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(41) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967.
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(43) E. Kováts, Helv. Chim. Acta, 41, 1915 (1958).

Reactions of 2,3-Diphenylthiirene 1,1-Dioxide with Nucleophiles

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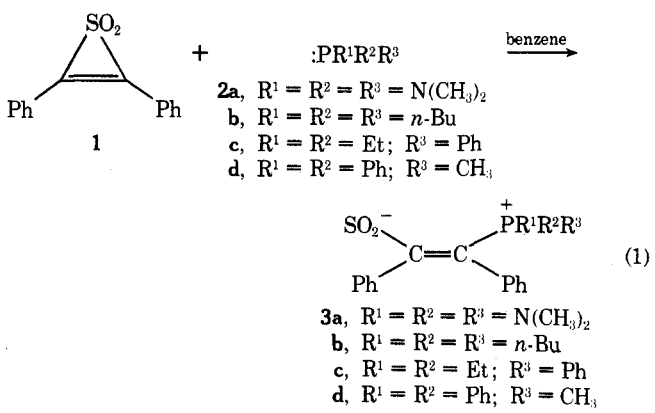
2,3-Diphenylthiirene 1,1-dioxide (1) reacts with tertiary phosphines, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), dimethylamine, sodium cyanide, and sodium benzenesulfinate in aprotic solvents by initial attack at the carbon centers of the three-membered ring. The reaction of 1 with dimethylamine in benzene gives a high yield of (*E*)-1,2-diphenyl-1-*N*,*N*-dimethylaminoethene. Tertiary phosphines and DBN react with 1 to give a new class of betaines. The complete X-ray structure of the betaine **3d** derived from 1 and diphenylmethylphosphine is reported. Cyanide and benzenesulfinate ions in DMF add across the carbon–carbon double bond in 1 to give an intermediate anion which undergoes electrocyclic ring opening to vinylsulfinates (**16** and **17**, respectively). These sulfinates were converted into their respective methyl sulfones (**18** and **19**) with methyl iodide.

Although the physical and chemical properties of cyclopropenones[1] indicate that these compounds enjoy a relatively high degree of stability owing to their aromatic character, the corresponding sulfones, thiirene 1,1-dioxides, are not sufficiently well characterized to draw a similar conclusion.[2] A good deal of information is now available on the reactions of cyclopropenones,[1] but far less is known about similar reactions with the unsaturated episulfones. In view of this, we have investigated the reactions of 2,3-diphenylthiirene 1,1-dioxide (1) with nucleophiles.

Results and Discussion

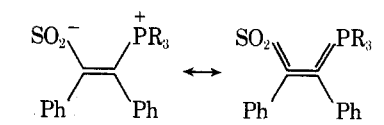
α,β-Unsaturated sulfones,[3] like other alkenes substituted with electron-withdrawing groups,[4] are susceptible to nucleophilic additions. Typical nucleophiles used are alkoxides, amines, thiolates, sulfinates, cyanide, and carbanions.[4] Tertiary phosphines also are reactive, but their reactions with the activated alkenes tend to be highly reversible.[5] Because of the nature of the strained ring system in 2,3-diphenylthiirene 1,1-dioxide (1), it seemed likely that 1 would react irreversibly with nucleophiles such as tertiary phosphines either by attack at the sulfur or α-carbon positions. Indeed, 1 reacted rapidly in benzene solvent with a number of reactive tertiary phosphines (2) to give 1:1 adducts in quantitative yield.[6] The structure of the adduct of 1 with diphenylmethylphosphine (**2d**) was established as **3d** by an X-ray crystallographic analysis.



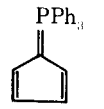
(1)

An ORTEP drawing of **3d** from the X-ray determination is given in Figure 2; bond lengths and angles are shown in Figure 1. The A and B phenyl rings, which are attached to the central C=C, are twisted by steric interactions out of the double bond plane by angles of 67 and 47°, respectively. The shortest ring A···ring B distance of 3.37 Å (Figure 2) is virtually identical with the 3.4-Å van der Waals thickness of an aromatic ring. The O(1)–S–O(2) and Ph–P–Ph angles are approximately bisected by the double bond plane, and the orientations of both the SO_2 and PCH_3Ph_2 groups appear to be governed by steric factors. Newman projections illustrating the conformations about C(2)–P and C(3)–S are given in Figure 3. The SO_2 group is pyramidal (the sum of the three angles around S is 315.9°; sum of three perfectly tetrahedral angles, 109.5°, is 328.5°), and with the assumption that the unshared electron pair on S (form I) is positioned, relative to the C and two O atoms, to give a S tetrahedron, it is clear that the SO_2's orientation maximizes the electron pair–P^+ interaction (S···P 3.20 Å).

The resonance structure extremes for **3d** are represented by canonical form I, a sulfinophosphonium betaine, and form II, a phosphonium ylide–sulfene.[7] Bond lengths (Figure 1) for the central P–C–C–S part of the molecule have the usual values for P–C, C=C, and C–S, all of which would pertain to structure I. The P–C(2) distance is typical of P–C (sp^2, phenyl) lengths; phosphonium ylides with some P=C character normally show a distance of about 1.72 Å. Several representative distances are given below.



I II

	$HOCH_2$-$SO_2^-Na^+$		CH_2=CH_2
Bond	C-S[9]	ring-C-P[10]	C-C[11]
Bond length, Å	1.838	1.718	1.34

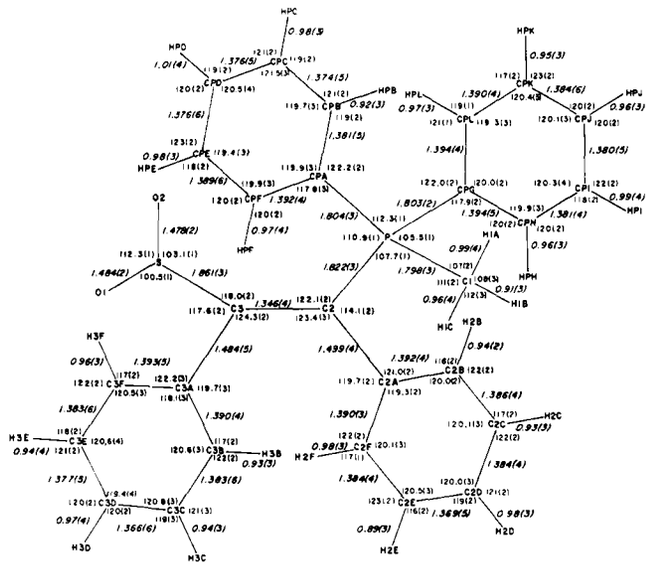
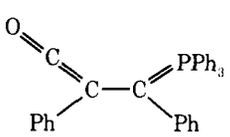


Figure 1. Bond lengths (Å) and angles (degrees) for **3d.** Estimated standard deviations are in parentheses.

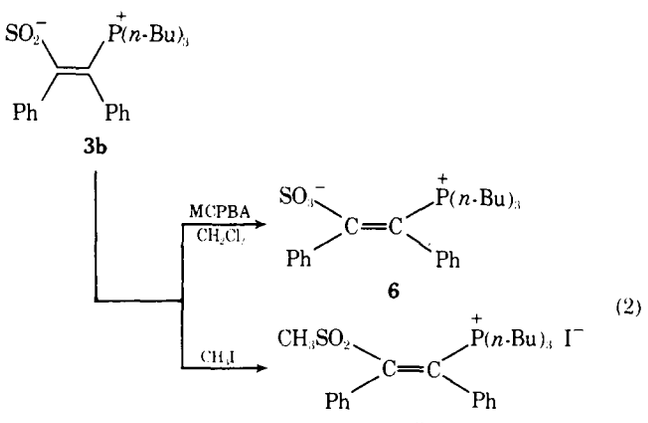
There is no bond length evidence for the P to S delocalization indicated by structure II. The pyramidal shape of the SO_2 and the orthogonal orientation of the S's electron pair to the C=C π electrons are further evidence for structure I.

In contrast to the betaines **3** resulting from the reactions of tertiary phosphines with 1, 2,3-diphenylcyclopropenone reacts with triphenylphosphine to give a 1:1 adduct which is properly represented by the phosphorane structure (**4**).[12]



4

Betaine **3b** reacted with methyl iodide to give the methylsulfonyl phosphonium iodide **5**, and **3b** was oxidized by *m*-chloroperoxybenzoic acid (MCPBA) to the sulfophosphonium betaine **6**.



(2)

5

Interestingly, the sulfinobetaines **3** are yellow-orange colored whereas the sulfobetaines **6** and **7** are colorless. The uv spectrum of **3d** is strongly solvent dependent: λ_{max} (CH_3CN) 390 nm (ϵ 394) and λ_{max} (CH_3OH) 350 nm (ϵ 350). Although it is tempting to ascribe the color of **3d** (bright orange) to a major contribution from the sulfene–ylide form (II), this must be discounted based on the X-ray data (vide supra). The absorption appears to be due to a charge transfer band (eq 3) which undergoes a blue shift going from acetonitrile to methanol, since hydrogen bonding of methanol to the sulfonyl group lowers the ground-state energy of **3d.**[13]

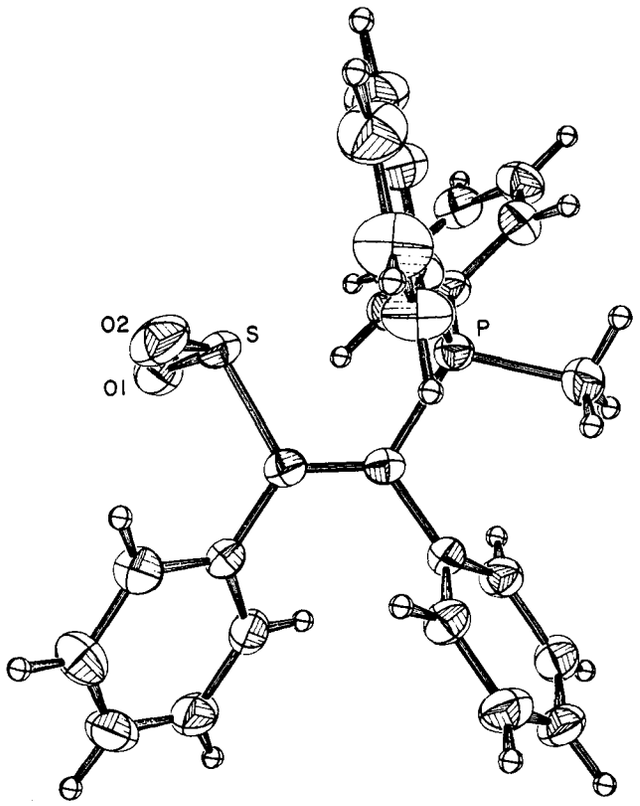
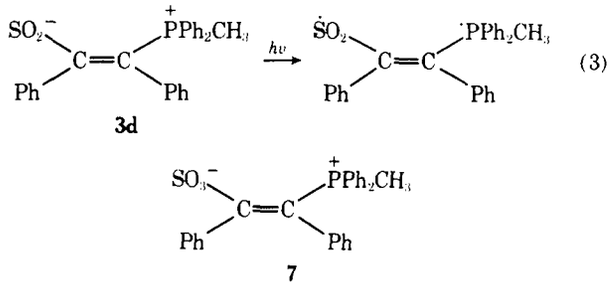


Figure 2. An ORTEP-II drawing of **3d.** The view is normal to the plane of the central C=C.

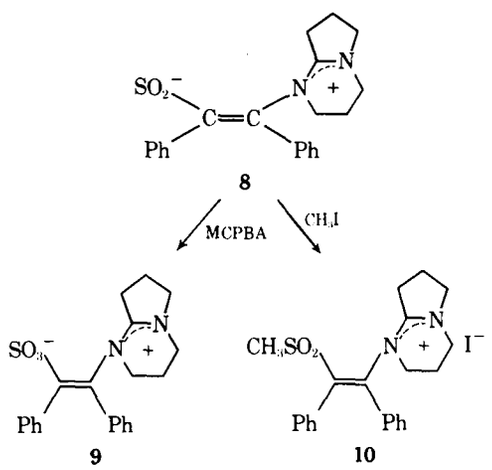


(3)

3d

7

In contrast to the reactions of tertiary phosphines, **1** does not react with typical tertiary amines (triethylamine and 1,4-diazabicyclo[2.2.2]octane).[14] However, **1** did react in benzene with the highly reactive tertiary amine, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), to give a 1:1 adduct, the betaine **8**.[6] The yellow-colored betaine **8** was oxidized to the



(4)

9 **10**

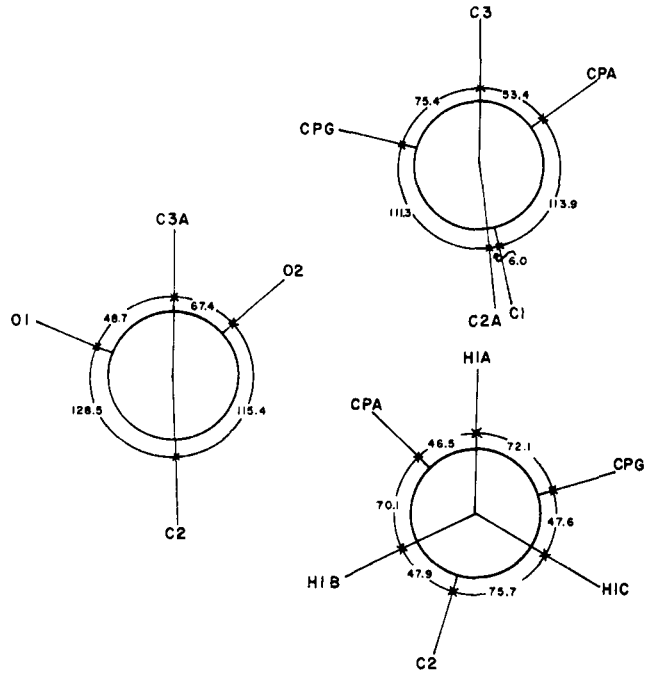
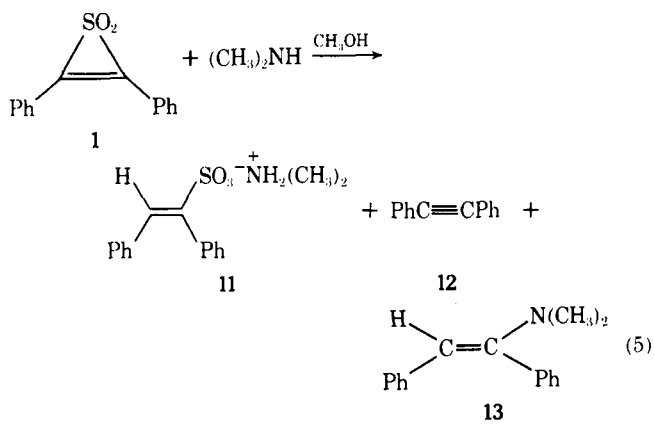


Figure 3. Newman projections for **3d.** Clockwise from the top right, the three projections are for C2 → P, C1 → P, and C3 → S. Dihedral angles are included.

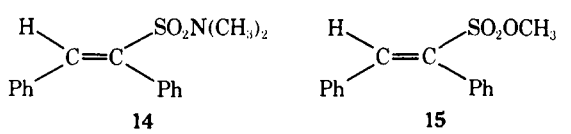
colorless betaine **9** and methylated with methyl iodide to give the sulfone **10.**

Although normal tertiary amines are unreactive toward **1**, dimethylamine reacts with **1** in methanol to give the dimethylammonium sulfonate **11**, a minor amount of diphenylacetylene **12**, and the vinylamine **13**. The salt **11** was



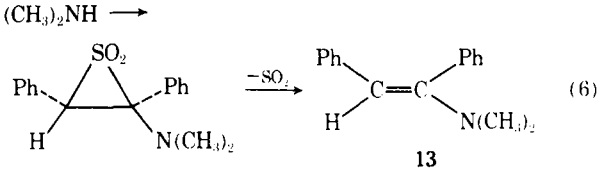
identified by its spectral data and conversion to the known *p*-toluidine salt of 1,2-diphenylethylene-1-sulfonic acid[15] (see Experimental Section).

A possible precursor of **11** is the sulfonamide **14**, which could conceivably have given **11** under the reaction conditions. However, **14** (for synthesis, see Experimental Section) was stable under conditions of eq 5, but methyl sulfonate **15** was rapidly converted to **11** with dimethylamine in



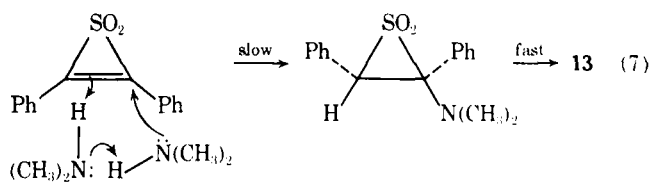
methanol. The methyl sulfonate **15** and diphenylacetylene result from the rapid reaction of **1** with methoxide ion,[16] which is produced by the methanolysis of dimethylamine in methanol. The methanolysis of dimethylamine can be suppressed by running the reaction of **1** with dimethylamine in the presence of dimethylammonium chloride. In the absence of added dimethylammonium chloride, **1** reacts with dimethylamine to give **11** and **13** in a ratio of ca. 8:1, whereas under the same conditions with added 1 *M* dimethylammonium hydrochloride, the ratio of **11:13** is ca. 1:8.

The overall structure of the vinylamine **13** was established through the use of spectroscopy and by the hydrolysis of **13** to benzyl phenyl ketone in quantitative yield. ^{1}H NMR spectroscopy and liquid chromatography showed that the sample of **13** was homogeneous with no indication of a mixture of isomers. Hauser, Taylor, and Ledford[17] reported the synthesis of a vinylamine whose structure they assigned as (*Z*)-1,2-diphenyl-1-*N*,*N*-dimethylaminoethene, mp 30°, from the base-catalyzed elimination of hydrogen cyanide from α-dimethylamino-α-phenylacetonitrile. Thermal elimination of hydrogen cyanide from the above nitrile gave "a liquid enamine" which they suggested was either a geometrical isomer of the 2-vinylamine or a mixture of *E* and *Z* isomers. The assigned stereochemistry of **13** (liquid at room temperature) was based on the above considerations as well as the probable mode of generation (eq 6).



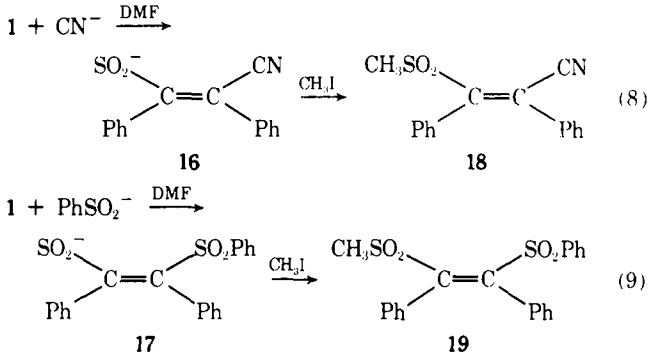
Amines typically add syn to activated olefins[18] and extrusion of sulfur dioxide from episulfones is known to occur with complete retention of configuration.[19]

The reaction of **1** with dimethylamine in benzene gives **13** in high yield accompanied by a small amount of the salt **11**, which presumably arises because of a small amount of water present. The ratio of **13:11** varies with amine concentration (see Experimental Section). A plot of log [**13**]/[**11**] vs. log [$(CH_3)_2NH$] for the reaction of **1** with dimethylamine in benzene gives a straight line (r = 0.994) whose slope is 1.05. This result indicates that in the reaction leading to **13**, the order of the reaction with respect to dimethylamine is one order higher than for the reaction leading to the salt **11**. Assuming that the reaction leading to **11** is first order in amine,[16] then the reaction leading to **13** is second order in amine, which is typical for the additions of amines to olefins in aprotic solvents.[3,4,18] The mechanism below is consistent with the above results and the observed syn addition of dimethylamine to **1**.[20]



At this point it appeared that anions such as alkoxide,[16] hydroxide,[16] and hydride[2a] ions and Grignard reagents[2a] attack the central sulfur atom, whereas neutral nucleophiles such as amines, phosphines, hydroxylamine,[2a] and hydrazine[2a] attacked exclusively the carbon–carbon double bond in the ring of **1**. However, cyanide and benzenesulfinate ions reacted with **1** in DMF to give the vinylsulfinates **16** and **17**, respectively; the sulfinates **16** and **17** were trapped with methyl iodide and isolated as their respective methyl sulfones, **18** and **19** (eq 8 and 9).

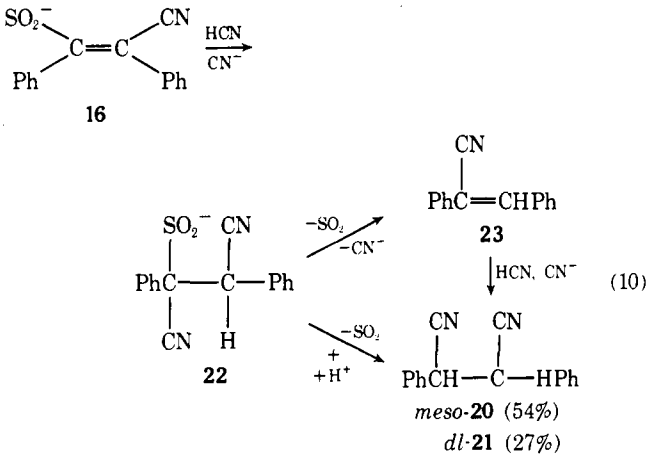
If reaction 8 is run in the presence of excess cyanide ion (ratio of CN^-:**1** of ca. 10:1) a high yield of *meso*- and *dl*-1,2-diphenyl-1,2-dicyanoethane (**20** and **21**) is obtained.[21]



(8)

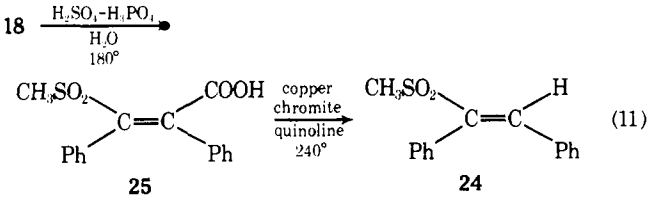
(9)

Under these reaction conditions, α-cyanostilbene (**23**) reacts with excess sodium cyanide in DMF to give **20** and **21** in the same ratio as found above. Although these reactions were run in dry DMF, there no doubt is a small amount of adventitious water present so that hydrogen cyanide could add to **16**. The resulting sulfinate **22** would undergo easily desulfination[22] to give **23** or **20** and **21**, directly (both **20** and **21** are epimerized by sodium cyanide in DMF to a 2:1 mixture of **20**:**21**).



(10)

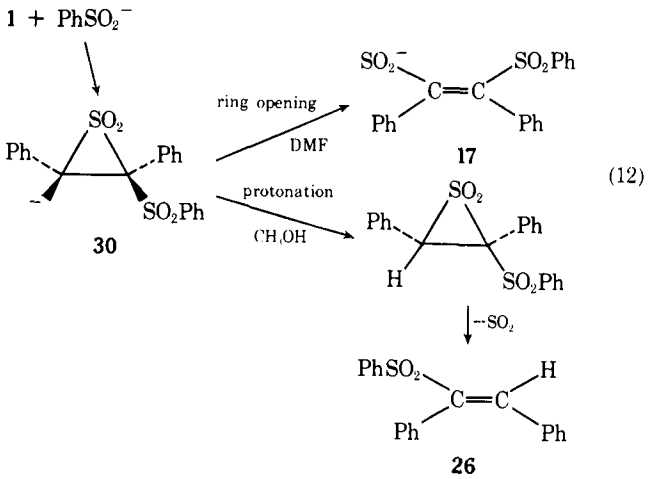
The stereochemical assignment for the vinyl sulfones **18** and **19** rests mainly on the mechanism of their formation; **18** was converted (eq 11) to **24**,[23] a compound which ap-



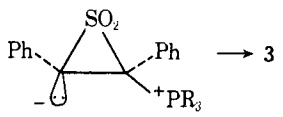
(11)

pears to have been reported earlier but assigned the *Z* configuration.[27]

The reaction of **1** with sodium benzenesulfinate follows a course dependent upon the solvent; in DMF, **17** is formed, but in methanol, **26** is formed (eq 12).[28] Proton transfers to carbanions are fast but well below diffusion controlled.[31] However, electrocyclic ring opening of carbanion **30** apparently is unable to effectively compete with protonation in methanol solvent.[32] The stereochemistry of these electrocyclic ring openings (e.g., **30** → **17**) appears to be governed by the principle of least motion.[33] Although one could argue that the configurationally more stable olefin **17** was the result of steric control, based on a steric argument (*Z*)-**16** should be less stable than its *E* isomer, and yet **16** is the observed product. The stereochemistry of the reactions of phosphines with **1** to give the betaines **3** could be the result either of the strong attraction of the incipient sulfonyl–phosphonium ion sites or of the ring opening of the intermediate betaine **31** accompanied with the least amount of motion of the atoms involved.



(12)



Conclusions

Unlike α,β-unsaturated ketones where nucleophiles add across both the carbon–carbon and carbon–oxygen double bonds, α,β-unsaturated sulfones normally react with nucleophiles to give only addition across the carbon–carbon double bond; the sulfonyl group is attacked by nucleophiles only with difficulty.[34] With α,β-unsaturated ketones, the more highly basic nucleophiles attack the carbonyl carbon while the less basic nucleophiles attack the β-carbon atom.[4b] This also seems to apply to the reactions of **1** with nucleophiles, since the strongly basic nucleophiles attack the sulfonyl sulfur atom while the less basic nucleophiles[35] prefer to attack the unsaturated carbon atoms of the ring.

Experimental Section

Melting points were taken on Fisher-Johns and Mel-Temp apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on a Varian Associates A-60D and Varian Associates EM 360 NMR spectrometers operating at ambient temperature. All spectra were taken in carbon tetrachloride or deuteriochloroform with tetramethylsilane (δ 0.00) as an internal standard unless otherwise specified. The ir spectra were taken on a Beckman IR-8 infrared spectrometer as solutions in carbon tetrachloride or as KBr pellets. The Raman spectrum of **18** was recorded on an instrument with a Coherent Radiation Laboratories Argon Ion Laser Model 52, Spec 1401 double spectrometer and EMI 9286-SR photomultiplier tube. The blue line 4880 Å was used. High-pressure liquid chromatography was performed on a Du Pont instrument 830 with a 4-ft analytical Permaphase octadecyl silane (ODS) column at ambient temperature. DMF was distilled once over phosphorus pentoxide in vacuo. Oxygen-free benzene was obtained by passing dry nitrogen through benzene for 15 min before use. Mass spectra were run by Dr. Martha Gay and elemental analyses were performed by Dr. Franz Kasler of the University of Maryland.

The details for the synthesis of the betaines **3**, **6**, **7**, **8**, and **9** and their physical properties are reported elsewhere.[6]

Reaction of 1 with Dimethylamine in Methanol. To a solution of 1.00 g (4.13 mmol) of the thiirene **1** in 150 ml of methanol at room temperature was added ca. 2 ml of dimethylamine. After 10 min, the solvent was removed in vacuo. Recrystallization of the solid residue from dichloromethane–hexane–ether gave 825 mg (65%) of **11**: mp 153°; MS *m/e* 260 [$M^+ - (CH_3)_2NH$]; ir (KBr) 3500 (N–H), 1200 and 1040 cm^{-1} (SO_3^-); ^{1}H NMR ($CDCl_3$) δ 2.4 (t, 6 H), 7.1–7.4 (m, 10 H), 7.6 (s, 1 H), 8.0–8.6 (m, 2 H).

Elemental analysis for **11** was unsatisfactory because the compound proved to be too hygroscopic.

Reaction of 1 with Dimethylamine in Benzene. To a solution

of 1.00 g (4.13 mmol) of 1 in 50 ml of distilled benzene was added 5 ml of dimethylamine. After 5 min, the solvent was removed in vacuo. The resulting yellow oil was put into a 10-ml round-bottom flask. Evaporative distillation (Kugelrohr apparatus, pot temperature 150°, 1 mmHg) gave 775 mg (84%) of (*E*)-1,2-diphenyl-1-*N*,*N*-dimethylaminoethene (**13**)[17] as a viscous yellow oil: ir (neat) 1600 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 2.70 (s, 6 H), 5.52 (s, 1 H), 6.65–7.1 (m, 5 H), and 7.3 (s, 5 H).

Hydrolysis of 13. To a 10-ml beaker with 200 mg (0.89 mmol) of the enamine **13** was added 2 ml of 6 *M* HCl. A white precipitate of 150 mg (86%) of deoxybenzoin was isolated, mp 59° (lit.[36] 60°). Identification was made by ^1H NMR, ir spectroscopy, and mixture melting point.

Preparation of (*E*)-1,2-Diphenylvinylsulfonyl Chloride. To a solution of 1.00 g (3.31 mmol) of **11** in 30 ml of Spectrograde chloroform was added 2.00 g (9.59 mmol) of phosphorus pentachloride. After stirring at room temperature for 3 hr, the solution was washed twice with 30 ml of saturated sodium bicarbonate solution, followed by 30 ml of water. The solvent was dried ($MgSO_4$) and removed in vacuo. Crystallization from methylene chloride–hexane gave 470 mg (49%) of the sulfonyl chloride: mp 130°; ir (CCl_4) 1630 (C=C), 1380 and 1175 cm^{-1} (SO_2); ^1H NMR ($DCCl_3$) δ 8.0 (s, 1 H), 7.6 (s, 5 H), and 7.1–7.4 (m, 5 H).

Anal. Calcd for $C_{14}H_{11}ClO_2S$: C, 60.32; H, 3.98. Found: C, 60.18; H, 4.14.

Preparation of *N*,*N*-Dimethyl-(*E*)-1,2-diphenylvinylsulfonamide (14). To a solution of 300 mg (1.08 mmol) of (*E*)-1,2-diphenylvinylsulfonyl chloride in 50 ml of dry benzene was added 0.3 ml of dimethylamine. The solution was held at reflux for 10 min. The solvent was removed in vacuo. Crystallization from ethanol–water gave 150 mg (47%) of the sulfonamide **14**: mp 153°; ir (CCl_4) 1620 (C=C), 1340 and 1150 cm^{-1} (SO_2); ^1H NMR ($DCCl_3$) δ 2.7 (s, 6 H), 7.1–7.4 (m, 5 H), 7.5 (s, 5 H), and 7.75 (s, 1 H); MS M^+ 287, 179 (PhC=CHPh), and 178 (PhC:CPh).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96. Found: C, 66.57; H, 6.20.

Hydrolysis of Methyl (*E*)-1,2-Diphenylvinylsulfonate (15) To a solution of 50 mg (0.18 mmol) of the sulfonate **15**[16b] in 20 ml of Spectrograde methanol was added ~0.5 ml of dimethylamine. The reaction was followed by TLC (silica gel–100% CH_2Cl_2) and was complete in about 1 hr. The solvent was removed in vacuo. Crystallization from methanol–ether gave a white precipitate of dimethylammonium (*E*)-1,2-diphenylvinylsulfonate (**11**), 45 mg (82%). Identification was made by comparison with the authentic sample.

Preparation of *p*-Toluidinium (*E*)-1,2-Diphenylvinylsulfonate. To a solution of 200 mg (0.66 mmol) of the sulfonate **11** in 5 ml of water was added to 1 ml of 6 *M* HCl followed by 100 mg (0.93 mmol) of *p*-toluidine in 5 ml of 6 *M* HCl. A precipitate formed instantaneously. After cooling in an ice bath, the precipitate was collected. Decolorization with neutral Norit and recrystallization from water gave 110 mg (45%) of the salt, mp 196° (lit.[15] 198°).

Qualitative Study of the Reaction of 2,3-Diphenylthiirene 1,1-Dioxide with Dimethylamine with and without Dimethylammonium Chloride. To a vial with ca. 5 mg of 2,3-diphenylthiirene 1,1-dioxide, ca. 5 mg of naphthalene, and 100 mg of dimethylammonium chloride in 1 ml of methanol was added 1 drop of dimethylamine. The reaction was followed by TLC (silica gel–100% methylene chloride) and was complete in about 10 min, at which time 10 drops of 6 *M* HCl was added. This reaction was repeated in the absence of dimethylammonium chloride. The reaction mixtures were analyzed by liquid chromatography (4-ft Permaphase ODS column, 60:40 methanol–water, room temperature, 1000 psi). The products were the ammonium sulfonate **11**, deoxybenzoin, and diphenylacetylene. Deoxybenzoin was isolated from a preparative scale reaction and identified by ir and ^1H NMR spectra and by comparison with an authentic sample. No sulfonamide **14** was detected. Retention times for ammonium sulfonate **11**, deoxybenzoin, sulfonamide **14**, and diphenylacetylene were 2.4, 13.2, 19.6, and 27.8 min, respectively (4-ft Permaphase ODS column, 30:70 methanol–water, room temperature, 1000 psi). The ratio of sulfonate **11**:deoxybenzoin:diphenylacetylene was 1:8:1 in the presence of dimethylammonium chloride but the ratio was 8:1:1 in the absence of dimethylammonium chloride.

Product Ratio Study of the Reaction of Dimethylamine with 1 in Benzene. Twenty milligrams of **1** was put into a 10-ml volumetric flask and dry benzene was added to the mark. A 50-ml volumetric flask with ca. 40 ml of dry benzene was weighed. Anhydrous dimethylamine was added and the weight of dimethylamine was obtained by difference in weight. Dry benzene was added to the mark. The amine solution was transferred to pipette into other volumetric flasks and diluted to the desired concentration. To a vial with 1 ml of **1** solution was added 1 ml of a standard amine solution at room temperature, and the course of the reaction was followed by TLC. After the reaction was complete, the benzene was removed by a steady stream of nitrogen, and methanol was added. The product ratio was analyzed by liquid chromatography (4-ft ODS column, 1000 lb, methanol–water, 40:60) with naphthalene as standard. No significant amount of diphenylacetylene was detected. The results of this experiment are given in Table I.

Table I
Product Ratio of the Reaction of 1 with Dimethylamine in Benzene

[Me_2NH], *M*	[Vinylamine **13**]/[sulfonate **11**]	[Me_2NH], *M*	[Vinylamine **13**]/[sulfonate **11**]
3.45	74.9	0.63	15.0
1.78	35.0	0.45	8.6
1.25	29.8	0.31	5.9
0.89	15.7	0.16	2.9

Reaction of 2,3-Diphenylthiirene 1,1-Dioxide (1) with Sodium Cyanide in DMF. To a solution of 1.00 g (4.13 mmol) of **1** in 10 ml of dry DMF was added in one portion, at room temperature, 215 mg (4.15 mmol) of sodium cyanide in 5 ml of dry DMF. A yellow color appeared immediately. After 10 hr, 1.0 ml of methyl iodide was added. After 3 hr, water was added carefully, and the resulting white precipitate was collected. Recrystallization from dichloromethane–hexane gave 750 mg (65%) of (*Z*)-1,2-diphenyl-2-cyanovinyl methyl sulfone (**18**): mp 161°; ir (KBr) 2940 (CH_3), 1315 and 1140 cm^{-1} (SO_2); Raman 2238 cm^{-1} (C≡N);[37] ^1H NMR ($CDCl_3$) δ 2.9 (s, 3 H) and 7.1–7.3 (m, 10 H); MS (70 eV) 283 (M^+) and 220 [$M^+ - (CH_3SO_2)$].

Anal. Calcd for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94. Found: C, 67.48; H, 4.63; N, 4.65.

Reaction of 1 with Excess Sodium Cyanide in DMF. A solution of 250 mg (1.08 mmol) of **1** and 500 mg (10 mmol) of sodium cyanide in 8 ml of DMF stood at ambient temperature for 15 hr. The solution was poured into 50 ml of water and extracted with three 30-ml portions of ether. A crystalline solid which was both water and ether insoluble was collected by filtration to give 130 mg (54%) of *meso*-1,2-dicyano-1,2-diphenylethane, mp 236–237° (lit.[38] 236–237°). The ether extracts were combined, and the ether was removed by rotary evaporation. The resulting material was chromatographed over 10 g of silica gel packed in hexane. Elution with 5% benzene in hexane gave 6 mg (3%) of diphenylacetylene. Elution with 20% ether in hexane gave 65 mg (27%) of (±)-1,2-dicyano-1,2-diphenylethane, mp 162–164° (lit.[38] 163–164°).

When α-cyanostilbene[38] was treated with sodium cyanide under the above conditions, an almost quantitative yield of *meso*- and (±)-1,2-dicyano-1,2-diphenylethane (2:1 ratio) was obtained. Treatment of either the meso or racemic diastereomer under the above conditions led to the same 2:1 mixture of diastereomers.

Acid Hydrolysis of 18. In a round-bottom flask containing 300 mg (1.06 mmol) of the sulfone **18** was added 4 ml of 85% phosphoric acid and 1 ml of 75% sulfuric acid. After being heated to 180° for 2 hr, the solution was cooled and ice water added carefully. The white crystals were collected and recrystallized from dichloromethane–hexane to yield 268 mg (86%) of (*Z*)-2,3-diphenyl-3-methylsulfonylacrylic acid (**25**): mp 198°; ir (KBr) 3500–2300 (OH), 1700 (C=O), 1320 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.9 (s, 3 H), 7.25–7.45 (m, 10 H), and 8.35 (s, 1 H).

Anal. Calcd for $C_{16}H_{14}O_4S$: C, 63.56; H, 4.67. Found: C, 63.72; H, 4.82.

Decarboxylation of 25. One milliliter of quinoline was added to a small test tube containing 100 mg (0.34 mmol) of the acid **25** and 20 mg of copper chromite catalyst. The test tube was heated to about 50° and evacuated with a vacuum pump for about 10 min to remove moisture. The tube was heated to 240° for 15 min. To the cooled yellow solution, 20 ml of ether was added, and the catalyst was removed by filtration. Quinoline was removed by extraction with two 10-ml portions of dilute hydrochloric acid, followed by 10 ml of saturated sodium chloride solution. After being dried ($MgSO_4$), the ether was removed in vacuo. Crystallization from carbon tetrachloride–hexane gave 37 mg (44%) of (*E*)-1,2-diphenylvinyl methyl sulfone (**24**): mp 117°; ir (KBr) 1320 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.8 (s, 3 H), 7.0–7.2 (m, 5 H), 7.45 (s, 5 H), and 7.82 (s, 1 H).

Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.47. Found: C, 69.81; H, 5.44.

Reaction of 1 with Sodium Benzenesulfinate in Methanol. One gram (4.13 mmol) of 1 was dissolved in 150 ml of Spectrograde methanol. Five grams (30.1 mmol) of sodium benzenesulfinate in 30 ml of methanol was added. After 4 days, the precipitate that had formed was collected to give 900 mg (68%) of (*E*)-1,2-diphenylvinyl phenyl sulfone (**26**), mp 182° (lit.[28] 182–183°).

Preparation of *threo*-2-Thiophenoxy-1,2-diphenyl-1-chloroethane. To a warm solution of 10 g (55 mmol) of *cis*-stilbene in 150 ml of glacial acetic acid was added rapidly 8 g (55 mmol) of phenylsulfenyl chloride.[39] After 5 min, the solution was poured over crushed ice. The aqueous solution was extracted twice with 150-ml portions of dichloromethane. The organic solution was washed with water and saturated $NaHCO_3$ followed by water. It was dried ($MgSO_4$) and the solvent was removed in vacuo. Crystallization from pentane–petroleum ether (bp 38–49°) gave 12.4 g (69%) of the sulfide: mp 47–49°; ^1H NMR ($CDCl_3$) δ 4.83 (d, J_{AB} = 7 Hz, 1 H), 5.40 (d, J_{AB} = 7 Hz, 1 H), and 7.1–7.5 (m, 15 H).

Anal. Calcd for $C_{20}H_{17}ClS$: C, 73.94; H, 5.28. Found: C, 74.20; H, 5.50.

Preparation of (*Z*)-1,2-Diphenylvinyl Phenyl Sulfone (27). To a solution of 1.0 g (3.1 mmol) of threo sulfide in 20 ml of Me_2SO was added 0.40 g (3.6 mmol) of potassium *tert*-butoxide in 10 ml of Me_2SO. The mixture was stirred at room temperature overnight, poured into 200 ml of ice water, and extracted twice by 50-ml portions of ether. The ether solution was dried ($MgSO_4$), and the solvent was removed in vacuo. Seventy milliliters of dichloromethane was added, followed by 2.0 g (ca. 10 mmol) of *m*-chloroperoxybenzoic acid (MCPBA). After standing for 3 hr at room temperature, the organic solution was washed twice with saturated sodium carbonate and once with water and dried ($MgSO_4$). The solvent was removed in vacuo. Crystallization from dichloromethane–hexane gave 700 mg (71%) of **27**, mp 131° (lit.[28] 133–134°). When the reaction was run in which the Me_2SO solution was warmed on a steam bath for 30 min and the resulting vinyl sulfide was oxidized with 30% hydrogen peroxide in acetic acid at 80° for 1 min, or with MCPBA in dichloromethane at room temperature for 6 hr, only sulfone **26** was isolated. However, when this reaction was run in which the Me_2SO solution was at room temperature overnight and the resulting vinyl sulfide was oxidized with 30% hydrogen peroxide in acetic acid at 80° for 1 min, **27** was isolated.

Isomerization of (*Z*)-1,2-Diphenylvinyl Phenyl Sulfone (27) to (*E*)-1,2-Diphenylvinyl Phenyl Sulfone (26). In a 50-ml flask containing 10 ml of ethanol was dissolved 100 mg (0.31 mmol) of **27**. The solution was treated with 5 ml of 0.2 *M* ethanolic sodium hydroxide and heated at reflux overnight. The solution was allowed to cool and water was added carefully. The crystals were collected and recrystallization from dichloromethane–hexane gave 40 mg (40%) of crystals, mp 180°. The infrared and ^1H NMR spectra were identical with those of **26**.

Preparation of (*Z*)-1,2-Diphenyl-2-methylsulfonylvinyl Phenyl Sulfone (19). To a solution of 220 mg (1.34 mmol) of sodium benzenesulfinate in 15 ml of dry DMF was added 300 mg (1.24 mmol) of 1. The solution turned yellow. The reaction was followed by TLC (silica gel–100% CH_2Cl_2), and was completed in about 30 min. One milliliter of methyl iodide was added, and the solution was heated at 40° for 1 hr. Water was added, and the solution was extracted three times with 20-ml portions of dichloromethane. The organic solution was dried ($MgSO_4$) and decolorized, and the solvent removed in vacuo. Crystallization from dichloromethane–hexane gave 150 mg (30%) of **19**: mp 172–173°; ir (KBr) 1310 and 1145 cm^{-1} (SO_2); ^1H NMR ($DCCl_3$) 3.37 (s, 3 H), 6.7–7.9 (m, 15 H).

Anal. Calcd for $C_{21}H_{18}O_4S_2$: C, 63.29; H, 4.56. Found: C, 63.35; H, 4.57.

X-Ray Analysis. Recrystallization of diphenylmethyl-(*Z*)-1,2-diphenylvinylsulfinophosphonium betaine (**3d**) from methanol–isopropyl ether gave suitable crystals for an X-ray diffraction analysis. The Laue symmetry, systematic absences, and rough values of the lattice constants were obtained from oscillation and Weissenberg X-ray photographs taken with Cu radiation. The final cell parameter and all intensity measurements were made with monochromatic Mo radiation (by diffraction from a highly oriented graphite crystal, $K\alpha\lambda$ = 0.71069 Å on a Picker FACS-I diffractometer). The crystal, a 0.12 × 0.28 × 0.29 mm parallelopiped with all angles approximately 90°, was mounted and aligned to place the [8, 0, −2] parallel to the ϕ axis of the instrument. The cell constants were calculated by the method of least square using 12 Bragg angles determined from manual measurements of $+2\theta$ and -2θ for each reflection; the average of $|2\theta_o - 2\theta_d|$ was 0.002°. The space group is $P2_1/c$, and cell parameters are a = 9.8970 (7), b = 15.822 (2), c = 15.728 (3) Å, β = 116.045 (6)°. The intensity data were measured using θ–2θ scan methods at a rate of 2° min^{-1} over 2θ range computed from 1.45° + 0.369° tan θ; 10-sec background measurements were made at the start and finish of each scan. Three standard reflections were measured every 100 reflections to monitor intensity fluctuations. Metal foil X-ray attenuators were automatically inserted into the diffracted beam to keep the maximum count rate below 15,000 counts sec^{-1}. A total of 4364 data were measured to a 2θ maximum of 50°; 4062 of the data (including 162 systematic absences) were unique; 2777 of the data were more than three standard deviations above background.[40]

The data were reduced and scaled, $|E|$'s were calculated, and the phases for 687 reflections (295+, 282−) were obtained in a straightforward way, using the direct methods program PHASE.[41] An E map computed with these 687 data revealed the 27 C, 2 O, S, and P atoms and a structure factor calculation gave an R index ($R = \Sigma|F_o - F_d|/\Sigma F_o$) of 0.241.

The structure was refined with the method of full matrix least squares, minimizing the function $\Sigma w(F_o - F_c)^2$; unit weights (w = 1) were used initially, but Hughes-type[42] weights (w = 1 if $F_o \leq 50$, $w = (50/F_o)^2$ if $F_o > 50$) were applied in the later refinement cycles. A reflection was included in the calculations only in those cases which I_c was greater than $3\sigma(I_o)$. Hydrogen atoms were located in a different map. The last stages of refinement used anisotropic temperature factors for C, O, S, and P, isotropic terms for H, and included a correction for isotropic secondary extinction [r^* = 0.0069 (2)[43]]. X-Ray scattering factors: C, O, S, P,[44] H.[45] The final R index was 0.036; the weighted R index $[(\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}]$ was 0.037. The atomic parameters and the calculated and observed structure factors are listed in the microfilm supplement.

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Registry No.—**1**, 5162-99-2; **11**, 56437-42-4; **13**, 56437-43-5; **14**, 56437-44-6; **15**, 16003-69-3; **18**, 56437-45-7; **19**, 56437-46-8; **24**, 56437-47-9; **25**, 56437-48-0; **26**, 53105-00-3; **27**, 5533-33-5; dimethylamine, 124-40-3; (*E*)-1,2-diphenylvinylsulfonyl chloride, 56437-49-1; phosphorus pentachloride, 10026-13-8; *p*-toluidine, 106-49-0; dimethylammonium chloride, 506-59-2; sodium cyanide, 143-33-9; *threo*-2-thiophenoxy-1,2-diphenyl-1-chloroethane, 56437-50-4; sodium benzenesulfinate, 873-55-2; *cis*-stilbene, 645-49-8; phenylsulfenyl chloride, 931-59-9.

Supplementary Material Available. A listing of observed and calculated structure factors appears in the 1974 microfilm edition of the Journal of the American Chemical Society following p 8094. Photocopies or microfiche (105 × 148 mm, 24× reduction, negatives) of that supplementary material may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W. Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-74-8087.

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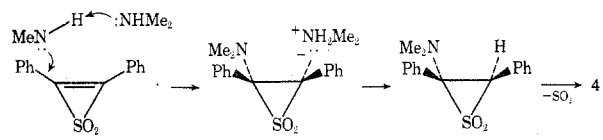
(20) This reaction, 7, for the sake of economy was represented as a cyclic concerted addition across the carbon–carbon double bond. A similar process was suggested for the addition of amines to *p*-tolyl vinyl sulfone in benzene.[3a] However, reaction 7 could take place stepwise.[4a]



(21) This same result is obtained if excess sodium cyanide in DMF is added to a solution of **16** generated in reaction 8. Treatment of **1** with sodium cyanide in methanol gave the methyl sulfonate **15**, the result of the reaction of **1** with methoxide ion.[16]
(22) C. J. M. Stirling, *Int. J. Sulfur Chem., Part B*, **6**, 277 (1971).
(23) Normally, hydrolysis of the cyano group and decarboxylation of the resulting acid would be expected to take place with no accompanying cis-trans isomerization.[24] However, since the observed product (**24**) is certainly the thermodynamic product,[25] it is possible that the conditions of one or both steps in reaction 11 are sufficient to cause isomerization. For example, oxidation (warm peracetic acid) of (*Z*)-1,2-diphenyl-1-benzylthioethene gave a mixture of both (*E*)- and (*Z*)-1,2-diphenyl-1-benzylsulfonylethene.[26]
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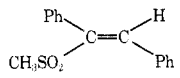
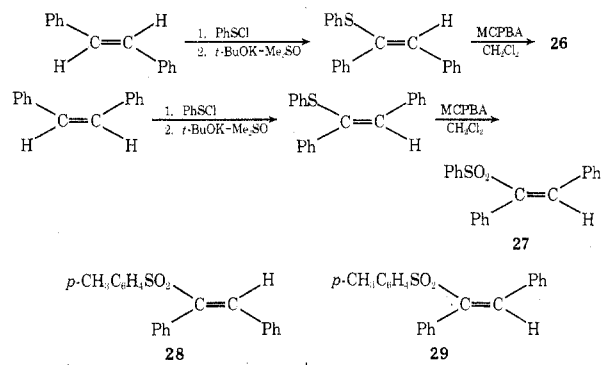
(27) The vinyl sulfone **24**, mp 117°, appears to have been assigned as the *Z* isomer i by earlier workers [M. Oki and A. Kimura, *Bull. Chem. Soc. Jpn.*, **38**, 682 (1965)], based solely on the expected stereochemistry of the base-initiated elimination of hydrogen chloride from *threo*-1-chloro-2-methylthio-1,2-diphenylethane to give (*Z*)-1,2-diphenylvinyl methyl sulfide. This sulfide was oxidized by peracetic acid to a vinyl sulfone, mp 118–119°, which was believed to be i. However, we feel, based on the expected stereochemistry of reactions 8 and 11 as well as the proof of structure for the vinyl sulfone **26**[28] (vide infra), that this sulfone assigned structure i is actually (*E*)-1,2-diphenylvinyl methyl sulfone (**24**).



i

(28) Apparently, sulfone **26** was isolated earlier from the reaction of benzenesulfonyl chloride with phenyllithium but was assigned the *Z* configuration (**27**); an isomeric sulfone said to be **26** was isolated when this reaction was run at low temperature [Y. Shirota, T. Nagai, and N. Tokura, *Tetrahedron*, **23**, 639 (1967)]. Implicit in these assignments was the assumption that (*Z*)-**27** is more stable than (*E*)-**26**. This is certainly not the case, as shown by Cristol and Pappas.[25b] We have synthesized stereospecifically sulfones **26** and **27**[29] (see below) and find that with sodium ethoxide in ethanol, **27** is isomerized to **26**.[30] Furthermore, the reported melting point and uv data for the two series of sulfones (**26** and **27** vs. **28** and **29**) are inconsistent; for the *p*-tolyl sulfones (**28** and **29**) the higher melting isomer had a higher λ_{max} and larger ϵ and was assigned the *E* configuration,[25] whereas for the phenyl sulfones **26** and **27**, the higher melting isomer (higher λ_{max} and larger ϵ) was assigned the *Z* configuration by Shirota. The earlier configuration assignments for **26** and **27** should be reversed.



(29) Treatment of *threo*-1-thiophenoxy-2-chloro-1,2-diphenylethane with potassium *tert*-butoxide in dimethyl sulfoxide (Me_2SO) at 25° followed by oxidation with either *m*-chloroperoxybenzoic acid in dichloromethane at 25° (6 hr) or oxidation with hydrogen peroxide in acetic acid at 80° (1 min), gave **27**. However, if the dehydrohalogenation was run in hot Me_2SO (steam bath, 30 min), oxidation led to the vinyl sulfone **26**. Apparently, the strongly basic conditions of potassium *tert*-butoxide in Me_2SO at elevated temperatures is sufficient to cause epimerization of the intermediate vinyl sulfide.
(30) Sodium benzenesulfinate in methanol does not cause the isomerization of **27** to **26**, and therefore sulfone **27** is not involved in the reaction of **1** with sodium benzenesulfinate in methanol.
(31) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 2960 (1967).
(32) Although triphenylphosphine does not react with **1** in benzene,[6] it does react in methanol to give at least five products from which a 30% yield of **3**, $R^1 = R^2 = R^3 =$ Ph, was isolated. This shows that the electrocyclic ring opening of **31** is at least competitive with protonation by methanol solvent.
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