Diphenylthiirene 1-Oxide. Synthesis, Characterization, and Reactivity

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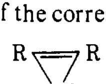
Abstract: The synthesis of 2,3-diphenylthiirene 1-oxide (**7**) by treatment of (±)-α,α'-dibromodibenzyl sulfoxide (**5**) with triethylamine in methylene dichloride solution is described. The sulfoxide **5** was obtained by careful oxidation of the free radical bromination product of dibenzyl sulfide, (±)-α,α'-dibromodibenzyl sulfide (**4**), by means of *m*-chloroperbenzoic acid. The structure of **7** was established by oxidation to the corresponding well-known sulfone (**1**, R = C_6H_5). Photolysis of **7** at 30 °C gave diphenylacetylene. Thermolysis of **7** appeared to be accompanied by ring expansion to the corresponding oxathiete derivative **10** as evidenced by the isolation of benzil. Reaction of **7** with hydroxylamine gave a mixture of α-benzil dioxime (**18**) and deoxybenzoin oxime (**17**). Treatment of **7** with phenyldiazomethane gave 3,4,5-triphenylpyrazole (**14**) and excess phenylmagnesium bromide led to the formation of phenyl triphenylvinyl sulfide (**15**). Synthesis of the *m*- and *p*-fluoro derivatives of **7** as well as the corresponding sulfones and ketones **20** followed by examination of their ^{19}F NMR spectra provided evidence for conjugative effects increasing in the order thiirene oxide < thiirene dioxide < cyclopropenone.

Following the synthesis of several thiirene 1,1-dioxides **1**[1] it was naturally of considerable interest to attempt the preparation of the corresponding monoxides **2**.[2] Although also potentially aromatic, such compounds would be of even greater novelty owing to the presence on the central sulfur atom of an unshared pair of electrons with its possible antiaromatic destabilizing influence. The modified Ramberg-Bäcklund reaction which had proved successful in the synthesis of aryl-substituted dioxides **1** also made possible the development of a general route to the corresponding monoxides via reaction of benzylic α,α'-dibromo sulfoxides with triethylamine.



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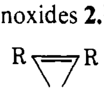

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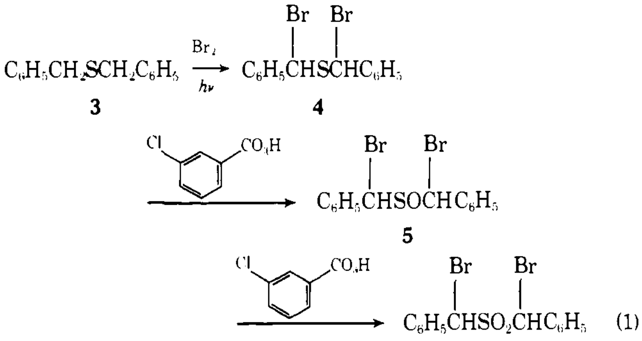
Previously[1] we brominated dibenzyl sulfide photolytically and oxidized the intermediate dibromo sulfide to obtain α,α'-dibromodibenzyl sulfone (**6**). We have now succeeded in stopping the oxidation at the sulfoxide stage by isolating and purifying the labile dibromo sulfide **4** and carefully oxidizing with 1 equiv of *m*-chloroperbenzoic acid (eq 1). The dibromo sulfide showed in the NMR spectrum, in addition to the phenyl peaks, two singlets at δ 6.34 and 5.55 in the ratio 4:1. The major component in the mixture was shown to be the racemic isomer by further oxidation to the known racemic sulfone.[1,3] The corresponding sulfoxide showed two one-proton singlets at δ 5.53 and 6.26 confirming its assignment as the racemic isomer.[4,5]

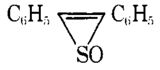


$$C_6H_5CH_2SCH_2C_6H_5 \xrightarrow[h\nu]{Br_2} C_6H_5\overset{Br}{C}HS\overset{Br}{C}HC_6H_5 \longrightarrow C_6H_5\overset{Br}{C}HSO\overset{Br}{C}HC_6H_5 \longrightarrow C_6H_5\overset{Br}{C}HSO_2\overset{Br}{C}HC_6H_5 \quad (1)$$

3 **4** **5** **6**

Upon refluxing a solution of racemic α,α'-dibromodibenzyl sulfoxide with excess triethylamine in methylene dichloride for 2 days triethylamine hydrobromide was precipitated and thiirene oxide **7** was isolated in about 50% yield. Treatment of **5** with aqueous sodium hydroxide also gave the desired compound, albeit in very low yield (ca. 9%). The structural assignment was verified by oxidation to the corresponding sulfone (**1**, R = C_6H_5) whose structure had previously been firmly established.[1] Subsequently X-ray analysis confirmed both structural assignments.[6]

Compound **7** is a snow-white, crystalline solid, mp 92.5–93.1 °C, which is far more stable thermally than either of the two saturated analogues **8** in spite of the significantly less angular strain of the dihydro derivatives. Both *cis*- and *trans*-**8** were found to undergo ready loss of sulfur monoxide on warming.[7] The sulfoxide **7** is also much more stable thermally than the corresponding sulfone **1** (R = C_6H_5). Clearly there can be no significant antiaromatic destabilizing effects ascribable to the presence of an unshared pair of electrons on the sulfur atom of sulfoxide **7**. Comparable electron-attracting conjugative influences must be operative in the case of both sulfoxide and sulfone. The greater stability of the sulfoxide presumably reflects the fact that sulfur dioxide is a better leaving group than sulfur monoxide since the same difference is observed between *cis*- and *trans*-**8** and the saturated sulfones **9**, the trans isomer of which is so unstable that it has never been isolated in a pure state.[8]



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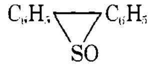

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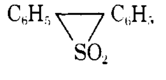

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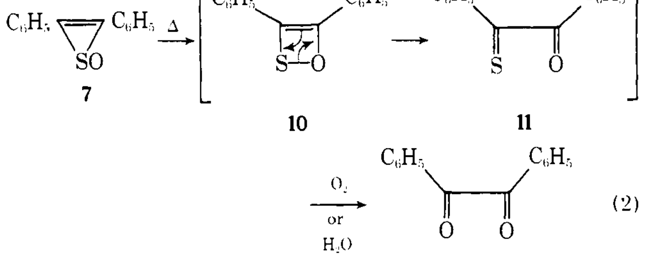
The sulfoxide **7** takes on a yellow surface color on exposure to direct sunlight. Irradiation with an ultraviolet source at 30°C in a quartz vessel gave diphenylacetylene. Thermolysis at 130°C gave benzil **12** as the only product which could be isolated. One can rationalize the formation of benzil as outlined in eq 2 by ring expansion to the oxathiete **10** followed by re-



7 **10** **11** **12** (2)

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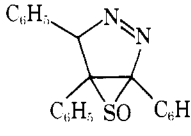
arrangement to monothiobenzil[9] **11** which might be expected to undergo hydrolysis or air oxidation to give benzil **12**.

Chemical Properties of Diphenylthiirene 1-Oxide. Oxidation of **7** to the corresponding sulfone has been described above. Attempts to reduce the carbon-carbon double bond under a variety of conditions (Pd/C, Pt sulfide/C, $Al(Hg)_x/H_2O$) failed. Raney nickel gave only dibenzyl. Treatment of **7** with phenyldiazomethane in ether resulted in the formation of 3,4,5-triphenylpyrazole (**14**) which presumably arises by loss of sulfur monoxide from the labile adduct **13**. The corresponding sulfone undergoes a similar reaction. With 2 equiv of phenylmagnesium bromide **7** was converted to phenyl triphenylvinyl sulfide (**15**) in 62% yield. The structure of **15** was established by an unambiguous synthesis from triphenylvinylmagnesium bromide (**16**) and benzenesulfenyl chloride.



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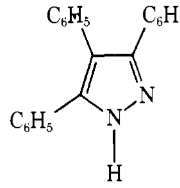

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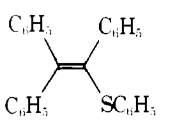

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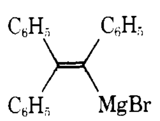

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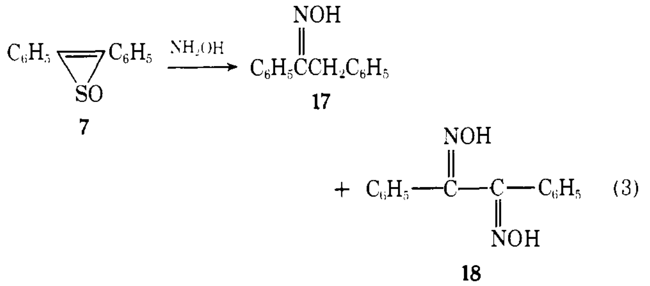
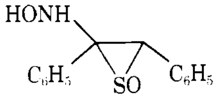
Formation of **15** from **7** can be rationalized by a variety of pathways depending on whether initial attack of the Grignard reagent occurs at the conjugated double bond or the sulfoxide function.[12]

Treatment of the sulfoxide with hydroxylamine gave a mixture of deoxybenzoin oxime **17** (36%) and α-benzil dioxime **18** (13%) (eq 3). The former is probably derived from the conjugate addition product **19**, the latter from monothiobenzil **11**.



In order to make a rough estimate of the nature of the conjugative effects present in the three-ring sulfoxides and their comparison with those of the corresponding sulfone and ketone we have prepared the *m,m′*- and *p,p′*-fluoro derivatives of the three systems **20** (Z = SO, SO_2, CO). Both of the sulfoxides were synthesized by techniques analogous to those described for **7**. The sulfones were obtained by the same general method previously described[1] for the parent diphenyl compound. Bis(*m*-fluorophenyl)thiirene dioxide (**21**) served as a convenient precursor of the corresponding cyclopropenone (eq 4). Taft and co-workers[13] have demonstrated the extreme sensitivity of ^{19}F shielding to intramolecular perturbation by ring substituents in fluorobenzenes. With such measurements these workers have developed generalized correlations which permit isolation of the inductive (σ_I) and conjugative (σ_R) effects. Table I lists the shielding parameters of the compounds studied and Table II lists the σ values calculated from these experimental observations. The σ_I value for the thiirene dioxide system is significantly higher than that of the monoxide which in turn is somewhat higher than that of the cyclopropenone reflecting the decreasing electron-withdrawing inductive effects of the three compounds. A similar order has been observed by Taft for simple sulfone, sulfoxide, and ketone substituents.[13b]



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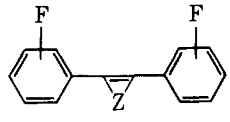
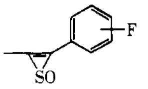
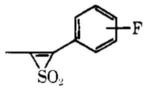
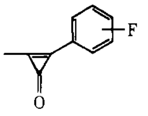


20, Z = SO, SO_2, CO

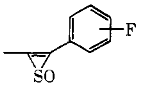
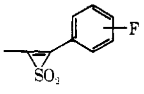
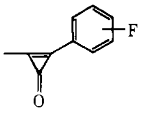
Comparison of σ_R values shows that the extent of the electron-withdrawing conjugative effect increases in the order thiirene oxide < thiirene dioxide < cyclopropenone. This also agrees with earlier studies on the relative order of conjugative interaction in simple sulfoxides and sulfones and indicates clearly that the greater thermal stability of the thiirene oxide relative to the dioxide cannot be related to conjugative interaction. These data are not of course pertinent to the question of whether these are simple conjugative interactions or involve cyclic conjugative effects with transmission through the sulfur atom.[15]

Table I. ^{19}F NMR Shielding Parameters of Substituted Fluorobenzenes (FC_6H_4X) (ppm)

X	solvent	$\int_H^{m\text{-}X}$	$\int_H^{p\text{-}X}$	$\int_{m\text{-}X}^{p\text{-}X}$
	$CHCl_3$	−2.73	−7.48	−4.75
	$CHCl_3$	−3.86	−10.19	−6.33
	$CHCl_3$[a]	−2.24	−9.65	−7.41

[a] The meta isomer was measured in CH_2Cl_2; bis(*p*-fluorophenyl)cyclopropenone was kindly provided by Dr. S. Tobey,[14] Dow Chemical Co.

Table II. Substituent Parameters of Substituted Fluorobenzenes (FC_6H_4X)

X	solvent	σ_I	σ_R
	$CHCl_3$	0.47	0.16
	$CHCl_3$	0.63	0.21
	$CHCl_3$[a]	0.40	0.25

[a] The meta isomer was measured in methylene dichloride.

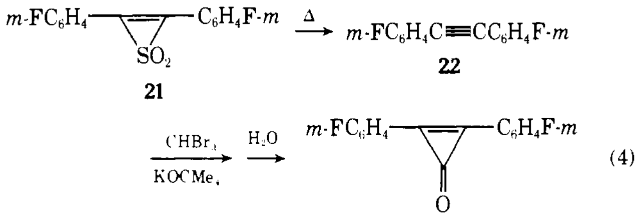
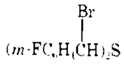
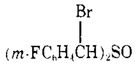
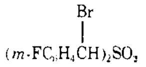
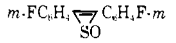
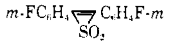
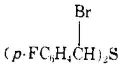


Table III. Fluorinated Sulfides, Sulfoxides, and Sulfones[a]

compd	yield, %	mp, °C (recryst solvent)	elemental anal.	^{1}H NMR spectrum (solvent), δ
$(m\text{-}FC_6H_4CH_2)_2S$	86	*b*	C, H, S	(CCl_4) 3.45 (s, 4, CH_2), 6.98 (m, 8, aryl)
 $(m\text{-}FC_6H_4\overset{Br}{\overset{\vert}{C}}H)_2S$	65	58.5-60 (ligroin)	C, H, Br, F, S	(CCl_4) 6.29 (s, 1, CH), 6.78-7.46 (m, 4, aryl)[c]
 $(m\text{-}FC_6H_4\overset{Br}{\overset{\vert}{C}}H)_2SO$	79	100-102 (C_6H_6-ligroin)	C, H, Br, F, O, S	($CDCl_3$) 5.47 (s, 1, CH), 6.25 (s, 1, CH), 7.30 (m, 8, aryl)
 $(m\text{-}FC_6H_4\overset{Br}{\overset{\vert}{C}}H)_2SO_2$	78	194-200 ($CHCl_3$)	C, H, Br, F, S	
	57	120-121 (C_6H_6-ligroin)	C, H, S	($CDCl_3$) 7.05-7.75 (m, aryl)
	90	129-131 dec (C_6H_6)	C, H, F, S	($CDCl_3$) 7.20-7.70 (m, aryl)
 $(p\text{-}FC_6H_4\overset{Br}{\overset{\vert}{C}}H)_2S$	59	61-62 (ligroin)	C, H	(CCl_4) 6.30 (s, 1, CH), 6.99 (m, 2, *m*-aryl), 7.47 (m, 2, *o*-aryl)[d]

[a] In each case the method used parallels a procedure described in detail in the Experimental Section or in a previous paper[1a] for an analogous compound. [b] Bp 115 °C (0.4 mm). [c] The appearance of a single at δ 5.53 integrating for 1/6 proton indicated contamination of the major racemic product by the meso isomer. [d] The appearance of a singlet at δ 5.53 integrating for 1/4 proton indicated contamination of the major racemic product by the meso isomer.

Experimental Section[16]

(+)-α,α′-Dibromodibenzyl Sulfide (4). To a gently refluxing solution of 107 g of dibenzyl sulfide in 1500 mL of anhydrous CCl_4 (distilled over P_2O_5) was added dropwise over a period of about 3 h a solution of 160 g of Br_2 in 200 mL of anhydrous CCl_4 while focusing a 275-W G.E. sunlamp on the refluxing solution from a distance of 0.5 in. The mixture was refluxed for an additional 3 h and evaporated in vacuo to give a violet-colored oil. To the oil was added 700 mL of ligroin (bp 67-71 °C) and the solution cooled in an ice bath. Filtration of the resulting white solid followed by quick washing with ligroin gave 100 g of white solid, mp 74-78.5 °C. The combined filtrate and washings were concentrated and cooled to give another 45 g of white solid, mp 74-79 °C. The combined crude dibromo sulfide (145 g, 78.3%) was recrystallized twice from ligroin to give 129 g (69.7%) of the dibromide, mp 78-81.2 °C. The analytical sample (ether) had mp 79.5-81 °C; NMR (CCl_4) δ 6.34 (s, 2, CHBr), 7.32 (m, 10, phenyl). The appearance of a singlet at δ 5.55 integrating for 1/4 proton indicates contamination by the meso isomer. The material could be stored without deterioration in a refrigerator at −15 °C, although it decomposed slowly on exposure to air at room temperature.

Anal. ($C_{14}H_{12}Br_2S$) C, H, S.

(±)-α,α′-Dibromodibenzyl Sulfoxide (5). To a stirred solution of 69 g (0.185 mol) of α,α′-dibromodibenzyl sulfide in 500 mL of anhydrous ether there was added dropwise over a period of 20 min with stirring and cooling in an ice bath a solution of 40 g (0.185 mol, based on 80% purity) of *m*-chloroperbenzoic acid[17] in 200 mL of anhydrous ether. After complete addition the mixture was allowed to come to room temperature. At the end of 4 h the solvent was removed in vacuo to give a white solid which was treated with saturated $NaHCO_3$ solution until gas evolution ceased. Filtration of the remaining solid followed by thorough washing with water and then 200 mL of cold (10-15 °C) EtOH gave 57.3 g (80%) of crude racemic-α,α′-dibromodibenzyl sulfoxide, mp 107-121 °C. Two recrystallizations from EtOH gave 40 g (55.7%) of the pure sulfoxide, mp 120-123 °C. The analytical sample (EtOH) had mp 121-123.5 °C; IR ($CHCl_3$) 1073 cm^{-1} (S═O); NMR ($CDCl_3$) δ 5.53 (s, 1, CHBr), 6.26 (s, 1, CHBr), 7.45 (m, 10, phenyl).

Anal. ($C_{14}H_{12}Br_2OS$) C, H, Br, S.

Oxidation of (±)-α,α′-Dibromodibenzyl Sulfoxide. To a stirred solution of 2.03 g of (±)-α,α′-dibromodibenzyl sulfoxide in 300 mL of anhydrous ether there was added dropwise a solution of 1.38 g (90%) purity) of *m*-chloroperbenzoic acid.[17] The mixture was refluxed for 48 h and the solvent removed in vacuo to give a white solid which was treated with saturated $NaHCO_3$ solution until gas evolution ceased. Filtration followed by washing with cold water and 15 mL of cold EtOH (10-15 °C) gave 1.95 g (92.2%) of the crude sulfone, mp 155-159 °C. Recrystallization from EtOH have 1.6 g (75.6%) of (±)-α,α′-dibromodibenzyl sulfone, mp 161-162.5 °C (lit[1] mp 157-159 °C), which was identified as the racemic isomer by the mixture melting point and comparison of IR and NMR spectra with those of an authentic sample.

2,3-Diphenylthiirene 1-Oxide (7). A stirred solution of 66 g (0.17 mol) of (±)-α,α′-dibromodibenzyl sulfoxide in 420 mL of CH_2Cl_2 and 86 g (0.85 mol) of NEt_3 (distilled over phenyl isocyanate) was refluxed gently for 48 h, cooled, and filtered and the solid was washed with 40 mL of cold (5-10 °C) CH_2Cl_2. The methylene dichloride solution was extracted with three 150-mL portions of 3 N HCl followed by two 100-mL portions of H_2O and dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was washed with 50 mL of cold (5-10 °C) ether-ligroin (bp 67-71 °C) (2:1) to give 16 g of tan-colored solid, mp 85-91 °C. Addition of 150 mL of ether-ligroin (bp 67-71 °C) (1:1) to the filtrate followed by boiling for 5 min, filtration, and cooling in a refrigerator (−15 °C) gave an additional 7 g of tan-colored solid, mp 84-90 °C. Decolorization by means of activated carbon (Darco G-60) and recrystallization of the combined crude solid (23 g, 60%) from ligroin gave 19.5 g (50.7%) of the vinylene sulfoxide, mp 92-93 °C. The analytical sample (from ether-ligroin and ligroin, bp 67-71 °C) had mp 92.5-93.1 °C; IR ($CHCl_3$) 1061 cm^{-1} (S═O); NMR ($CDCl_3$) δ 7.52 (m, 6, *m*- and *p*-phenyl), 7.87 (m, 4, *o*-phenyl); UV (95% EtOH) nm (log ε) 220 (4.41), 227.5 (4.40), 292.5 sh (4.40), 299 (4.45), 310 sh (4.38).

Anal. ($C_{14}H_{10}OS$) mol wt 226.28; C, H, O, S; mol wt (osmometric in EtOAc) 228.

Oxidation of 2,3-Diphenylthiirene 1-Oxide. To a stirred solution of 1.13 g of **7** in 15 mL of methylene dichloride there was added dropwise a solution of 1.13 g of *m*-chloroperbenzoic acid (95%)[18] in 20 mL of methylene dichloride. The solution was refluxed for 20 h, washed with three 15-mL portions of saturated $NaHCO_3$ solution followed by two 15-mL portions of water, dried ($MgSO_4$), and evaporated in vacuo. The residual solid was recrystallized from benzene-ligroin (bp 67-71 °C) (1:1) to give 0.27 g of crude **1** (R = C_6H_5). Concentration of the filtrate followed by chromatographic separation of the residue on silica gel with elution by benzene-chloroform (1:1) gave an additional 0.1 g of **1** (R = C_6H_5) as well as 0.12 g of recovered sulfoxide **7**. The combined crude sulfone (0.37 g, 30%) was recrystallized from benzene to give 0.25 g (20.7%) of 2,3-diphenylthiirene 1,1-dioxide, mp 116-126 °C dec (lit.[1] mp 116-126 °C dec), which was identified by mixture melting point and comparison of IR and NMR spectra with those of an authentic sample.

Bis(*p*-fluorobenzyl) Sulfide. To a well-stirred solution of 26.5 g (0.185 mol) of *p*-fluorobenzyl chloride in 150 mL of ethanol there was added slowly a solution of 28 g (0.117 mol) of sodium sulfide nonahydrate in 15 mL of water. The mixture was refluxed gently over a steam bath for 1 day. Most of the ethanol was removed under reduced pressure over a steam bath, the remaining mixture cooled, and 800 mL of water added. The resulting mixture was extracted with three 50-mL portions of ether. The combined ether extracts were washed with 100 mL of water, dried over anhydrous magnesium sulfate, and filtered. Evaporation of the ether under reduced pressure and vacuum distillation of the resulting residue yielded 19.3 g (83%) of an oil, bp 115 °C (0.3 mm), which soon solidified, mp 60-63 °C. One recrystallization from ligroin (bp 67-71 °C) afforded 17 g (73.5%) of bis(*p*-fluorobenzyl) sulfide, mp 63.7-64.5 °C. An analytical sample was prepared by an additional recrystallization from ligroin (bp 67-71 °C): mp 64-64.8 °C; NMR (CCl_4) δ 3.41 (s, 4, methylene), 7.00 (m, 8, aromatic).

Anal. ($C_{14}H_{12}F_2S$) C, H, S, F.

2,3-Bis(*p*-fluorophenyl)thiirene 1-Oxide. Generally the intermediate bis(α-bromobenzyl) sulfoxide was isolated and purified prior to reaction with triethylamine. In the present case the crude dibromide is used without isolation. To a well-stirred cold solution (ice bath) of 14 g (0.0343 mol) of bis(α-bromo-*p*-fluorobenzyl) sulfide in 150 mL of anhydrous ether was added dropwise over a period of 10 min a solution of 7.4 g (0.0343 mol based on 80% purity) of *m*-chloroperbenzoic acid[17] in 60 mL of anhydrous ether. After complete addition the mixture was allowed to come to room temperature. At the end of 4 h the ether was removed in vacuo to afford a gummy, white solid which was dissolved in 100 mL of chloroform. The chloroform solution was washed with three 25-mL portions of saturated sodium bicarbonate solution and two 30-mL portions of water, dried over anhydrous magnesium sulfate, and filtered. Evaporation in vacuo over a 50 °C water bath yielded 14 g of a slightly orange-colored oil. To a solution of 14 g of the crude oil in 80 mL of methylene dichloride was added 21.8 g (0.215 mol) of triethylamine (distilled over phenyl isocyanate) and the mixture gently refluxed. At the end of 24 h the mixture was filtered and the solid washed with 20 mL of cold (5-10 °C) methylene dichloride. The brown methylene dichloride solution was washed with three 30-mL portions of 3 N hydrochloric acid followed by two 25-mL portions of water, dried over anhydrous magnesium sulfate, and filtered. Evaporation of most of the methylene dichloride caused crystallization of a tan-colored solid which was filtered and washed with 15 mL of a cold 2:1 mixture of ether-ligroin (bp 67-71 °C) to give 2.7 g of a tan-colored solid, mp 149-151 °C. Addition of 15 mL of a 1:1 mixture of ether-ligroin (bp 67-71 °C) to the filtrate followed by boiling for 1 min, filtration, and cooling in a refrigerator (−15 °C) overnight gave an additional 0.4 g of tan-colored solid, mp 146-150 °C. The combined tan-colored solid (3.1 g, 34.5%) was decolorized with activated carbon (Darco G-60) and recrystallized twice from a 1:4 mixture of benzene-ligroin (bp 67-71 °C) to afford 2.5 g (27.8%) of the thiirene oxide, mp 151-154 °C dec. An analytical sample, mp 157-160 °C dec, was prepared by two additional recrystallizations from a 1:3 mixture of benzene-ligroin (bp 67-71 °C); IR ($CHCl_3$) 1065 cm^{-1} (S=O); NMR ($CDCl_3$) δ 7.31 (m, 4, *m*-phenyl), 7.93 (m, 4, *o*-phenyl).

Anal. ($C_{14}H_8F_2OS$) C, H, S.

2,3-Bis(*p*-fluorophenyl)thiirene 1,1-Dioxide. Generally the intermediate bis(α-bromobenzyl) sulfide and sulfoxide were isolated and purified prior to reaction with triethylamine. In the present case neither of these intermediates is isolated. To a stirred solution of 11.5 g of bis(*p*-fluorophenyl) sulfide in 150 mL of anhydrous CCl_4 there was added dropwise over a period of 1.5 h a solution of 14.7 g of Br_2 in 50 mL of CCl_4 while irradiating with a General Electric 275-W sunlamp placed 0.5 in. from the flask. The solution was stirred at room temperature for an additional 4 h and the solvent removed from a water bath at 50 °C with the aid of a water aspirator. The pink-colored residue was dissolved in 30 mL of anhydrous ether, the solution cooled in an ice bath, and a solution of 30 g of *m*-chloroperbenzoic acid[17] (80% pure) in 140 mL of ether added over a period of 10-15 min. The solution was stirred in the ice bath for 2 h and then at room temperature for 24 h followed by evaporation in vacuo. To the residue there was added a solution of 25 g of $NaHCO_3$ in 300 mL of H_2O and the mixture stirred at room temperature for 8 h. The cream-white powder was filtered, washed with water, and recrystallized from EtOH to give 8 g of the dibromo sulfone (mp 120-135 °C; IR (Nujol) 1333, 1136 cm^{-1}), which was pure enough to use in the subsequent cyclization. The crude dibromo sulfone (8 g) was dissolved in 100 mL of CH_2Cl_2, 6.53 mL of triethylamine added, and the solution refluxed with stirring for 4 h. The mixture was extracted with two 50-mL portions of water, and dried ($MgSO_4$) and the solvent was removed in vacuo to give a solid which upon recrystallization from benzene gave 3.8 g (29.7%) of the thiirene dioxide as white, flaky crystals: mp 141-148 °C dec; IR (Nujol) 1250, 1149 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.1-7.9 (m, aromatic).

Anal. ($C_{14}H_8F_2SO_2$) C, H, F.

Bis(*m*-fluorophenyl)acetylene. Five grams (0.018 mol) of bis(*m*-fluorophenyl)thiirene 1,1-dioxide in a 10-mL Erlenmeyer flask was heated in a 175 °C oil bath. The compound melted immediately and an evolution of sulfur dioxide was observed. The greenish oil solidified soon after removing the flask from the oil bath to give 3.75 g (97.5%) of crude bis(*m*-fluorophenyl)acetylene, mp 61-62 °C. An analytical sample, mp 62-62.5 °C, was prepared by recrystallization from ligroin (bp 67-71 °C) followed by sublimation, NMR (CCl_4) δ 6.75-7.40 (m, aromatic).

Anal. ($C_{14}H_8F_2$) C, H, F.

2,3-Bis(*m*-fluorophenyl)cyclopropenone. Bis(*m*-fluorophenyl)-acetylene (2.05 g) was converted to the cyclopropenone by the method of Vol'pin and Breslow.[19] There was obtained 0.45 g (20.4%) of the ketone, mp 152-156 °C dec. An analytical sample, mp 155-158 °C dec, was obtained by two recrystallizations from a 2:1 mixture of ligroin (bp 67-71 °C) and benzene, IR ($CHCl_3$) 1850 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.54 (m, aromatic).

Anal. ($C_{15}H_8F_2O$) C, H, F.

Photodecomposition of 2,3-Diphenylthiirene 1-Oxide. A solution of 1 g (0.004 42 mol) of 2,3-diphenylthiirene 1-oxide in 500 mL of benzene was irradiated under a positive nitrogen pressure with a 450-W Hanovia lamp no. 79A36 at 30 °C. At the end of 3 h the solution was evaporated under reduced pressure to afford 0.76 g (96.5%) of a solid, mp 55-60 °C. Recrystallization from 75% ethanol yielded 0.68 g (86.5%) of diphenylacetylene, mp 60-62 °C (lit.[20] mp 60-61 °C), which was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Thermal Decomposition of 2,3-Diphenylthiirene 1-Oxide. Into a semimicrosublimation apparatus was put 0.5 g of the sulfoxide. The apparatus was then heated at 130 °C in an oil bath for 24 h. Some greenish-yellow solid was observed on the condenser and an additional quantity sublimed under the reduced pressure of a water aspirator. At the end of 30 h 0.2 g of a greenish-yellow solid, mp 90-93 °C, was obtained. Recrystallization from *n*-hexane yielded 0.15 g (32.3%) of benzil, mp 95-96 °C (lit.[21] mp 95-96 °C), which was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample. The remaining brownish-orange residue was not further investigated, although its infrared spectrum indicated the presence of additional benzil as well as other unidentified compounds. Upon refluxing a benzene solution of the thiirene 1-oxide for 40 h it was possible to recover 93% of the unreacted starting material.

Treatment of 2,3-Diphenylthiirene 1-Oxide with Phenyldiazomethane. A solution of phenyldiazomethane in ether was prepared from azibenzil according to the procedure of Yates and Shapiro[22] from 4.8 g of sodium hydroxide, 90 mL of water, 60 mL of methanol, and a solution of 3.34 g (0.015 mol) of azibenzil in 75 mL of ether. To the stirred red phenyldiazomethane solution (ca. 0.01 mol) was added 2.26 g (0.01 mol) of 2,3-diphenylthiirene 1-oxide. The solution became yellow in color after 3 h and a white precipitate appeared after 5 h. Upon filtration of the mixture after 22 h there was obtained 0.4 g of a white solid, mp 175-250 °C. Recrystallization from ethanol yielded 0.28 g (9.45%) of 3,4,5-triphenylpyrazole, mp 263-264.5 °C (lit.[23] mp 265 °C), identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Evaporation of the ether solution from the original reaction mixture under reduced pressure at room temperature afforded a yellow oil. Chromatography of the oil on silica gel and elution with a 5:1 mixture of benzene-ligroin (bp 67-71 °C) led to the isolation of 0.15 g of *trans*-stilbene, mp 120-123 °C (lit.[24] mp 124 °C). Upon subsequent elution with methanol there was recovered 0.8 g (35.4%) of 2,3-diphenylthiirene 1-oxide.

Treatment of 2,3-Diphenylthiirene 1-Oxide with Hydroxylamine. To a stirred solution of 30 g (0.0132 mol) of the thiirene oxide in 80 mL of dioxane was added dropwise a solution of 7.2 g of NaOAc and 9 g of $H_2NOH \cdot HCl$ in 80 mL of water. The mixture was stirred at room temperature for 4 days and evaporated in vacuo and the residue was treated with 100 mL of CH_2Cl_2. Filtration followed by thorough washing with cold water (15 °C) gave 0.45 g of white solid, mp 223-224 °C dec. Recrystallization from EtOH gave 0.4 g (12.6%) of α-benzildioxime, mp 245-245.5 °C dec (lit.[25] mp 244 °C), which was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

The original CH_2Cl_2 filtrate was evaporated under reduced pressure to give a brown oil which was chromatographed on SiO_2 with a 1:1

mixture of benzene–ligroin (bp 67–71 °C) to give 1.1 g of a solid, mp 95–97.5 °C. Recrystallization from a 1:1 mixture of EtOH–H_2O gave 1.0 g (36%) of deoxybenzoin oxime, mp 96.5–98 °C (lit.[26] mp 98 °C), identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Treatment of 2,3-Diphenylthiirene 1-Oxide with Excess Phenylmagnesium Bromide. An ethereal solution of phenylmagnesium bromide (0.01 mol) was prepared from 1.57 g (0.01 mol) of bromobenzene and 0.24 g (0.01 mol) of magnesium in 70 mL of anhydrous ether under a positive nitrogen pressure. To this solution was added 1 g (0.004 42 mol) of 2,3-diphenylthiirene 1-oxide at room temperature. A yellow precipitate formed immediately. The mixture was refluxed for 8 h and cooled, and sufficient saturated ammonium chloride solution was added to cause solution of most of the precipitate which had formed. The mixture was filtered and the residue was washed with 10 mL of ether and 10 mL of water. The two layers were separated and the organic layer extracted with 15 mL of saturated sodium bicarbonate solution. The extract was added to the aqueous solution. The combined aqueous solution was cooled in an ice bath, acidified with 3 N hydrochloric acid, and extracted with three 80-mL portions of ether. The combined ether extracts were washed once with 50 mL of water, dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure to give 1 g (62.2%) of a yellow solid, mp 140–142 °C. Recrystallization once from ligroin (bp 67–71 °C) yielded pale yellow crystals, mp 143–145 °C, which were identified as triphenylvinyl phenyl sulfide (**15**) by elemental analysis, mixture melting point, and comparison of its infrared and nuclear magnetic resonance spectra with those of an authentic sample prepared by the method described below. An analytical sample, mp 143.5–145 °C, was prepared by two recrystallizations from ligroin (bp 67–71 °C); IR ($CHCl_3$) 1582 cm^{-1} (C=C); NMR ($CDCl_3$) δ 6.84–7.39 (m, aromatic).

Anal. ($C_{26}H_{20}S$) C, H, S.

Triphenylvinyl Phenyl Sulfide (15). Benzenesulfenyl chloride (7.9 g) was prepared from 6.6 g (0.06 mol) of benzenethiol and chlorine according to the procedure of Lecher and Holschneider.[27] A solution of triphenylvinylmagnesium bromide (0.05 mol) was prepared from 18 g (0.0538 mol) of bromotriphenylethylene, 1.5 g of magnesium, and a catalytic amount of iodine in 400 mL of anhydrous ether under a positive pressure of nitrogen according to the method of Koelsch.[28] To the ethereal solution of triphenylvinylmagnesium bromide (0.05 mol) was added dropwise a solution of 7.8 g (0.0545 mol) of benzenesulfenyl chloride in 40 mL of anhydrous ether. The mixture was refluxed for 10 h and cooled, and sufficient saturated ammonium chloride solution was added to cause solution of most of the precipitate which had formed. The mixture was filtered and the residue washed with 20 mL of water. The two layers were separated and the water layer was cooled, acidified, and extracted with two 100-mL portions of ether. The combined ether extracts were washed with 100 mL of water, dried over anhydrous magnesium sulfate, and filtered. Evaporation of the solvent under reduced pressure afforded 10 g of a yellow solid, mp 142–145 °C. Recrystallization from ligroin (bp 67–71 °C) yielded 9 g (49.4%) of triphenylvinyl phenyl sulfide, mp 143–144.5 °C.

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