca.* 5°, 100 ml of water was added, and the reaction mixture was extracted three times with ether. The ether extracts were dried at −20° over $MgSO_4$. The ether was removed at −5°. A crude oil (33 g) remained that was dissolved in petroleum ether (bp 40–60°) and then immediately cooled to −50°. By this means there was obtained 5 g (9% yield) of an unstable white solid that was chiefly *trans*-2,5-dimethyl-1,3,4-thiadiazolidine; nmr (CCl_4) δ 1.47 (d, J = *ca.* 7 Hz, 6, CH_3) and 4.63 (m, 2, methine H) (the NH resonances were not observed); ir (Nujol) 3250 cm^{-1}.

The above solid (5 g, 42 mmol) and diethyl azodicarboxylate (10 g, 57 mmol) were dissolved in 200 ml of ether and stored overnight at 5°. Working at about 5°, the hydrazo ester was removed and the ether solution was washed with 100 ml of a cold aqueous solution of 10 g of sodium metabisulfite. The solution was dried over $MgSO_4$ and the ether was thereafter removed to leave 3.05 g of crude *trans*- (chief product) and *cis*-2,5-dimethyl-Δ^3-1,3,4-thiadiazoline, which was used immediately without characterization. The crude mixture was dissolved in 5 ml of ether and dimethyl acetylenedicarboxylate (15 ml, excess) was added. The temperature of the solution was gradually raised by distilling off the ether; vigorous gas evolution occurred. The temperature eventually reached 120°. Distillation afforded a mixture of **4c** and **4d** (6.5 mmol, 25%), bp 80–110° (1 mm).

The isomers were separated by preparative glpc using an SE-30 stainless steel column. Compound **4c** had ir (neat) 1050, 1215, 1375, 1435, 1645, 1720, and 2950 cm^{-1}; nmr (CCl_4) δ 1.43 (broad d, J = *ca.* 7 Hz, 6, CH_3), 3.75 (s, 6, OCH_3), and 4.52 (complex m, 2, 2,5-H).

Anal. Calcd for $C_{10}H_{14}O_4S$: C, 52.16; H, 6.13; S, 13.92. Found: C, 51.80; H, 6.13; S, 13.62.

Owing to a shortage of material no other analyses of any derivatives or of the cis isomer were carried out.

Compound **4d** had ir (neat) 1020, 1050, 1090, 1200, 1270, 1370, 1430, 1650, 1720, 2900–3000 cm^{-1}; nmr (CD_3OD) δ 1.52 (broad d, J = *ca.* 7 Hz, 6, CH_3), 3.78 (s, 6, OCH_3), and 4.41 (complex m, 2, 2,5-H).

***cis*-2,5-Dimethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-oxide (20d)** was prepared by allowing **4d** (50 mg, 0.218 mmol) dissolved in 1 ml of cold distilled methylene chloride to react with *m*-chloroperbenzoic acid (43.3 mg, 0.217 mmol) dissolved in 3 ml of methylene chloride. After stirring overnight the solution was washed with aqueous Na_2SO_3 solution and thereafter with water. After drying over $MgSO_4$ evaporation of the solvent yielded 53 mg

Table VI

Diene	Ir, cm^{-1}	Pmr, δ	Anal., %
6	2900–3000, 1740, 1455, 1380, 1260, 1220[a]	1.12 (s, 9, (*E*)-*t*-Bu), 1.22 (s, 9, (*Z*)-Bu), 3.64 (s, 6, 4,5-OCH_3) 5.72 (s, 1,3-H), 6.67 (s, 1, 6-H)[b]	Calcd: C, 68.15; H, 9.29[c] Found: C, 67.74; H, 9.07
7	*a*	1.09 (s, 18, (*E*)-*t*-Bu), 3.67 (s, 6,3,5-OCH_3), 6.72 (s, 2,3,6-H)[b]	*c*
8	*a*	1.06 (s, 18, (*Z*)-*t*-Bu), 3.75 (s, 6,3,5-OCH_3), 5.37 (s, 2,3,6-H)[b]	*c*
13	2900–3000, 1770, 1720, 1630, 1430, 1210, 1080[a]	1.68 (s, 6, (*E*)-CH_3), 2.13 (s, 6, (*Z*)-CH_3), 3.58 (s, 6,3,4-OCH_3)[b]	Calcd: C, 63.71; H, 8.03 Found: C, 63.38; H, 8.03
14	2900, 1700, 1620, 1420, 1240, 1200, 1010, 750[a]	1.81 (d, *J* = 7.5 Hz, (*E*)-CH_3), 2.18 (d, *J* = 7.5 Hz, 3 (*Z*)-CH_3), 3.72 (s, 6,3,4-OCH_3), 6.12 (q, *J* = 7.5 Hz, 1, (*E*)-vinyl H), 7.04 (q, *J* = 7.5 Hz, 1, (*Z*)-vinyl H)[d]	Calcd: C, 60.59; H, 7.12 Found: C, 60.53; H, 7.19
15	2900, 1700, 1620, 1420, 1230, 1030, 760[a]	1.69 (d, *J* = 7.5 Hz, 6, (*E*)-CH_3), 3.72 (s, 6, 3,4-OCH_3), 7.15 (q, *J* = 7.5 Hz, vinyl H)[d]	Calcd: C, 60.59; H, 7.12 Found: C, 60.21; H 7.22
16	2950, 1710, 1630, 1430, 1190, 1010[d]	2.04 (d, *J* = 7.0 Hz, 6, (*E*)-CH_3), 3.72 (s, 6, 3,4-OCH_3), 6.29 (q, *J* = 7.0 Hz, 2, vinyl H)[e]	*g*
17	1725, 1635, 1220, 1250[a]	1.04, 1.07 (overlapping t, 6, *J* = 7.0 Hz, 1,8-CH_3), 2.15 (m,[f] 2,7-CH_2), 2.62 (m,[f] 2,2-CH_2), 3.66, 3.67 (overlapping s, 6, OCH_3), 5.28 (t, 1, *J* = 7.5 Hz, (*E*)-H), 6.75 (t, 1, *J* = 7.5 Hz, (*E*)-H)[b]	Calcd: C, 63.69; H, 8.04 Found: C, 63.39; H, 8.06
18	*g*	0.94 (t, *J* = 7.0 Hz, 6,1,8-CH_3), 1.95 (m,[f] 4, 2,7-CH_2), 3.60 (s, 6, 4,5-OCH_3), 6.80 (t, *J* = 7.4 Hz, 2,3,6-H)	*g*

[a] Measured neat; **7** and **8** not determined separately. [b] In CCl_4. [c] Mixture of **6**, **7**, and **8**. [d] In $CDCl_3$. [e] In CD_3OD. [f] Confirmed by decoupling experiments. [g] Not measured separately.

(0.215 mmol, 99% yield) of **20d** as an oil: nmr (CD_3OD) δ 1.54 (broad d, *J* = 7.5 Hz, 6, CH_3), 3.85 (s, 6, OCH_3), and 4.01 (complex m, 2 H, 2,5-H). Only one isomer could be detected; the somewhat lower shifts of the methyl groups in **20d** compared to **20c** (below) as well as the selectivity of oxidation leads to the tentative conclusion that the sulfoxide bond is located anti to the methyl groups.

***trans*-2,5-Dimethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-oxide (20c)** was prepared as described for **20d** using **4c** (791 mg, 3.44 mmol). There was obtained 710 mg (2.71 mmol, 79% yield) of **20c:** nmr ($CDCl_3$) δ 1.47 (broad d, *J* = 7.5 Hz, 6, CH_3), 3.80 (s, 3, OCH_3), 3.83 (s, 3, OCH_3), and 4.14 (complex q, *J* = *ca.* 7 Hz, 2 H, 2,5-H); ir (neat) 1070 cm^{-1}.

***cis*-2,5-Dimethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-dioxide (19d)** was prepared in the same manner as described for **20d** using **4d** (45 mg, 0.195 mmol) and *m*-chloroperbenzoic acid (76 mg, 0.390 mmol) in 1 ml of dry, cold methylene chloride. Work-up gave 43 mg (0.165 mmol, 85% yield) of **19d** as a white solid: nmr (CD_3OD) δ 1.43 (d, *J* = 7.0 Hz, 6, CH_3), 3.83 (s, 6, OCH_3), and 4.14 (q, *J* = 7.0 Hz, 2, 2,5-H).

***trans*-2,5-Dimethyl-3,4-dicarbomethoxy-2,5-dihydrothiophene *S*-dioxide (19c)** was prepared as described for **20d** using **4c** (1.38 g, 6 mmol) and *m*-chloroperbenzoic acid (2.39 g, 15 mmol). There was obtained 1.57 g (6 mmol, 100% yield) of **19c:** nmr ($CDCl_3$) δ 1.52 (d, *J* = 7.2 Hz, 6, CH_3), 3.85 (s, 6, OCH_3), and 4.10 (broad q, *J* = 7.2 Hz, 2, 2,5-H); ir (neat) 1320, 1135 cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_6S$: C, 45.79; H, 5.38; S, 12.23. Found: C, 45.77; H, 5.35; S, 12.24.

Photochemical Experiments. Most of the photochemical reactions were carried out using a Rayonet R.P.R. 100 photochemical reactor equipped with 16 2537-, 3000- or 3500-Å lamps. The reaction vessels consisted of cylindrical quartz irradiation tubes with either 0.25 in. i.d. and 2 ml capacity, 2.05 in. i.d. and 0.5 l. capacity, or 3 mm i.d. and 0.5 ml capacity. The latter tube fit in a Varian A-60D spectrometer probe and was used for experiments in which the instability of starting material or products required immediate nmr analysis. Degassing was accomplished by at least five freeze–thaw cycles. The irradiated solutions were also monitored by glpc (6 ft × 0.125 in., 10% Carbowax 20M or 10% SE-30 on Chromosorb W AW 80–100 mesh at 200°). Some preparative-scale reactions were done using a Hanau TQ-81 lamp provided with Vycor glass filters. Low-temperature reactions were carried out in the quartz nmr tube mentioned above using an adapted temperature control unit from an esr apparatus to maintain the temperature; the light source was a Philips SP-500 superhigh-pressure lamp. Quantum yields were determined using ferrioxalate actinometry.

Remarks on Individual Irradiations. The spectra of the diene products are described in Table VI. In the case of dihydrothiophenes **4** considerable attention was paid to the isolation and identification of vinyl episulfide intermediates. (In the irradiations of compounds **19** and **20,** when followed by pmr, no trace of an intermediate could be detected. Unfortunately, temperatures in solution could rarely be brought lower than about −20° because of the tendency of the compounds to precipitate.) The vinyl episulfides (spectra given in text) were isolated by carefully concentrating a freshly irradiated solution of **4a** in ether and injecting the solution on a 4-ft glass Carbowax column held at 200°. The effluent was fed through a 10:1 stainless steel splitter connected to a heated outlet and a flame detector, respectively. The material was essentially blown through the column (retention time about 2 min). In this manner about 70–80% pure samples of **9** and **10** were obtained, the pmr spectra of which were obtained with aid of a CAT system. In independent experiments **9** and **10** were shown to be the only products detectable from **4a** directly after irradiation (nmr and glpc). On adding triphenylphosphine at room temperature desulfurization occurred before nmr spectra could be run; the products, **6** and **7,** were formed in the same ratio as **9** and **10**. To establish that **9** and **10** were monomeric, a 200-mg sample of **4c** was irradiated to 23% conversion. Determination of the molecular weight by osmometry in ethyl acetate gave a value of 311.1 ± 4.0 for four measurements. The molecular weight of **4a** (and **9** and **10**) is 314. If **9** and **10** were dimeric the observed molecular weight would have been 314 + (0.103 × 628) = 378. Both **9** and **10** exhibited in the mass spectrum parent peaks at *m/e* 314 with a cracking pattern completely different from that observed with **4a**.

The vinyl episulfides from **4e** were isolated in a manner similar to that described above. A reasonably pure (about 70%) sample of the precursor to **17** was isolated. Overlap with the absorptions for **17** prevents complete assignment. The following partial nmr spectrum was obtained: nmr (CCl_4) δ 2.57 (q, *J* = *ca.* 7 Hz, 2, allylic CH_2CH_3), 3.57–3.90 (complex m, 1, methine H on episulfide ring), and 6.42 (t, *J* = 7.2 Hz, vinyl H). From chemical shift considerations (text) the ethyl group and carboalkoxy group on the double bond are considered to be cis. Desulfurization with triphenylphosphine produced exclusively **17.** Although the precursor to diene **18** was clearly apparent in glpc traces, isolation in sufficient quantities to allow spectral identification was not possible. Because of the symmetry of diene **18,** there exists no ambiguity in the structure of its precursors; the carboalkoxy group and the ethyl group on the three-membered ring must be trans.

A vinyl episulfide (**12a**) was also detected as an intermediate in the photochemical reactions of **4b.** This succeeded only in CD_3OD and the intermediate seemed to be quite unstable. A sample of **4b** was irradiated to 32% conversion and a single new product was detected by nmr (94% yield). In CD_3OD this product had singlet absorptions for four different methyl groups at δ 1.71, 1.91, 1.99, and 2.14. The methoxy peaks could not be located with certainty. Treatment with triphenylphosphine immediately gave **13**. A sample of **13** (0.5 g, 2.21 mmol) and *m*-chloroperbenzoic acid (1.0 g, 5 mmol) were dissolved in 90 ml of carbon tetrachloride and held at 80° for 20 hr. Work-up gave 0.69 g of crude material that was reasonably pure vinyl epoxide **12b**. Purification by thin layer chromatography gave a sample: ir (neat) 2950, 1710, 1620, 1430, 1370, 1280, 1210, 1060, 1000, 790, and 730 cm^{-1}; nmr (CCl_4) δ 1.23 (s, 3, CH_3), 1.34 (s, 3, CH_3), 1.93 (s, 3, CH_3), 2.12 (s, 3, CH_3), and 3.72 (s, 6, OCH_3). The close resemblance to the spectrum of the vinyl episulfide **12a** is to be noted.

Pyrolysis Reactions. Pyrolyses on a gram scale were carried out in a quartz apparatus of standard design consisting of a 30-cm long tube filled with glass shards and heated by electric ovens held at the desired temperature. The tube was connected on one side to a distillation flask (containing starting material, heated by an air bath) and on the other side to two cold traps hooked in series to cool the products. The system was evacuated to 0.05–0.1 mm pressure.

Pyrolyses on a milligram scale could most easily be carried out in tubes, heated in an air bath, or by pyrolysis in a glass injection port of a gas chromatograph.

All diene products were identified by comparison with authentic dienes obtained from photochemical experiments. In the case of **20b**, for which anomalous results were obtained, the pyrolysis was carried out with 429 mg (1.56 mmol) at 540° (0.1–0.4 Torr). An oil (322 mg) was collected in the cold trap. This was separated into **13** (13%), **21** (19%), **22** (6%), and **23** (62%). Compound **13** was identified by comparison with a known sample (Table VI). Product **21** had ir (CCl_4) 1720, 1650, 1630, 1075 and 1035 cm^{-1}; nmr (CCl_4) δ 1.67 (d, J = 7 Hz, 3, CH_3), 1.70 (s, 3, CH_3), 2.22 (s, 3, CH_3), 3.70 (s, 3, OCH_3), 3.77 (s, 3, OCH_3), and 6.86 (q, J = 7 Hz, 1, vinyl H). These nmr data can be reconciled only with **21**. The relatively low field absorption of the vinylic proton indicates it as being cis to the carbomethoxy group. Compound **21** has mass spectrum parent m/e 212 (calcd for $C_{11}H_{16}O_4$, 212).

Product **22** had ir (CCl_4) 1710 and 1430 cm^{-1}; nmr (CCl_4) δ 1.80 (s, 3, CH_3) 2.12 (d, J = 8 Hz, 3, CH_3), 2.15 (s, 3, CH_3), 3.16 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), and 5.93 (q, J = 8 Hz, 1, vinyl H); mass spectrum parent m/e 212 (calcd for $C_{11}H_{16}O_4$, 212). This compound is clearly an isomer of **21**; the higher shift of the vinyl proton indicates that it is trans to the carboalkoxy group.

Compound **23** had ir (CCl_4) 1740, 1720, 1640, 1090, and 1040 cm^{-1}; nmr (CCl_4) δ 1.78 (s, 6, CH_3), 2.02 (s, 3, CH_3), 3.62 (s, 3, OCH_3), 3.65 (s, 3, OCH_3), 4.07 (broad s, 1, CH), 4.78 (broad s, 1, vinyl H), and 4.88 (broad s, 1, vinyl H); mass spectrum parent m/e 226 (calcd for $C_{12}H_{18}O_4$, 226). The fact that two apparently equivalent methyl groups are present was not readily rationalized. However, this was shown to be an accident of chemical shift by using $Eu(thd)_3$ as shift reagent. The δ 1.78 peak in CCl_4 in the presence of 0.3 equiv of $Eu(thd)_3$ separated into separate absorptions at δ 1.99 and 2.05; the methoxy absorptions were at δ 3.92 and 4.00. With 0.7 equiv of $Eu(Thd)_3$ the δ 1.78 peak had separated into a doublet at δ 2.45 and 2.55; the methoxy peaks were at δ 4.44 and 4.85; no other significant changes occurred in the spectrum. These data are all fully consistent with structure **23**.

Acknowledgment. We greatly appreciate several illuminating conversations with Dr. M. J. Janssen of this department. Drs. J. de Wit and W. D. Weringa provided much aid with obtainment and interpretation of pmr spectra. The Netherlands Research Foundation (ZWO) provided a research assistantship for W. L. Prins.[32] We are indebted to Professors D. M. Lemal and N. D. Epiotis for a free exchange of views concerning the interpretations offered here.

Registry No.—**4a**, 30465-51-1; **4b**, 36614-53-6; **4c**, 50443-46-4; **4d**, 50443-47-5; **4e**, 30465-50-0; **4f**, 30646-53-8; **6**, 32016-99-2; **7**, 32017-00-8; **8**, 3207-01-9; **12b**, 51667-98-2; **13**, 6117-26-6; **14**, 51667-95-9; **15**, 51667-96-0; **16**, 51667-97-1; **17**, 32016-97-0; **18**, 32016-98-1; **19a**, 36611-67-3; **19b**, 36614-55-8; **19c**, 50443-40-8; **19d**, 50443-42-0; **20a**, 36611-66-2; **20b**, 36614-54-7; **20c**, 50443-39-5; **20d**, 51744-50-4; **21**, 50443-49-7; **22**, 50443-50-0; **23**, 50443-51-1; *trans*-2,5-dimethyl-1,3,4-thiadiazolidine, 51667-99-3.

References and Notes

(1) (a) For an authoritative discussion of 1,3-dipolar additions, see R. Huisgen, *Angew. Chem.*, **75**, 604 (1963); R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968). (b) For recent theoretical aspects chiefly concerning orientation, see K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Amer. Chem. Soc.*, **95**, 7287 (1973); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973).

(2) It is not common that one can reverse a 1,3-dipolar or a Diels–Alder cycloaddition by irradiating the cycloadduct. This generalization is based of course to a great extent on negative evidence, since it is hard to document reactions that do not occur. A review of this and related matters will appear: R. M. Kellogg, *Advan. Heterocycl. Chem.*, in press. An important exception is found in the photochemistry of a five-membered ring system containing several heteroatoms; 1,3-dipolar species are (apparently) sometimes produced. It is possible that the presence of lone pairs on heteroatoms aids in releasing severe orbital symmetry imposed restrictions on allowed transition state geometries.[3] See, for examples, R. W. Hoffmann and H. J. Luthardt, *Chem. Ber.*, **101**, 3861 (1968); K. K. Meyer, *Tetrahedron Lett.*, 319, 325 (1968); P. Scheiner, *J. Org. Chem.*, **34**, 199 (1969); P. Scheiner and J. F. Dinda, Jr., *Tetrahedron*, **26**, 2619 (1970).

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(5) (a) P. Scribe, D. Hourdin, and J. Wiemann, *C. R. Acad. Sci., Ser. C*, **268**, 178 (1969); (b) P. Scribe, M. R. Monot, and J. Wiemann, *Tetrahedron Lett.*, 5157 (1967); (c) S. J. Cristol, G. A. Lee, and A. L. Noreen, *ibid.*, 4175 (1971).

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(10) (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, pp 184–192; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1966, pp 710–742. (c) For related argumentation, see, for example, B. M. Trost, *Accounts Chem. Res.*, **3**, 120 (1970); J. J. Gajewski and C. N. Shih, *J. Org. Chem.*, **37**, 64 (1972).

(11) This absorption could not be resolved in the CAT spectrum from some **7** present as a contaminant.

(12) The triplet level of dimethyl maleate seems not to be known with certainty. A singlet–triplet absorption is seen at 333 nm (86 kcal/mol): E. S. Albone, *J. Amer. Chem. Soc.*, **90**, 4663 (1968). The lowest triplet must be *ca.* 69 kcal/mol, however, since benzophenone readily sensitizes reactions.

(13) J. Iden and Y. Yura, *Tetrahedron Lett.*, 3491 (1968).

(14) K. Kondo and A. Negishi, *Tetrahedron*, **27**, 4821 (1971).

(15) B. J. Hutchinson, K. K. Andersen, and A. R. Katritzky, *J. Amer. Chem. Soc.*, **91**, 3839 (1969).

(16) At moderate temperature (*ca.* 100°), sulfur monoxide may be trapped by dienes: (a) P. Chao and D. M. Lemal, *J. Amer. Chem. Soc.*, **95**, 920 (1973); (b) D. M. Lemal and P. Chao, *ibid.*, **95**, 922 (1973); (c) R. M. Dodson and R. F. Sauers, *Chem. Commun.*, 1189 (1967); (d) A. G. Anastassiou and B. Y.-H. Chao, *ibid.*, 979 (1971); (e) see also Y. L. Chow, J. N. S. Tam, J. E. Blier, and H. H. Szmant, *ibid.*, 1604 (1970); C. K. Bradsher and D. F. Lohr, *J. Org. Chem.*, **31**, 978 (1966); R. M. Dodson and J. P. Nelson, *Chem. Commun.*, 1159 (1969).

(17) For recent critical discussions of orbital symmetry factors, see (a) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972); (b) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *ibid.*, **5**, 402 (1972). (c) Professor N. D. Epiotis has indicated to us that he is engaged in calculations on "stretched" thiophenes, the geometry of which can correspond to **24** in the configuration drawn. Professor Epiotis has emphasized, and correctly to our minds, the crudeness of the generic term "biradical."

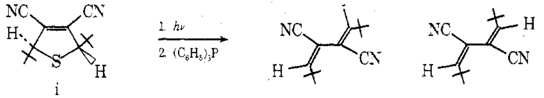
(18) H. E. Zimmermann, *Advan. Photochem.*, **1**, 183 (1963).

(19) (a) For a review of thiyl radicals, see R. M. Kellogg, "Methods in Free Radical Chemistry," Marcel Dekker, New York, N. Y., 1969, pp 1–120. (b) W. C. Lumma, Jr., and G. A. Berchtold, *J. Amer. Chem. Soc.*, **89**, 2761 (1967); *J. Org. Chem.*, **34**, 1566 (1969); P. Y. Johnson and G. A. Berchtold, *ibid.*, **35**, 584 (1970); K. K. Maheshwari and G. A. Berchtold, *Chem. Commun.*, 13 (1969); A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, **93**, 1304 (1971); P. Y. Johnson, *Tetrahedron Lett.*, 1991 (1972); J. Kooi, H. Wynberg, and R. M. Kellogg, *Tetrahedron*, **29**, 2135 (1973).

(20) See, for example, P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and H. H. Hattaway, Jr., *J. Amer. Chem. Soc.*, **95**, 7058 (1973), and references cited therein. This applies to π–π^* excited states of olefins; in **4** we do not know if the lowest excited state (presumably a triplet) is n–π^* or π–π^*. The ready cis-trans isomerization of virtually all olefinic systems on excitation certainly suggests that twisting about the double bond is a very important process.

(21) An alternative is that the barriers to isomerization in the allylic portions of the biradical are low. The barrier in the allyl radical itself is calculated to be 12 kcal/mol: S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968. Whether this fairly high barrier is applicable here in unknown.

(22) (a) Carboalkoxy groups are not essential chromophores. Compound i, formed from addition of the appropriate thiocarbonyl ylide to dicyanoacetylene, is transformed rapidly on irradiation to unstable prod-

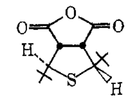


i

ii (major)

iii (minor)

ucts that on treatment with triphenyl phosphine yield ii and iii. (b) After much effort compound iv was prepared in abominable yield by addition of the thiocarbonyl ylide to acetylenedicarboxylic acid followed by dehydration with dicyclohexylcarbodiimide. All other routes attempted failed utterly. It could not be obtained, however, in sufficient quantity or purity to allow investigation of the effect of geometrical constriction.



iv

(23) For a review, see O. P. Strausz, *Organosulfur Chem.*, 11 (1967).

(24) Landolt-Börnstein, Vol. II, Part 4, Springer-Verlag, West Berlin, 1961, pp 180–184.

(25) (a) S. Saito, *Tetrahedron Lett.*, 4961 (1968); (b) W. H. Breckenridge and T. A. Miller, *J. Chem. Phys.*, **56**, 465 (1972).

(26) (a) H. Mackle, *Tetrahedron*, **19**, 1159 (1963); (b) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4861 (1968).

(27) R. G. Pearson, *J. Amer. Chem. Soc.*, **94**, 8287 (1972).

(28) For a simple molecular orbital description, see W. Moffit, *Proc. Roy. Soc., Ser.* **A**, **200**, 409 (1950).

(29) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(30) We are much indebted to Professor D. M. Lemal for an incisive discussion concerning the questions of "allowedness" in these compounds. Professor Lemal's analysis will be published by his group in due course.

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(32) A portion of this work has been abstracted from the Ph.D. Thesis of W. L. Prins, submitted Sept 1973.

Rearrangement of the Tricyclic Orthothio Esters Derived from Mercaptoacetic Acid and Alkanedithiols. Crystal Structure of a Rearrangement Product

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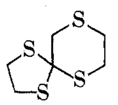
Equimolar amounts of mercaptoacetic acid and ethanedithiol undergo acid-catalyzed condensation to produce a tricyclic ortho ester, 1,4-dithiane-2,5-dione bis(ethylene thioketal). Dissolving this substance in concentrated sulfuric acid followed by quenching with water results in formation of a highly rearranged tricyclic disulfide. By X-ray crystallography the structure of this rearrangement–oxidation product was determined to be 1-[2-(1,3-dithiolanylidene)]-2,3,6,9-tetrathiaspiro[4.4]nonane. Similar condensation and rearrangement reactions were observed when 1,3-propanedithiol was used instead of ethanedithiol. A reaction mechanism involving acid-catalyzed dissociation and recombination is formulated to account for these rearrangements.

Orthothio esters of several simple carboxylic acids have been prepared,[1] generally by straightforward methods involving the direct condensation of the acid, an ester, or its chloride with 3 equiv of the RSH component. The ortho ester **1** of mercaptoacetic acid was described by Backer and Wiggerink[2] as the product resulting from the condensation of chloroacetyl chloride with ethanedithiol. Schöberl and Wiehler[3] prepared symmetrical ortho esters of type **3** by treating dithioglycolide (**2**) with various mercaptans. Boron trifluoride catalyzed self-condensation of mercaptoacetic acid produced the orthothio ester **3b.** Schöberl and Wiehler also described an unusual reaction of their compounds of type **3**, namely their nitration in nitric acid which produced the 1,4-dithiin derivatives **4**.



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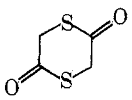

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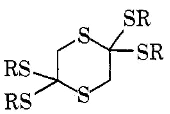
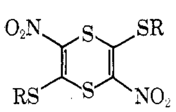
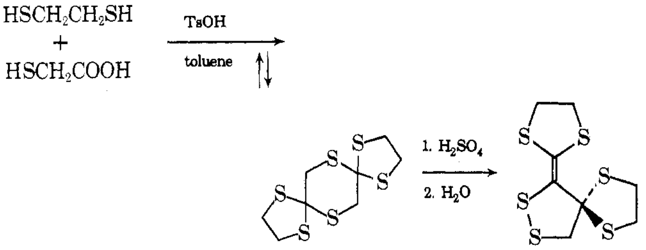


3a, R = phenyl, benzyl
b, R = CH_2COOH



4

The possibility of utilizing compounds of type **4** as progenitors of protected α-mercaptoamino acids evoked our interest in the orthothio esters of mercaptoacetic acid. During the course of our work with compounds of this type, we had occasion to prepare the tricyclic ortho ester **5**, which is easily done, albeit in modest yield, by the direct, acid-catalyzed condensation of equimolar quantities of ethanedithiol and mercaptoacetic acid. The structure of



5

6

this high-melting, poorly soluble, colorless substance is evident from its nmr and mass spectra. The former consists of two signals, an AB quartet at 3.49 ppm (J = 6 Hz)