ether was added 6.4 ml (0.080 mol) of acetyl chloride. An ice bath was used to cool the reaction mixture during the addition. The solution was stirred at room temperature for 24 hr; the pyridinium hydrochloride was filtered off and the solution was washed with 5% HCl, water, saturated sodium bicarbonate solution, saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. After filtration of the magnesium sulfate, the solvent was removed by rotary evaporation and the product was distilled, bp 90–93° (5 mm).

***trans*-Propenylbenzene-*1-d*.** A solution of 7.0 g (0.039 mol) of 1-acetoxy-1-phenylpropane-*1-d* in 50 ml of ether was passed through a column of glass beads at 400° at the rate of 5 drops/min. The pyrolysis was conducted under a stream of dry nitrogen and the product dropped into a collection vessel which had been cooled to −70° in a Dry Ice–isopropyl alcohol bath. The crude olefin was dissolved in ether and washed with saturated sodium bicarbonate solution until no more CO_2 evolved. The ethereal solution was then dried over magnesium sulfate, filtered, and the solvent removed by rotary evaporation. The relative areas of 1 to 3 for the vinyl and methyl proton resonance, the absence of allylic coupling in the methyl resonance the simplified splitting of the vinyl resonance and the absence of the low-field portion of the vinyl resonance as compared to *trans*-propenylbenzene all confirm the structure of the *trans*-propenyl-*1-d*.

Product Studies. The molar concentrations of reactants employed in this work were varied in order to achieve desired ratios of reactants and to ensure solubility. In a typical experiment utilizing a 1:1 ratio of reactants, 0.27 g of Na_2PdCl_4, 0.12 g of phenylcyclopropane, and 6 ml of 2:1 glyme–water were placed in a flask fitted with a reflux condenser. The flask was maintained at 75° for 2 hr during which time palladium precipitation was observed. After cooling the flask to room temperature, the contents were removed with 40 ml of water and the organic product was extracted with two 20-ml portions of ether. After drying the solution with magnesium sulfate the ether solvent was removed to the extent necessary to allow for the analysis desired, *i.e.*, either vpc, nmr, or ir.

Controls were designed to determine if the products and reactants were stable to the finely divided palladium which is produced in the reaction. Palladium was obtained from one reaction by filtration and used in examining the stability of each organic substance under the reaction condition. Of importance to this study is the absence of isomerization of phenylcyclopropane to *trans*-propenylbenzene under the reaction conditions.

Thiirene Dioxides. Synthesis, Characterization, and Reactivity[1]

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Abstract: The synthesis of 2,3-diphenylthiirene 1,1-dioxide (**12**) by a modified Ramberg–Bäcklund reaction is described. α,α'-Dibromodibenzyl sulfone (**11**) was obtained by (a) bromination of dibenzyl sulfide followed by oxidation or (b) brominative decarboxylation of α,α'-diphenylsulfodiacetic acid (**13**). Without separation of the mixture of diastereomeric dibromides, treatment with triethylamine in refluxing methylene dichloride gave **12**. The structure of **12** was established by reduction to the corresponding dihydro derivative, *cis*-2,3-diphenylthiirane 1,1-dioxide (**21**), by means of aluminum amalgam in wet ether. Reaction of **12** with phenyldiazomethane gave α-diazobenzyl 1,2-diphenylvinyl sulfone (**19**). Three alkyl-substituted thiirene dioxides were obtained by a general method which involves generation of a sulfene from an α-bromoalkanesulfonyl chloride and triethylamine in the presence of a diazoalkane. Interaction of the sulfene and diazo compound leads to a bromoepisulfone which is dehydrobrominated by means of triethylamine or a stronger base. The method was applied to the synthesis of the monomethyl (**32**), dimethyl (**38**), and 2-methyl-3-phenyl (**39**) derivatives. The most unusual property of the thiirene dioxides is their marked stability relative to their saturated analogs, a fact which is suggestive of special conjugative effects.

Previously the only stable, isolable compounds incorporating a heteroatom in a cyclopropene ring system were derivatives of the 1-azirine[2] and 1-diazirine[3] systems (**1** and **2**, respectively). Furthermore


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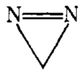
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not a single compound of this type had been synthesized with the heteroatom substituted at position 3 as in **3** (M = O, NH, S, etc.) although several such compounds have been postulated as transient intermediates.[4] In fact special instability has been suggested for those species in this class which bear an unshared electron pair on the heteroatom.[4a,b,e,5]

As part of a general survey of the synthesis of such 3-heteracyclopropenes we have now succeeded in pre-

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[1] (a) Abstracted in part from the Ph.D. Theses of Louis V. McAdams, III, 1966, and John W. Spiewak, 1969, University of Massachusetts; (b) a portion of this work has appeared in preliminary form: L. A. Carpino and L. V. McAdams, III, *J. Amer. Chem. Soc.*, **87**, 5804 (1965); L. A. Carpino and R. H. Rynbrandt, *ibid.*, **88**, 5682 (1966).

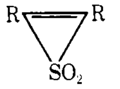
[2] For a brief review, see A. Hassner and F. W. Fowler, *ibid.*, **90**, 2869 (1968).

[3] E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967.

[4] (a) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **86**, 4866 (1964); (b) J. K. Stille and D. D. Whitehurst, *ibid.*, **86**, 4871 (1964); (c) J. Meinwald and D. H. Aue, *ibid.*, **88**, 2849 (1966); (d) R. Huisgen and H. Blaschke, *Chem. Ber.*, **98**, 2985 (1965); (e) D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Commun.*, 147 (1969); (f) J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966); (g) O. P. Strauss, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Amer. Chem. Soc.*, **89**, 4805 (1967); (h) O. M. Nefedow and M. N. Manakow, *Angew. Chem.*, **78**, 1039 (1966).

[5] (a) D. T. Clark, *Theor. Chim. Acta*, **15**, 225 (1969). (b) For a review of the concept of anti-aromaticity as applied to hydrocarbons, see R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **7**, 565 (1968).

paring derivatives of the first examples in this category, the thiirene dioxides **4**.[6] On the basis of a naive analogy with the now well-known cyclopropenones (**5**) the thiirene dioxides were of special interest as a possible new non-benzenoid aromatic system in which aromaticity effects, if any, would require transmission through the d orbitals of the sulfur atom.[7] A hint that the possible analogy between **4** and **5** might have some validity is found in the similarity between the properties reported for the labile thiophene sulfone[9] (**6**) and the transient cyclopentadienone[10] (**7**). If the demonstrated instability of **6** were in fact related to its "anti-Hückel" nature, **4** would be expected to be relatively stable in comparison with the corresponding saturated analogs as is true for the cyclopropenones[11a] relative to the cyclopropanones.[11b] It is recognized, however, that the analogy between sulfones **4** and **6** on the one hand and ketones **5** and **7** on the other may be no more than superficial. Although sulfones of this type have not specifically been treated from a theoretical point of view, extrapolation[12] from discussions of related compounds suggests, according to one approach, that no through-conjugation would be possible in **4** and **6** because of the directional properties of the available d orbitals. From another picture one might expect conjugation effects to be important but not necessarily any Hückel-type periodicity effects.



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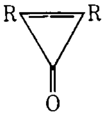

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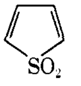

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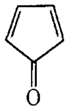

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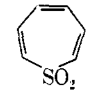

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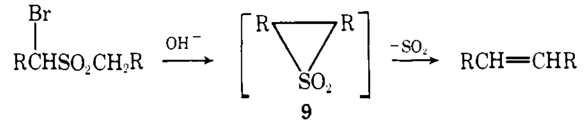
In view of this confused situation[13] it seemed worthwhile to obtain appropriate derivatives of **4** for study of their chemical and spectral properties in order to come to some conclusions regarding their fundamental electronic nature. The 7-ring analog of **4**, thiepin dioxide (**8**), has been synthesized[14] and although it shows little resemblance to tropone there is some question as to how its lack of planarity affects its properties. From nmr[15] and crystallographic[16] data there is some evidence for the importance of conjugative effects in **8**.

In considering approaches to the synthesis of thiirene dioxides we first explored the possible use of the Ramberg–Bäcklund reaction[17] (eq 1) since compelling evidence had been presented by Bordwell and coworkers[18] establishing the intermediacy of episulfones (**9**) in this process. Although no episulfone had ever been isolated from such a reaction these compounds have been synthesized in other ways and exhibit the properties expected of a true intermediate.[19] By utilizing an α,α- or α,α'-dihalosulfone it seemed possible that conditions might be found for the dehydrohalogenation of the halogenated episulfone formed in the first step.[20] The only previous reference we have been able to locate regarding the possible existence of a thiirene dioxide was in the work of Scholnick,[23] who rationalized the formation of phenylacetylene on treatment of benzyl dibromomethyl sulfone with sodium hydroxide by invoking the intermediacy of the monophenyl derivative.



9 (1)

For ease of operation diphenylthiirene dioxide (**12**) was made the target of initial synthetic studies. Bromination of dibenzyl sulfide (**10**) by means of bromine followed by oxidation of the intermediate α,α'-dibromo sulfide gave α,α'-dibromodibenzyl sulfone (**11**) as a mixture of the meso and racemic diastereomers (eq 2). The α,α'-orientation is assigned on the basis of an alternate unequivocal route to **11** involving brominative decar-

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(6) Previously[1b] we have made use of the descriptive "vinylene sulfone" terminology. At the insistence of the reviewers and editors we now substitute systematic *Chem. Abstr.* nomenclature.

(7) For the first systematic listing of these compounds, see M. E. Volpin, Y. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962). The silicon and germanium derivatives described in this work as being the first members of this series have been shown to be dimeric.[8]

(8) (a) F. Johnson and R. S. Gohlke, *Tetrahedron Lett.*, 1291 (1962); (b) R. West and R. E. Bailey, *J. Amer. Chem. Soc.*, **85**, 2871 (1963).

(9) W. J. Bailey and E. W. Cummins, *ibid.*, **76**, 1932, 1936, 1940 (1954).

(10) (a) C. H. DePuy, M. Isaks, K. L. Eilers, and C. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964); (b) for a review, see M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965).

(11) (a) A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(12) For recent reviews relating to d orbital participation in conjugative effects, see (a) M. J. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–440; (b) W. G. Salmond, *Quart. Rev., Chem. Soc.*, **22**, 253 (1968); (c) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(13) Recently a new way of looking at sulfones such as **6** has been suggested as part of the development of the concept of spiroconjugation; see H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967).

(14) W. L. Mock, *ibid.*, **89**, 1281 (1967).

(15) M. P. Williamson, W. L. Mock and S. M. Castellano, *J. Magn. Resonance*, **2**, 50 (1970).

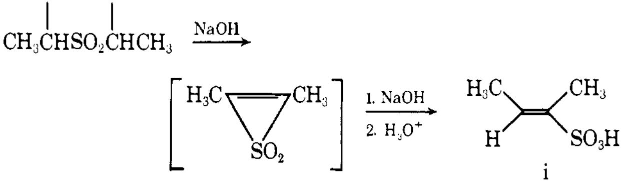
(16) H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock, *J. Amer. Chem. Soc.*, **90**, 4501 (1968).

(17) L. Ramberg and B. Bäcklund, *Ark. Kemi Mineral. Geol.*, **13A**, (27), 1 (1940); *Chem. Abstr.*, **34**, 4725 (1940).

(18) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1951).

(19) (a) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963); (b) N. P. Neureiter, *ibid.*, **88**, 558 (1966); (c) H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916); (d) G. Hesse, E. Reichold, and S. Majmudar, *ibid.*, **90**, 2106 (1957).

(20) In the original description of Ramberg and Bäcklund[17] it is mentioned without experimental detail or other discussion that α,α'-dichlorodiethyl sulfone, on treatment with aqueous sodium hydroxide, gives the sulfonic acid (i). We considered this to be circumstantial evidence for the intermediacy of dimethylthiirene dioxide which would be expected to suffer hydroxide attack to yield i. Recently Paquette[21] and Bordwell[22] and their coworkers have provided substantial evidence for the intermediacy of thiirene dioxides under ordinary Ramberg–Bäcklund conditions.

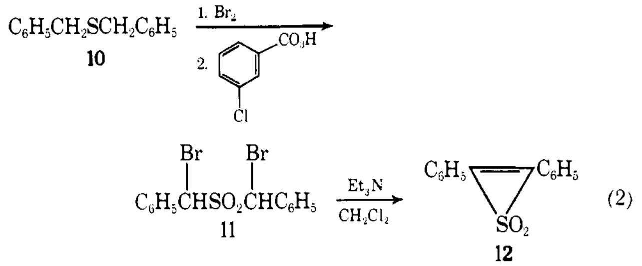


i

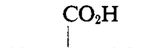
(21) (a) L. A. Paquette and L. S. Wittenbrook, *J. Amer. Chem. Soc.*, **89**, 4483 (1967); (b) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967); (c) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **90**, 6790 (1968).

(22) F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968).

(23) F. Scholnick, Ph.D. Thesis, University of Pennsylvania, 1955. For more recent work, see ref 21 and 22.



boxylation of the corresponding sulfone dicarboxylic acid **13**. Both routes gave a mixture of the same two



$(C_6H_5\overset{CO_2H}{C}H)_2SO_2$ **13**

$C_6H_5CCl_2SOCH_2C_6H_5$ **14**

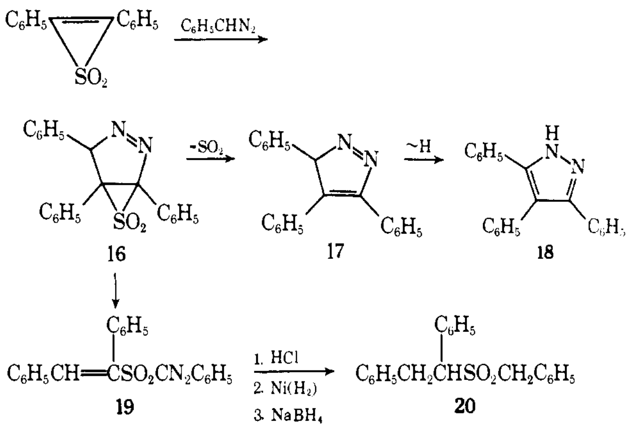
$C_6H_5CCl_2SO_2CH_2C_6H_5$ **15**

isomeric dibromides, the configurations of which were subsequently determined by crystallographic methods.[24] In contrast to bromination, chlorination of **10** by means of *N*-chlorosuccinimide[25] gave the α,α- (**15**) rather than the α,α'-dichlorosulfone. Unequivocal evidence for the α,α-orientation for **15** was obtained by stopping the oxidation at the stage of the corresponding sulfoxide **14**, the nmr spectrum of which showed an AB quartet at δ 3.8 (J = 14 cps) thus establishing the presence of a methylene group adjacent to the asymmetric sulfoxide function.[26,27]

Treatment of the mixture of meso and racemic dibromosulfones (**11**) with triethamine[28] led to the isolation of a compound of molecular formula $C_{14}H_{10}O_2S$ to which structure **12** can confidently be assigned on the basis of its spectral and chemical properties.[29] The infrared spectrum of **12**, a stable, snow-white crystalline solid, mp 116–126° dec, proved to be anomalous in that the asymmetric stretching frequency for the SO_2 group was outside the normal range.[30,31] From the ultraviolet spectrum the conjugated double bond of **12** could be clearly recognized by appearance of the spectrum typical of the 1,2-diphenylcyclopropene chromophore.[32,33]

Although the spectral data are consistent with formulation **12** the structure proof rests on two unique chemical transformations of the compound. The first involved reaction of **12** with phenyldiazomethane which led to the formation of two compounds identified as 3,4,5-triphenylpyrazole (**18**) and α-diazobenzyl 1,2-diphenylvinyl sulfone (**19**). While the pyrazole (**18**) might conceivably have been derived by reaction of diphenylacetylene with the diazo compound it was shown in a separate experiment that these reactants did not give **18** under conditions which caused ready reaction of the vinylene sulfone and phenyldiazomethane. The pyrazole, obtained in 6% yield, is therefore thought to arise from the initially formed 1,3-dipolar cycloaddition product (**16**) by loss of sulfur dioxide (Scheme I).

Scheme I



Concurrently the diazosulfone **19** may be formed from **16** in a ring-opening process analogous to that which has been demonstrated to follow the cycloaddition of tosyl azide to certain enamines.[34,35] As a class, α-diazosulfones have been unknown until recently.[36] Formation of **19** clearly establishes the presence of two carbon–sulfur bonds in the original sulfone. Unambiguous proof of structure **19** (stereochemistry unassigned) was obtained by its transformation into the known sulfone **20** as outlined in Scheme I.

The second transformation of the thiirene dioxide which bears on the structural assignment was more definitive in that the three-membered ring was maintained during the reaction. This involved reduction of the double bond by means of aluminum amalgam[37] at −45° in wet ether to give *cis*-2,3-diphenylthiirane dioxide **21** (Scheme II). The dihydro derivative **21** was made for comparison purposes by two general episulfone syn-

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(24) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968). Professor Bordwell has kindly informed us that the lower melting isomer has the meso configuration.

(25) The use of sulfuryl chloride leads to the formation of the same compound; see L. A. Paquette, *ibid.*, **86**, 4089 (1964).

(26) M. Nishio and T. Ito, *Chem. Pharm. Bull.*, **13**, 1392 (1965).

(27) M. Nishio *ibid.*, **15**, 1669 (1967).

(28) Compare (a) L. A. Carpino, P. H. Terry, and S. D. Thatte, *Tetrahedron Lett.*, 3329 (1964); and (b) R. Breslow, J. Posner, and A. Krebs, *J. Amer. Chem. Soc.*, **85**, 234 (1963).

(29) Substitution of α,α-dichlorosulfone (**15**) for the dibromo compound (**11**) gave a mixture consisting of about equal quantities of **12** and **15**. Since it proved difficult to separate **12** from unreacted **15** this method proved unsuitable as a preparative technique.

(30) (a) D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.* 2442 (1949); (b) L. J. Bellamy and R. L. Williams, *ibid.*, 863 (1957); (c) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961); (d) P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta*, **16**, 1312 (1960); (e) O. Exner, *Collect. Czech. Chem. Commun.*, **28**, 935 (1963).

(31) In the case of a wide variety of compounds containing SO_2 groups (sulfones, sulfonates, sulfonamides, sulfonyl halides, etc). a precise internal correlation is observed between the asymmetric and symmetric stretching frequencies of the SO_2 group.[30b,c] The exact positions of absorption are thought to be due primarily to the inductive effects of the groups attached to the sulfur atom. A shift of the asymmetric band to higher or lower frequencies is always accompanied by a comparable high- or low-frequency shift of the symmetric band. In contrast the thiirene dioxide **12**, in comparison with other aliphatic and aromatic sulfones, shows a marked shift of the asymmetric absorption to lower frequencies accompanied by a lesser shift of the symmetric band to higher frequencies with the result that the Bellamy–Williams correlation no longer holds for this compound. Although no explanation can be offered at present for this anomaly it must in some way be associated with the unusual ring strain and/or specific conjugative effects of the unsaturated 3-ring system. That ring strain alone cannot be responsible for the effect is shown by the fact that the saturated analogs of **12**, the episulfones, fall neatly on the Bellamy–Williams correlation line.

(32) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958).

(33) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

(34) R. Fusco, G. Bianchetti, R. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).

(35) An even closer analog which involves the reaction of diphenylcyclopropenone with 2-diazopropane has recently been described: M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2659 (1969). Cycloadditions of this type make the thiirene dioxides useful synthetic intermediates. For a description of some related cycloadditions, see M. H. Rosen and G. B. Bonet, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN 11.

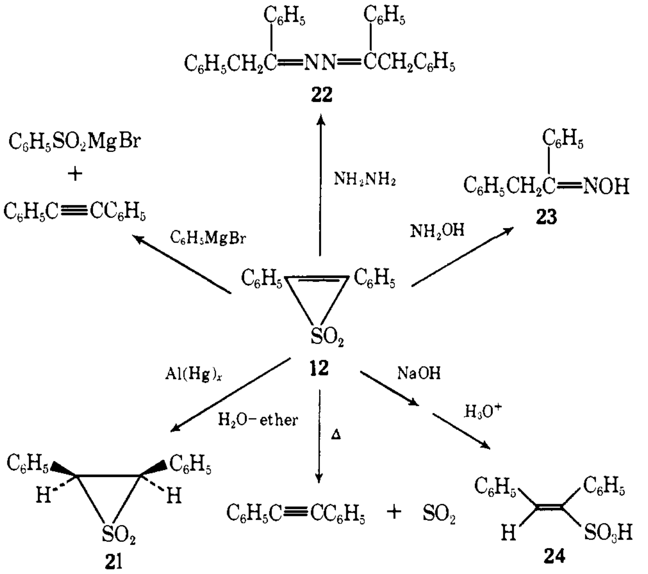
(36) A. M. van Leusen and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **84**, 151 (1965).

(37) L. A. Carpino, *J. Org. Chem.*, **34**, 461 (1969).

theses: (a) treatment of phenyldiazomethane with sulfur dioxide[38a] and (b) treatment of phenylmethanesulfonyl chloride with triethylamine in the presence of phenyldiazomethane.[38b,39]

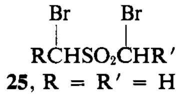
Although not structurally definitive, other reactions of the thiirene dioxide which have been examined are consistent with structure **12** (see Scheme II). Thermal

Scheme II



decomposition to diphenylacetylene and sulfur dioxide occurred by heating briefly at the melting point or by refluxing for several hours in benzene. Attempted diimide reduction using potassium azodicarboxylate[40] was complicated by the known[41] disproportionation of diimide to hydrazine and nitrogen. Addition of the azodicarboxylate to an acetic acid solution of **12** led to the isolation of a small amount of desoxybenzoin azine (**22**). The azine was apparently formed by reaction of the vinylene sulfone with hydrazine since in a separate experiment these two reactants were shown to give **22** in 75% yield. Similarly treatment of **12** with hydroxylamine gave desoxybenzoin oxime (**23**) in 80% yield. Both of these reactions can be rationalized as initial nucleophilic additions to the α,β-unsaturated sulfone system followed by loss of sulfur dioxide and tautomerization. Although Grignard reagents add to the β-carbon of ordinary α,β-unsaturated sulfones,[42] in the case of **12** phenylmagnesium bromide gives diphenylacetylene and the salt of benzenesulfinic acid (isolated as benzyl phenyl sulfone). Lithium aluminum hydride reacts similarly. These reactions are thus comparable to the ring opening observed with aqueous sodium hydroxide which, as expected on the basis of the results obtained on treatment of the dibromosulfone **11** with sodium hydroxide, gives unsaturated sulfonic acid **24**.

It was not possible to extend the Ramberg–Bäcklund reaction to the synthesis of the alkyl-substituted analogs of **12** since aliphatic α,α- and α,α'-dibromosulfones proved too weakly acidic to react with an organic base such as triethylamine. Stronger bases such as aqueous sodium hydroxide react with these dibromosulfones but the thiirene dioxides which are clearly formed as intermediates do not survive the drastic reaction conditions.[21,22] Dibromosulfones **25**, **26**,[43] and **28** were unaffected by treatment with triethylamine in refluxing


$$\overset{Br}{RCH}SO_2\overset{Br}{CH}R'$$

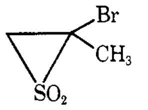
25, $R = R' = H$
26, $R = R' = CH_3$
27, $R = C_6H_5$; $R' = H$

$RCH_2SO_2CHBr_2$
28, $R = CH_3$
29, $R = C_6H_5$

$C_6H_5CH_2SO_2CH_2Br$
30

methylene dichloride. Even the monophenylated derivatives **27** and **29**[44] were either unreactive toward triethylamine or, depending on the conditions, were reduced to **30**.[45]

To avoid this difficulty the Ramberg–Bäcklund intermediates were synthesized in another way.[46] Thus, episulfone **31**, available by reaction of α-bromoethanesulfonyl bromide with triethylamine in the presence of diazomethane, was dehydrobrominated by treatment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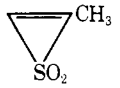
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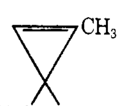
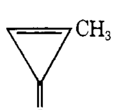
with triethylamine in ether at 0–5° to give sulfone **32**. Structure **32** was confirmed by elemental analysis, decomposition above its melting point to sulfur dioxide and methylacetylene, and its spectral characteristics. In the infrared spectrum the SO_2 bands appeared at positions comparable to those observed in the case of **12**. Since the sulfone bands of **12** are unique this constitutes strong evidence for structure **32**. The nmr spectrum is also consistent with the 3-ring structure. The methyl and vinylic protons are found ($CDCl_3$) at δ 2.50 and 9.04. By way of comparison trimethylcyclopropene (**33**) and methylcyclopropenone (**34**) show these absorptions at (a) δ 2.00 and 6.66 and (b) 2.40 and 8.70, respectively.[47,48] The ^{13}C–H coupling constant observed for the vinylic proton of **32** (J = 230–232 Hz)


33


34

is that expected for a vinylic proton attached to a three-membered ring (the corresponding data for **33** and **34** are 218 and 213 Hz, respectively).[47,48]

In view of the high ^{13}C–H coupling constant observed for **32** it is not unusual that this compound reacts with

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[38] (a) This method was also developed independently by N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, 31, 349 (1966); (b) G. Opitz and K. Fischer, *Angew. Chem.*, 77, 41 (1965).

[39] Formulation **21** rests on these alternate synthetic routes (admittedly not unequivocal), spectral characteristics, the fragmentation to *cis*-stilbene, and analogy with the dimethyl derivative, the structure of which has been established by X-ray diffraction techniques [R. Desiderato and R. L. Sass, *Acta Crystallogr.*, 23, 430 (1967)].

[40] (a) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Lett.*, 347 (1961); (b) S. Hünig, H.-R. Müller, and W. Thier, *ibid.*, 353 (1961); (c) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *J. Amer. Chem. Soc.*, 83, 3725 (1961).

[41] J. Thiele, *Justus Liebigs Ann. Chem.*, 271, 127 (1892).

[42] E. P. Kohler and H. Potter, *J. Amer. Chem. Soc.*, 57, 1316 (1935).

[43] K. Jönsson, Dissertation, Lund University, Lund, Sweden, 1929.

[44] J. M. Williams, Jr., Ph.D. Thesis, Northwestern University, Evanston, Ill., 1966.

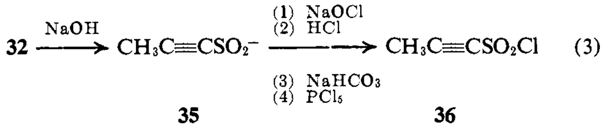
[45] Similar results have recently been reported.[21a,44]

[46] Compare G. Opitz and K. Fischer, *Z. Naturforsch.*, *B*, 18, 775 (1963).

[47] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 85, 99 (1963).

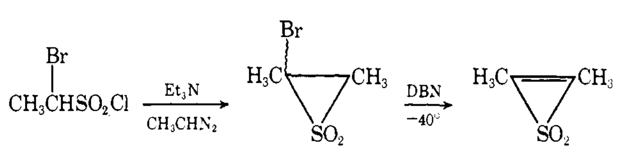
[48] R. Breslow and L. J. Altman, *ibid.*, 88, 504 (1966).

sodium hydroxide in a manner different from that observed in the case of **12**. As previously described, reaction at the acidic proton appears to be followed by rupture of the ring to give an unstable acetylenic sulfinate **35** (eq 3).[1b] Oxidation to the more stable sulfonate followed by treatment with phosphorus pentachloride gave the acetylenic sulfonyl chloride **36**, the structure of which follows from its elemental analysis and spectral characteristics (see Experimental Section).

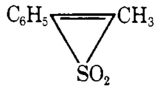


$$\mathbf{32} \xrightarrow{\text{NaOH}} \underset{\mathbf{35}}{CH_3C{\equiv}CSO_2^-} \xrightarrow[\text{(3) NaHCO}_3\ \text{(4) PCl}_5]{\text{(1) NaOCl}\ \text{(2) HCl}} \underset{\mathbf{36}}{CH_3C{\equiv}CSO_2Cl} \quad (3)$$

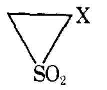
In extending our new thiirene dioxide synthesis to the dimethyl analog **38** it was found that alcohol-free[49,50] solutions of diazoethane must be used to avoid destruction[51] of the intermediate sulfene and a stronger base such as 1,5-diazabicyclo[4.3.0]non-5-ene[52] (DBN) is required for the elimination (eq 4). The properties of **38** were similar to those of **32**. Both showed only end absorption in the ultraviolet region. A similar method was used for the synthesis of the mixed 2-methyl-3-phenyl derivative (**39**). In the case of **40** and **41** most bases caused desulfonylation rather than dehydrohalogenation. For example, addition of 1,4-diazabicyclo[2.2.2]octane to a solution of **41** in deuteriochloroform followed by immediate nmr examination showed complete conversion to vinyl iodide.



37 **38** (4)



39



40, X = Br
41, X = I

Electronic Effects. The most remarkable property of diphenylthiirene dioxide is its great stability relative to its saturated analogs in spite of its additional angle strain, a result which parallels the cyclopropenone–cyclopropanone case.[53] Conjugative effects of the phenyl substituents cannot be solely responsible since a similar stability difference is observed for the corresponding mono- and dimethyl derivatives. In fact the dimethyl derivative **38** proved to be slightly more stable toward thermal fragmentation than the diphenyl derivative **12**. A similar, although more pronounced, effect was noted in a study of the decarbonylation of di-*n*-propyl- and diphenylcyclopropenone which showed that the latter decomposed five times faster than the former at 190°.[56] In the sulfone series the difference between **38** and **12** is only about 1.2 at 75°. It is not clear what significance should be attached to this slight difference which could represent a greater stabilizing influence of the alkyl groups on the thiirene dioxide or greater stabilization by the phenyl groups of the transition state for fragmentation. One estimate[44] suggests that the thermal decomposition of episulfone **21** is about 10^3 times as rapid as that of the thiirene dioxide **12**. On the basis of the present data it is not possible to conclude whether this stability is to be associated with simple conjugative effects of the α,β-unsaturated sulfone system or should be related to possible through-conjugation. Thermochemical studies[57] showed no significant stabilization due to simple conjugation in the case of thiete sulfone. While this suggests that special conjugative effects may be operable in the case of the thiirene dioxides, a clear answer to this question must await the availability of appropriate thermochemical data in the 3-ring series. The dipole moment of sulfone **12** (5.63 D)[58] is only slightly greater than that reported for diphenyl sulfone (5.12 D).[59] By contrast the moment of diphenylcyclopropenone (5.14 D)[33] is much larger than that of benzophenone (3.00 D). Although this suggests significantly less conjugative interaction in the case of the thiirene dioxide, definitive conclusions cannot be reached until studies on more suitable models are complete.[58] It is interesting in this connection that the unconjugated cyclopropene **33** shows long-range coupling between the methyl and vinylic protons (J = 1.1 Hz) whereas the nmr absorptions of the conjugated ketone **34** are reported to be singlets. Coupling of the same magnitude as in **33** is observed for **32** (J = 1.1 Hz). If the extent of such allylic coupling can be considered a measure of bond order[60] these data argue for significantly less interaction in the sulfone than in the ketone. From the data so far available no clear picture emerges as to the electronic nature of this new class of heterocycles. Additional and more refined spectral and structural studies are in progress.

Experimental Section[61]

α,α-Dichlorodibenzyl Sulfoxide (14). To a stirred solution of 21.4 g of dibenzyl sulfide in 200 ml of anhydrous CCl_4 was added 34.0 g of *N*-chlorosuccinimide. The mixture was refluxed for 3

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(49) The diazomethane synthesis of F. Arndt ("Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, pp 165, 461) was modified by the use of *N*-nitroso-*N*-ethylurea.

(50) Compare D. Kubik and V. I. Sternberg, *Chem. Ind.* (*London*), 248 (1966).

(51) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(52) H. Oediger, H.-J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(53) See ref 11. The difference is greater in the ketone case since episulfones are generally isolable, even though rather unstable, whereas cyclopropanones are generally not isolable under ordinary conditions. In addition the cyclopropenones are far more stable thermally[54] and toward base-catalyzed[55] ring opening than the corresponding sulfones.

(54) Diphenylcyclopropenone has a half-life[33] of about 5 min at 190° whereas diphenylthiirene dioxide decomposes instantaneously at its melting point.

(55) F. G. Bordwell and S. C. Crooks, *J. Amer. Chem. Soc.*, **91**, 2084 (1969).

(56) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

(57) H. Mackle, D. V. McNally, and W. V. Steele, *Trans. Faraday Soc.*, **65**, 2060 (1969).

(58) We are indebted to Drs. Otto Exner and V. Jehlicka, Czechoslovak Academy of Sciences, Prague, for this measurement which was taken in benzene solution. A comprehensive study of the dipole moments of several aryl- and alkyl-substituted thiirene dioxides and their saturated analogs is now being carried out in our laboratories.

(59) V. Baliah and S. Shanmuganathan, *Trans. Faraday Soc.*, **55**, 232 (1959).

(60) (a) S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964); (b) P. Raoul and J. Ville, *Bull. Soc. Chim. Fr.*, 1670 (1959); (c) P. L. Corio and I. Weinberg, *J. Chem. Phys.*, 31, 569 (1959).

(61) Melting and boiling points are uncorrected. Infrared spectra were obtained on Beckmann IR-5 and IR-10 and Perkin-Elmer 247B and 510 instruments, ultraviolet spectra on Cary 14 and PE 202 spectrometers, and nmr spectra on an A-60 unit with TMS as internal standard. Elemental analyses were carried out by Charles Meade and associates, University of Massachusetts Microanalytical Laboratory,

hr, cooled, filtered, and evaporated at 50° with a water aspirator. The residue was dissolved in 100 ml of anhydrous ether, the solution cooled in an ice bath and treated with 18.2 g of perphthalic acid over a period of 30 min. The mixture was allowed to stir at room temperature for 24 hr, the mixture filtered to remove precipitated phthalic acid, and the filtrate evaporated at room temperature under reduced pressure to an oil which solidified upon trituration with ligroin (bp 30–40°). After several recrystallizations from benzene–ligroin (bp 90–120°) (1:1) there was obtained 8.1 g (27%) of the dichloro sulfoxide, mp 85–90°. The analytical sample had mp 86.5–89.5° (C_2H_5OH); ir ($CHCl_3$) 9.2 μ (SO), nmr ($CDCl_3$) δ 3.8 (AB quartet, J_{AB} = 14 Hz, 2 H, CH_2), 7.55 (m, 10 H, phenyl). Further oxidation by means of *m*-chloroperbenzoic acid gave the corresponding sulfone **15**, mp 133.5–135° (lit.[25] mp 134–135°).

Anal. Calcd for $C_{14}H_{12}Cl_2OS$: C, 56.21; H, 4.01; Cl, 23.71; S, 10.72. Found: C, 55.85; H, 4.25; Cl, 23.57; S, 10.84.

α,α′-Diphenylthiodiglycolic Acid. To a mixture of 223 g of α-bromophenylacetic acid and 1250 ml of water there was added 158 g of sodium carbonate dissolved in 700 ml of water. The resulting solution was treated with a cold solution (10–15°) of 104 g of Na_2S (60–62% fused flakes) in 700 ml of water (initially prepared by warming to dissolve the sulfide). The mixture was stirred for 3 hr at room temperature, heated to the boiling point, filtered while hot, and acidified with HCl (3 *N*). Upon cooling and filtering there was obtained 123 g (78%) of the crude acid, mp 120–140°. Further purification was unnecessary in carrying out the subsequent reactions. After many recrystallizations from nitromethane the meso isomer, mp 177–180° (lit.[62] mp 179–180°), was obtained in a pure state.

α,α′-Dibromodibenzyl Sulfone (11). (A) From α,α′-Diphenylthiodiglycolic Acid. A solution of 24.8 g of crude α,α′-diphenylthiodiglycolic acid (mp 120–140°) in 250 ml of glacial acetic acid was cooled in an ice bath and 37.4 g of 30% H_2O_2 added over a period of 30 min. The mixture was stirred at room temperature for 3 days and if a precipitate was present it was removed by warming. There was added a solution prepared from 30 g of Br_2 in 150 ml of water containing 30 g of KBr. A 275-W G. E. sunlamp was focused on the mixture from a distance of 10 mm. At 50° gas evolution began and a solid was precipitated. During irradiation the solution was gradually heated to 80° and held at this point for 30 min. The mixture was then cooled, filtered, and the solid washed with 200 ml of water and 100 ml of cold ethanol (5–10°) to give 10 g (30%) of crude sulfone, mp 130–145°. The mixture of diastereomers was used without purification in the next step. By recrystallization from ethanol it was possible to separate two isomeric dibromides. The meso[24] isomer had mp 155–157.5°; ir ($CHCl_3$) 7.41, 8.62, 8.79 μ (SO_2); nmr ($CDCl_3$) δ 5.75 (s, 2 H, CHBr), 7.45 (m, 10 H, phenyl).

Anal. Calcd for $C_{14}H_{12}Br_2O_2S$: C, 41.60; H, 3.00; Br, 39.55; S, 7.93. Found: C, 41.81; H, 3.11; Br, 39.82; S, 8.05.

The racemic[24] isomer had mp 162–164°; ir ($CHCl_3$) 7.49, 8.66, 8.80 μ (SO_2), nmr ($CDCl_3$) δ 6.27 (s, 2 H, CHBr), 7.40 (m, 10 H, phenyl).

Anal. Found: C, 41.66; H, 3.02; Br, 39.71; S, 8.13.

(B) From Dibenzyl Sulfide. To a gently refluxing solution of 22.7 g of dibenzyl sulfide in 300 ml of CCl_4 (distilled over P_2O_5) there was added over 1.5 hr 35.2 g of Br_2 in 100 ml of CCl_4 while shining a 275-W G. E. sunlamp on the solution from a distance of 10 mm. After refluxing for 3 hr the CCl_4 was removed by distillation from a water bath (50°) at reduced pressure. The residual oil was treated with 50 ml of anhydrous ether, the solution cooled in an ice bath, and 65 g of *m*-chloroperbenzoic acid (80%) in 300 ml of anhydrous ether added over 30 min. The mixture was brought to room temperature and stirred for 2 days. The ether was allowed to evaporate spontaneously or by means of an air jet and the residual solid treated with saturated $NaHCO_3$ solution until gas evolution ceased. Filtration of the solid followed by washing with 200 ml of water and 100 ml of cold ethanol (10–15°) gave 12.8 g (30%) of the crude sulfone, mp 140–155°. The crude mixture of diastereomers was used for further work. By repeated recrystallization from ethanol the same two isomeric dibromides as described in method (A) could be obtained in pure form. In addition, in one case only, a third dibromide, mp 146.5–148.5°, was obtained which is believed to be a polymorphic modification of the isomer, mp 155–157.5° on the basis of infrared and nmr spectral comparisons.

Anal. Calcd for $C_{14}H_{12}Br_2O_2S$: C, 41.60; H, 3.00; Br, 39.55; S, 7.93. Found: C, 41.54; H, 2.98; Br, 39.52; S, 8.02.

2,3-Diphenylthiirene 1,1-Dioxide (12). To a solution of 63.6 g of crude α,α′-dibromodibenzyl sulfone (mp 130–145°) in 400 ml of CH_2Cl_2 there was added 50.5 g of triethylamine and the solution refluxed gently for 3 hr. The solution was washed with two 200-ml portions of dilute HCl (3 *N*) followed by 100 ml of water. Evaporation of the CH_2Cl_2 by distillation from a water bath at 30° with the aid of a water aspirator followed by washing of the residue with 50 ml of cold ethanol (5°) gave 34.1 g (90%) of the crude sulfone, mp 116–126° dec. Recrystallization from benzene gave 26.5 g (70%) of the thiirene dioxide as a snow-white solid, mp 116–126° dec (varies with rate of heating); ir (CCl_4) 7.85, 8.59 μ, ($CHCl_3$) 7.95, 8.66 μ (SO_2); uv max (95% C_2H_5OH) 222.5 mμ (log ϵ = 4.26), 296 (4.34), 307 (4.41), 322 (4.27); nmr ($CDCl_3$) δ 7.55 (m, phenyl).

Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.40; H, 4.17; S, 13.23; mol wt, 242. Found: C, 69.62; H, 4.11; S, 13.18; mol wt (vapor osmometry in $CHCl_3$ and C_6H_6, respectively), 245, 253.

Thermal Decomposition of 2,3-Diphenylthiirene 1,1-Dioxide. A small beaker containing 0.85 g of the thiirene dioxide was placed in an oil bath at 120–130° for 5 min. Vigorous gas evolution occurred. After cooling, the resulting oil solidified to give 0.6 g (97%) of diphenylacetylene, mp 57–60° (lit.[63] mp 58–59°), identified by mixture melting point and comparison of the infrared spectrum with that of an authentic sample. Another decomposition was carried out by heating in a sealed tube at 125–140° for 2 days a solution of 0.73 g of **12** and 0.2 g of *trans*-1,2-diphenylbenzocyclobutene[64,65] in 40 ml of CCl_4. Upon cooling and filtering there was obtained 0.1 g (42%) of 1,3-diphenyl-1,3-dihydroisothianaphthene 2,2-dioxide, mp 226–229° dec (lit.[64] mp 232.5–234°), identified by mixture melting point and infrared spectral comparison with an authentic sample.

Treatment of 2,3-Diphenylthiirene 1,1-Dioxide with Sodium Hydroxide. A mixture of 3.3 g of NaOH, 2.04 g of **12**, and 60 ml of water was refluxed for 30 min, the resulting solution cooled, made strongly acidic with HCl (3 *N*), and treated with 1.77 g of *p*-toluidine. An immediate precipitate separated. Cooling and filtering gave 2.7 g (90%) of the *p*-toluidine salt of 1,2-diphenylethylene-1-sulfonic acid (**24**), mp 195–199° dec (lit.[25] mp 198° dec) identified by infrared spectral comparison with an authentic sample. The same compound was obtained by direct treatment of α,α′-dibromodibenzyl sulfone with sodium hydroxide.

Aluminum Amalgam Reduction of 2,3-Diphenylthiirene 1,1-Dioxide. To a mixture of 1 g of **12** in 100 ml of water-saturated ether ("fat extraction" ether containing 0.5% ethanol) cooled to −45° by means of a Dry Ice–acetone bath was added 10 g of freshly prepared Hahn-Thieler aluminum amalgam.[37] The mixture was stirred for 1 hr at −45° and then filtered through Celite filter aid. The mixture remaining on the filter aid was extracted with 100 ml of $CHCl_3$ and the solution evaporated to give the unreacted vinylene sulfone in 50% recovery. Evaporation of the filtrate from the original reaction mixture by means of a rapid air jet at room temperature gave 0.25 g of a pale yellow solid, mp 74–105° dec. The infrared spectrum showed this to be mainly *cis*-2,3-diphenylthiirane dioxide **21** contaminated by small amounts of the unreacted thiirene dioxide and *trans*-stilbene. One recrystallization from $CHCl_3$–ether (1:1) gave 0.08 g (16% based on recovered starting material) of the episulfone, mp 78–84° dec, identified by comparison of its infrared spectrum with that of an authentic sample.

***cis*-2,3-Diphenylthiirane 1,1-Dioxide (21).** To a solution of phenyldiazomethane (0.012 mol) in 75 ml of ether cooled to 8–10° there was added simultaneously from two burets a solution of 2.29 g of phenylmethanesulfonyl chloride in 100 ml of ether and one of 1.32 g of triethylamine in 25 ml of ether. The addition required 3 min after which the mixture was stirred at 8–10° for 30 min, washed with 175 ml of water, evaporated, and the residue recrystallized from $CHCl_3$–ether. There was obtained 0.62 g (21%) of the episulfone (**21**): mp 84–86° dec (lit.[66] mp 83–85° dec); ir (CCl_4) 7.43, 8.62, ($CHCl_3$) 7.49, 8.67 μ (SO_2); nmr ($CDCl_3$) δ 4.8 (s, 2 H,

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(62) T. Mazonski and B. Prajsnar, *Zesz. Nauk. Politech. Slask. Chem.*, (7), 17 (1961); *Chem. Abstr.*, **62**, 13079*d* (1965).

(63) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 1 (1928).

(64) F. R. Jensen and W. E. Colman, *J. Amer. Chem. Soc.*, **80**, 6149 (1958).

(65) L. A. Carpino, *ibid.*, **84**, 2196 (1962).

(66) J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); *Can. J. Chem.*, **44**, 819 (1966).

CH), 7.15 (m, 10 H, phenyl). Upon standing at room temperature in the solid state or in solution the sulfone decomposed in 2–3 days to *cis*-stilbene. The episulfone **21** was also obtained from phenyldiazomethane and SO_2.

Treatment of 2,3-Diphenylthiirene 1,1-Dioxide with Hydrazine. To a stirred solution of 2 g of **12** in 50 ml of dioxane was added 2 g of 85% hydrazine hydrate. After 2 days standing at room temperature the solution was decanted from a small amount of insoluble tacky material and evaporated at 50° under reduced pressure to a yellow oil which solidified on standing. After several recrystallizations from ethanol there was obtained 1.2 g (75%) of desoxybenzoin azine (**22**), mp 160–163° (lit.[67] mp 164°), identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Treatment of 2,3-Diphenylthiirene 1,1-Dioxide with Hydroxylamine. To a stirred solution of 1.2 g of **12** in 40 ml of dioxane was added a solution of 2.4 g of sodium acetate and 3 g of hydroxylamine hydrochloride in 40 ml of water. After 9 hr at room temperature the solution was evaporated under reduced pressure from a water bath at 50° to a yellow oil. The oil was dissolved in ether, the solution dried ($MgSO_4$) and evaporated, and the residual semisolid material recrystallized from 50% aqueous ethanol to give 0.8 g (76%) of desoxybenzoin oxime (**23**), mp 92.5–95.5° (lit.[68] mp 98°), identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Treatment of 2,3-Diphenylthiirene 1,1-Dioxide with Phenyldiazomethane. To an ethereal solution of phenyldiazomethane prepared from 11 g of azibenzil according to the method of Yates and Shapiro[69] there was added 7.2 g of **12**. The mixture was stirred for 20 hr and filtered to give 0.9 g of a white solid, mp 160–245°, which after recrystallization from ethanol afforded 0.5 g (6%) of 3,4,5-triphenylpyrazole (**18**), mp 259–261° (lit.[70] mp 265°), identified by elemental analysis, mixture melting point and infrared spectral comparison with an authentic sample. Evaporation of the ether filtrate from the original reaction mixture under reduced pressure at room temperature gave an orange solid which was recrystallized from ether and ethanol–ether (1:1) to give 4.8 g (44%) of **α-diazobenzyl 1,2-diphenylvinyl sulfone** (**19**), mp 109.5–111.5° dec; the analytical sample had mp 112–114° dec; ir ($CHCl_3$) 4.82 μ (C=N=N), 6.15 μ (C=C), 7.55, 8.58, 8.79 μ (SO_2); nmr ($CDCl_3$) δ 7.3 (m, 15 H, phenyl), 7.8 (s, 1 H, =CH).

Anal. Calcd for $C_{21}H_{16}N_2O_2S$: C, 69.97; H, 4.48; N, 7.77; S, 8.89. Found: C, 70.11; H, 4.24; N, 7.72; S, 9.07

α-Chlorobenzyl 1,2-Diphenylvinyl Sulfone. Gaseous HCl was bubbled very slowly into a stirred solution of 2.3 g of α-diazobenzyl 1,2-diphenylvinyl sulfone in 150 ml of ice-cold ether until the orange color was discharged. The resulting yellow solution was washed with 50 ml of saturated $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated under reduced pressure at room temperature to a yellow solid which was recrystallized from ethanol to give 1.2 g (51%) of α-chlorobenzyl 1,2-diphenylvinyl sulfone as white crystals: mp 129.5–131°; ir ($CHCl_3$) 6.15 μ (C=C), 7.58, 8.62, 8.83 μ (SO_2); nmr ($CDCl_3$) δ 5.41 (s, 1 H, CHCl), 7.95 (s, 1 H, =CH), 7.40 (m, 15 H, phenyl).

Anal. Calcd for $C_{21}H_{17}ClO_2S$: C, 68.37; H, 4.65; Cl, 9.61; S, 8.69. Found: C, 68.29; H, 4.95; Cl, 9.56; S, 8.86.

Benzyl 1,2-Diphenylvinyl Sulfone. A mixture of 4.5 g of α-chlorobenzyl 1,2-diphenylvinyl sulfone, 7 g of Raney nickel (previously washed five times with 95% ethanol and five times with anhydrous ethanol), and 3 g of NH_4OAc in 150 ml of anhydrous ethanol and 50 ml of anhydrous dioxane was hydrogenated for 5 hr on a Parr apparatus at 40 psi. The mixture was filtered, evaporated to dryness under reduced pressure at 50°, and the residue treated with 100 ml of $CHCl_3$ and 150 ml of water. Separation of the $CHCl_3$ layer, drying ($MgSO_4$), and evaporation at 45° under reduced pressure gave a solid which was recrystallized from ethanol to give 3.2 g (80%) of the sulfone: mp 156–158° (lit.[71] mp 158°); ir ($CHCl_3$) 6.15 μ (C=C), 7.62, 8.62, 8.85 μ (SO_2); nmr ($CDCl_3$) δ 4.15 (s, 2 H, CH_2), 7.40 (m, 16 H, =CH and phenyl).

Benzyl 1,2-Diphenylethyl Sulfone (20). To a solution of 1 g of benzyl 1,2-diphenylvinyl sulfone in 50 ml of dioxane and 50 ml of ethanol was added 1 g of $NaBH_4$ dissolved in 20 ml of water. After refluxing for 15 hr solvent was removed at 50° under reduced pressure. The residual solid was dissolved in 30 ml of water and 30 ml of $CHCl_3$ and the chloroform layer dried (Na_2SO_4) and evaporated. Recrystallization of the residue from 50% aqueous ethanol gave 0.9 g (90%) of **20**, mp 120.5–123° (lit.[72] mp 123.5–125°), identified by mixture melting point and infrared spectral comparison with an authentic sample.

α,α′-Dibromodimethyl Sulfone (25). To a stirred solution of 56 g of sulfodiacetic acid dissolved in 500 ml of acetic acid there was added at 100° over a 3-hr period 160 g of bromine dissolved in 1000 ml of water containing 100 g of potassium bromide. After complete addition the solution was refluxed for 30 min and evaporated at 70° with the aid of a water aspirator to a volume of 500 ml. The remaining solution was cooled to room temperature and poured into 2 l. of crushed ice. Filtration gave 30.5 g (40%) of white solid, mp 65–80°. Two recrystallizations from carbon tetrachloride gave 22 g (28.5%) of the dibromo sulfone, mp 81–84°. The analytical sample had mp 83–84.5°; ir ($CHCl_3$) 7.46, 8.42, 8.75 μ (SO_2); nmr ($CDCl_3$) δ 4.69 (s, CH_2).

Anal. Calcd for $C_2H_4Br_2O_2S$: C, 9.53; H, 1.60; Br, 63.44; S, 12.72. Found: C, 9.96; H, 1.87; Br, 63.52; S, 12.83.

Dibromomethyl Ethyl Sulfone (28).[73] To a solution of 90 g of $NaHCO_3$ in 550 ml of H_2O there was added slowly 46 g of mercaptoacetic acid. The flask was fitted with a dropping funnel and an efficient reflux condenser. With stirring and heating to 60–70° 55 g of ethyl bromide was added over a period of 1.5 hr after which the mixture was heated at this temperature for another 11 hr, cooled, carefully acidified with HCl and extracted with three 300-ml portions of ether. The combined extracts were dried (Na_2SO_4) and distilled to give 43 g (72%) of crude thioethoxyacetic acid, bp 61–64° (0.2 mm). The crude acid was dissolved in 200 ml of glacial HOAc and 100 ml of 30% H_2O_2 was added portionwise with cooling over a 3-hr period. The temperature was maintained at 40–50° (caution is required since the reaction is very exothermic and may show an induction period). The solution was cooled in an ice bath to 10° and treated slowly with a solution of 115 g of Br_2 in 450 ml of 30% KBr while irradiating with a 275-W GE sunlamp. After the end of the addition the temperature was allowed to rise to 50–60° and held at this point for 1 hr. The solution was then cooled, diluted to 1.5 l. with H_2O, neutralized with Na_2CO_3, and extracted with two 400-ml portions of ether. The extracts were washed with Na_2CO_3, H_2O, dried (Na_2SO_4), and solvent removed. The residue was recrystallized from CCl_4 to give 26 g (28%) of the sulfone, mp 54.5–56°; ir ($CHCl_3$) 7.45, 8.64, 8.83 μ (SO_2); nmr ($CDCl_3$) δ 1.52 (t, 3, CH_3), 3.52 (q, 2, CH_2), 6.33 (s, 1, $CHBr_2$).

Anal. Calcd for $C_3H_6BrO_2S$: C, 13.55; H, 2.26; Br, 60.10; S, 12.05. Found: C, 13.67; H, 2.41; Br, 60.38; S, 12.03.

α-Phenylthiodiacetic Acid. A suspension of 36 g of methyl mercaptoacetate and 90 g of $NaHCO_3$ in 550 ml of water was heated at about 80° for 30 min (until a homogeneous solution formed). There was then added 71 g of α-bromophenylacetic acid and the solution maintained at 80–90° for 1 hr, cooled, acidified with dilute HCl, and extracted twice with 250-ml portions of ether. The extracts were dried (Na_2SO_4), the solvent removed and the residue recrystallized twice from water to give 45 g (60%) of the acid as white crystals: mp 128–129°; nmr (D_2O) δ 3.22 (s, 2, CH_2), 4.79 (s, 1, CH), 7.24 (s, 5, C_6H_5).

Anal. Calcd for $C_{10}H_{10}O_4S$: C, 53.10; H, 4.42; S, 14.20. Found: C, 52.95; H, 4.55; S, 14.06.

Dibromomethyl α-Bromobenzyl Sulfone. A solution of 42 g of α-phenylthiodiacetic acid in 250 ml of glacial HOAc was treated with 51 g of 30% H_2O_2. The solution was stirred overnight at room temperature (the temperature gradually rose spontaneously to about 75° and then began to drop again). Solvent was removed on a rotary evaporator below 35° until a volume of 125 ml remained, 200 ml of H_2O was added, and the solution extracted with ether after saturating with NaCl. Removal of ether from the dried (Na_2SO_4) extracts gave a solid which was partially purified by digesting with hot $CHCl_3$, filtering and discarding the filtrate. The crude solid (22 g, 47%) had mp 140–144° and was used as such in the next step. Recrystallization from $CHCl_3$ raised the melting point to 154–155° but an analytically pure sample was not obtained. A solution of 2.58 g of α-phenylsulfoacetic acid in 8 ml of HOAc and 4 ml of H_2O was cooled to 10° in an ice bath and treated dropwise with stirring with a solution of 4.8 g of Br_2 in 15 ml

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of 30% KBr solution while irradiating with a 275-W G. E. sunlamp. The temperature was maintained near 10° during the addition and for an additional 30 min after which the temperature was raised to 50° for 1 hr. The solution was cooled, diluted with 75 ml of H_2O, extracted several times with ether, and the combined extracts were washed with 20% Na_2CO_3 solution. After drying (Na_2SO_4) removal of ether on a rotary evaporator gave a yellow oil which slowly crystallized to give 3.54 g (76%) of the sulfone; after recrystallization from CCl_4 the sulfone had mp 92.5–93.5°; nmr ($CDCl_3$) δ 6.37 (s, 1, *CH*Br or *CH*C_6H_5), 6.42 (s, 1, *CH*Br or *CH*C_6H_5), 7.5 (m, 5, C_6H_5).

Anal. Calcd for $C_8H_7Br_3O_2S$: C, 23.60; H, 1.72; Br, 58.90; S, 7.88. Found: C, 23.55; H, 1.86; Br, 59.01; S, 8.00.

Bromomethyl α-Bromobenzyl Sulfone (27). A slurry of 0.5 g of dibromomethyl α-bromobenzyl sulfone in 25 ml of 75% methanol was treated dropwise with stirring over a period of 1 hr with a solution of 0.25 g of $NaHSO_3$ in 15 ml of 75% methanol. After stirring for an additional 1.5 hr at room temperature the solution was diluted with 200 ml of cold H_2O and extracted with two 100-ml portions of ether. After drying over Na_2SO_4 removal of solvent gave a solid which was recrystallized from absolute ethanol to give 0.3 g (75%) of the sulfone as white crystals: mp 85–86°; ir ($CHCl_3$) 7.50, 8.70, 8.80 μ (SO_2); nmr ($CDCl_3$) δ 4.45 (q, 2, CH_2Br), 6.15 (s, 1, CHBr), 7.45 (m, 5, C_6H_5).

Anal. Calcd for $C_8H_8Br_2O_2S$: C, 29.20; H, 2.44; Br, 48.70; S, 9.97. Found: C, 29.10; H, 2.54; Br, 49.07; S, 9.93.

If this reaction is carried out at reflux temperature the product is benzyl bromomethyl sulfone (**30**), mp 140–141° (lit.[44] mp 142.3°), identified by comparison with an authentic sample obtained by reduction of benzyl dibromomethyl sulfone.[22,23,74]

2-Iodothiirane 1,1-Dioxide (41). Treatment of diazomethane in dry ether with ICH_2SO_2Cl[75] and Et_3N according to the method described for the 2-bromo-2-methyl analog gave the episulfone in 36–50% yield. After recrystallization from ether (−78°) the sulfone had mp 78–81°; ir ($CHCl_3$) 7.49, 8.40, 8.69 μ (SO_2); nmr ($CDCl_3$) δ 3.05 (q, 1, J = 9.3 and 7.0 Hz), 3.82 (q, 1, J = 10.5 and 9.3 Hz) and 4.75 (q, 1 H, J = 10.5 and 7.0 Hz).

Anal. Calcd for $C_2H_3IO_2S$: C, 11.02; H, 1.39; O, 14.68. Found: C, 11.25; H, 1.40; O, 14.55.

2-Bromothiirane 1,1-Dioxide (40). Treatment of diazomethane in dry ether with $BrCH_2SO_2Cl$[76] and Et_3N according to the method described for the 2-bromo-2-methyl analog gave the episulfone in 49% yield. After recrystallization from ether (−78°) the sulfone had mp 73° dec; ir ($CHCl_3$) 7.45, 8.55 μ (SO_2); nmr ($CDCl_3$) δ 3.20 (q, 1, J = 9.8 and 6 Hz), 3.80 (t, 1, J = 10 Hz) and 4.80 (q, 1, J = 10 and 6 Hz).

Anal. Calcd for $C_2H_3BrO_2S$; C, 14.00; H, 1.75; Br, 46.70; S, 18.80. Found. C, 13.97; H, 2.00; Br, 46.73; S, 18.75.

α-Bromoethanesulfonyl Chloride. A mixture of 100 g of 1,1-dibromoethane,[77] 68 g of Na_2SO_3, 50 ml of ethanol, and 500 ml of water was refluxed with stirring for 48 hr. The resulting solution was evaporated on a steam bath and the residue heated to dryness in an oven at 85°. The dried solid was pulverized and cautiously treated with 330 g of PCl_5 while cooling in an ice bath. After the initial spontaneous reaction had subsided the mixture was heated for 0.5 hr on a steam bath, cooled, and poured over 2 Kg of crushed ice with vigorous stirring. When the ice had melted the mixture was extracted with three 200-ml portions of CH_2Cl_2 and the extracts were washed twice with water, 10% $NaHCO_3$ solution, and water. Drying ($MgSO_4$) and distillation gave 52.5–69 g (48–63%) of the sulfonyl chloride, bp 52–54° (0.6 mm). The analytical sample had bp 40° (0.5 mm); ir ($CHCl_3$) 7.24, 8.42, 8.59, 8.69 μ (SO_2); nmr ($CDCl_3$) δ 2.22 (d, 3, J = 6.5 Hz, CH_3), 5.40 (q, 1, J = 6.5 Hz, CH).

Anal. Calcd for $C_2H_4BrClO_2S$: C, 11.58; H, 1.93; Br, 38.52; Cl, 17.09; S, 15.45. Found: C, 11.55; H, 2.00; Br, 38.35; Cl, 17.00; S, 15.40.

Treatment with anhydrous NH_3 in ether at 0–10° followed by washing with H_2O, removal of solvent and recrystallization from benzene gave **α-bromoethanesulfonamide**: mp 70.5–71.5°; ir ($CHCl_3$) 7.40, 8.45, 8.75 μ (SO_2); nmr (D_2O) δ 2.04 (d, 3, CH_3), 5.25 (q, 1, CHBr).

Anal. Calcd for $C_2H_6BrO_2NS$: C, 12.80; H, 3.19; Br, 42.50; N, 7.45; S, 17.10. Found: C, 12.95; H, 3.34; Br, 42.58; N, 7.33; S, 17.25.

2-Bromo-2-methylthiirane 1,1-Dioxide (31). A 500-ml flask containing 260 ml of ethereal diazomethane[80] solution (0.084 mol of CH_2N_2) was fitted with $CaCl_2$ drying tubes and two burets. The solution was cooled in an ice bath, stirred and there was added at the same rate a solution of 15 g of α-bromoethanesulfonyl chloride in 35 ml of dry ether from one buret and 7.29 g of dry triethylamine in 35 ml of dry ether from the second buret. After the addition (8 min) the mixture was stirred for 75 min at 0–5°, the $Et_3N \cdot HCl$ was removed by filtration and the solvent removed at 0–5° on a rotary evaporator with the aid of a water aspirator. The residue was recrystallized from ether to give 8.5–9.6 g (62–70%) of the episulfone: mp 57.5–58.5° dec; ir ($CHCl_3$) 7.50, 8.67, 8.96 μ (SO_2); nmr ($CDCl_3$) δ 2.27 (s, 3, CH_3), 3.41 (s, 2, CH_2).

Anal. Calcd for $C_3H_5BrO_2S$: C, 19.47; H, 2.72; Br, 43.19; S, 17.32. Found: C, 19.46; H, 2.99; Br, 42.88; S, 17.38.

2-Methylthiirene 1,1-Dioxide (32). To 9.6 g of **31** in 300 ml of dry ether at 0–5° there was added 5.16 g of triethylamine and the solution stored at this temperature for 3–4 days, filtered, and the residue extracted with 150 ml of dry ether. The combined ether filtrates were evaporated and the crude solid recrystallized from ether (cooling in a Dry Ice–methanol bath) to give 1.2–2.7 g (22–51%) of the vinylene sulfone as snow-white needles: mp 59–60° (dec at 90–100°); ir ($CHCl_3$) 6.22 (C=C) and 7.82, 8.42 μ (SO_2); nmr ($CDCl_3$) δ 2.50 (d, 3, J = 1.1 Hz, CH_3), 9.04 (q, 1, J = 1.1 Hz, CH).

Anal. Calcd for $C_3H_4O_2S$: C, 34.63; H, 3.87; S, 30.79; mol wt, 104. Found: C, 34.53; H, 3.56; S, 30.90; mol wt (osmometric in $CHCl_3$), 110.

***cis*- and *trans*-2-Bromo-2,3-dimethylthiirane 1,1-Dioxide (37).** To a solution of diazoethane[49] (0.064 mol) in 265 ml of dry ether there was added from two burets as described for the monomethyl analog solutions of (a) 10.18 g of α-bromoethanesulfonyl chloride in 25 ml of dry ether and (b) 7.11 g of dry triethylamine in 25 ml of dry ether. Treatment of the reaction mixture as in the case of **31** gave after four recrystallizations from ether a small amount of the mixed episulfones: mp 60.5–62° dec (softening at 57°); ir ($CHCl_3$) 7.55, 8.50 μ (SO_2); nmr ($CDCl_3$) δ 1.65 (m, 3, *CH*$_3$CH), 2.27 (m, 3, *CH*$_3$CBr), and 3.15 (q, 1, CH_3*CH*). The mixture could be stored at −70°; after less than 1 hr at room temperature complete decomposition to a mixture of *cis*- and *trans*-2-bromo-2-butenes occurred.

Anal. Calcd for $C_4H_7BrO_2S$: C, 24.13; H, 3.54; S, 16.10. Found: C, 24.20; H, 3.59; S, 15.98.

2,3-Dimethylthiirene 1,1-Dioxide (38). To a 500-ml, three-necked, round-bottomed flask fitted with $CaCl_2$ drying tubes and two burets there was added 145 ml of ethereal diazoethane[49] (0.046 mol). The solution was cooled in a NaCl–ice bath and with stirring there was added over 8.5 min from the two burets solutions of (a) 8.51 g of α-bromoethanesulfonyl chloride in 25 ml of dry ether and (b) 4.96 g of dry Et_3N in 25 ml of dry ether. After stirring for 50 min in the brine bath the $Et_3N \cdot HCl$ was filtered and washed with ether. The combined ether filtrates were cooled to −70° in a Dry Ice–acetone bath and a solution of 5.09 g of 1,5-diazabicyclo[4.3.0]-5-nonene (DBN)[81] in 20 ml of dry ether was added dropwise over a period of 7 min. The mixture was stirred for 40 min at −70°, allowed to come to room temperature, and then evaporated from a water bath at 25° with a rotary evaporator. The residual yellow mass was dissolved in 250 ml of $CHCl_3$, the solution washed once with 170 ml of ice water in a separatory funnel. Drying of the $CHCl_3$ solution ($MgSO_4$) and evaporation at 25° with a rotary evaporator gave a yellow mass to which 5–10 ml of dry ether was added. This caused formation of a white solid which on filtration gave 1.8 g (36.6%) of the crude sulfone, mp 96.5–98° dec. Recrystallization by solution in refluxing ether followed by cooling at −18° gave 1.22 g (25%) of the pure thiirene dioxide: mp 101–101.5° dec (varies with the rate of heating); ir ($CHCl_3$) 7.96, 8.58 μ (SO_2); Raman (solid) 1685 cm^{-1} (C=C), 1233, 1166 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.28 (s, CH_3).

Anal. Calcd for $C_4H_6O_2S$: C, 40.66; H, 5.12; S, 27.14; mol wt, 118.2. Found: C, 40.88; H, 4.97; S, 26.96; mol wt (osmometric in benzene), 129.

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(74) Scholnick[23] reports mp 106–107°. This may represent a polymorphic form of the compound.

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Thermal Decomposition of 2,3-Dimethylthiirene 1,1-Dioxide (38). A sample of the thiirene dioxide was heated briefly in an oil bath at 120–130° and the evolved gases passed through a solution of aqueous NaOH into an infrared gas cell. The infrared spectrum of the gas was identical with that of an authentic sample of 2-butyne.

Phenyldiazomethane.[82] To a suspension of 23.2 g of 95% hydrazine in 67 ml of ether there was added with stirring and ice bath cooling over a period of 100 min a solution of 35.3 g of benzaldehyde in 100 ml of ether. After 1 hr at 0–10° and 24 hr at room temperature the ether layer was washed once with 100 ml of H_2O and stored in a refrigerator for future use (173 ml of the solution contained *ca.* 0.33 mol of the benzalhydrazone). To 43 ml of this wet ethereal solution there was added 350 ml of anhydrous ether and 70 g of anhydrous Na_2SO_4. The mixture was protected from the atmosphere with a $CaCl_2$ tube, cooled in an ice bath, stirred, and treated portionwise with 100 g of activated MnO_2[84] added over a period of 25 min from a solids-addition tube. After 1.5 hr at 0–10° the mixture was filtered, and the solid washed with ether until the washings were nearly colorless. The ether filtrates amounted to 406 ml. By benzoic acid titration the yield was 53% (yields ranged from 43 to 76%). The solution could be concentrated at 0–5° to *ca.* 0.4 *M* without loss of the diazo compound.

2-Methyl-3-phenylthiirene 1,1-Dioxide (39). A solution of 4.98 g of α-bromoethanesulfonyl chloride in 25 ml of dry ether was diluted with 62 ml of ethereal phenyldiazomethane[82] (0.024 mol) in a 500-ml flask fitted with a $CaCl_2$ drying tube and an addition funnel containing a solution of 4.85 g of Et_3N in 50 ml of dry ether. At room temperature with stirring one-half (25 ml) of the amine solution was added over a period of 5 min. The temperature rose to 34° at which point an ice bath was placed under the reaction mixture and the remaining 25 ml of the amine solution was added over another 5-min period. The mixture was stirred in the ice bath for 1.2 hr and filtered. The insoluble portion was dissolved in 100 ml of $CHCl_3$, the solution washed with one 50-ml portion of water, dried ($MgSO_4$), and evaporated with a rotary evaporator. The residue was dissolved in 220 ml of a refluxing mixture (4.5:1) of ether–ligroin (bp 88–98°), and the mixture filtered and concentrated on a steam bath to the cloud point. Storage at −18° for 65 hr have 0.6 g (13.7%) of the vinylene sulfone. An analytical sample was obtained by recrystallization from ether–ligroin (bp 88–98°) (4:1) and a trace of CH_2Cl_2 by cooling to Dry Ice–acetone temperatures: mp 117–118° dec; ir ($CHCl_3$) 7.95, 8.56 μ (SO_2); uv[85] (95% C_2H_5OH) 256 mμ (log ϵ = 4.19), nmr ($CDCl_3$) δ 2.55 (s, 3, CH_3), 7.51 (s, 5, C_6H_5).

Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 60.02; H, 4.63; S, 17.81.

1-Propynesulfonyl Chloride (36). A 1 *N* solution of NaOCl was freshly prepared by passing Cl_2 into a solution of 3 g of NaOH in 15 ml of water and 15 g of crushed ice. The mixture was cooled externally in an ice bath during passage of the Cl_2. After several minutes the solution became acidic whereupon chlorination was stopped and the solution made basic by the addition of a small amount of concentrated NaOH solution. Separately 3 g of 2-methylthiirene dioxide (**32**) was slowly added to 30 ml of 2 *N* NaOH solution at 0–5°. The resulting solution, maintained at 0–5°, was immediately titrated[86] with the freshly prepared NaOCl solution, the end point being determined by frequent testing for excess NaOCl by means of starch–iodide paper. The solution was then slowly acidified in the cold with concentrated HCl and then made basic by the addition of $NaHCO_3$ solution. The solution was evaporated by a current of dry air and the resulting solid further dried in a vacuum desiccator and then suspended in 75 ml of CCl_4 and treated with 14 g of PCl_5 with agitation. The mixture was refluxed for 24 hr, poured over 100 g of crushed ice, and stirred thoroughly. The CCl_4 layer was washed with water and 10% $NaHCO_3$, dried ($MgSO_4$), and the solvent removed at room temperature with the aid of a water aspirator. The resulting oil was distilled to give 1.4 g (35%) of the sulfonyl chloride, bp 60–62° (6 mm). A sample for elemental analysis was obtained by preparative glpc on a silicone gum rubber column (SE-30) operating at 140–150°: ir (CCl_4) 4.51 μ ($C{\equiv}C$), 7.20, 8.46 μ (SO_2); nmr (CCl_4) δ 2.28 (s, CH_3).

Anal. Calcd for $C_3H_3ClO_2S$: C, 26.00; H, 2.16; Cl, 25.60; S, 23.14. Found: C, 26.22; H, 2.34; Cl, 25.07; S, 23.14.

Comparison of the Rates of Thermal Decomposition of 2,3-Dimethyl- and 2,3-Diphenylthiirene 1,1-Dioxides. At least eight $CHCl_3$ solutions of each of the two sulfones were prepared in the range 0.05–0.95 *M*. For an absorption band near 10 μ shown to be absent in the spectra of SO_2 and the two acetylenic decomposition products, a concentration–absorbance curve was made up for each compound. Straight lines were observed in accordance with Beer's law except for slight deviation below 0.15 *M*, and above 0.7 *M*.

Soft glass tubes (6 × 110 mm) were sealed at one end and a small volume (about 0.10 ml) of a $CHCl_3$ solution of the thiirene dioxide was introduced. The tubes were immediately cooled in liquid nitrogen for 15–20 sec, rapidly sealed with an oxygen–propane torch, and immersed in a constant-temperature bath at 74.5–75.5°. Tubes were periodically withdrawn and cooled, and the absorbance was measured. From these results and the standard curves, first-order plots yielded straight lines (through at least two half-lives) from which the rate constants and half-lives were calculated. Half-lives for the dimethyl and diphenyl derivatives were 199 and 169 min, respectively.

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(82) Satisfactory results in the synthesis of 2-methyl-3-phenylthiirene dioxide were not obtained until a new method for the preparation of phenyldiazomethane was devised which could be used to obtain in high yield alcohol-free solutions of the compound. The method was adapted from that of Gutsche and Jason[83] except that activated manganese dioxide[84] was used as oxidant.

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(84) The manganese dioxide was precipitated from potassium permanganate by and on activated carbon: L. A. Carpino, *J. Org. Chem.*, **35**, 3971 (1970).

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