pirator), giving 10.1 g of a yellow oil which was filtered through 20 g of silica gel with 3% ethyl acetate/hexane. After solvent evaporation, a yellow solid was obtained which was stirred with methanol (50 mL) and filtered to give white crystals. Sublimation (60–70 °C (0.08 mm)) gave 5.20 g, mp 76–78 °C. Concentration of the methanol to 15 mL and cooling gave an additional 1.48 g of product (total yield 82%). No evidence for adduct formation from the contaminating 1,1-dimethylbutadiene was found. The crystalline product was identified as **15**: IR ($CBrCl_3$) 1710 cm^{-1}; NMR ($CDCl_3$) δ 5.43 (1 H, br d, J = 6 Hz), 3.2 (1 H, d, J = 17 Hz), 2.68 (1 H, d, J = 17 Hz), 2.61 (1 H, qd, J = 7, 6 Hz), 2.36 (3 H, s), 1.97 (3 H, s), 1.75 (3 H, br s), 1.09 (3 H, d, J = 7 Hz); exact mass, m/e 216.0642 (calcd for $C_{10}H_{16}OS_2$ 216.0643).

2-Acetyl-3,6-dihydro-3-methyl-2-(methylthio)-2*H*-thiopyran (14). The same procedure was used as described for the preparation of **15** (20-mmol scale). Sublimation (50–60 °C (0.08 mm)) gave **14** as white crystals: mp 61–63 °C (79%); IR ($CBrCl_3$) 1705 cm^{-1}; NMR ($CDCl_3$) δ 5.75 (2 H, m), 3.29 (1 H, br d, J = 17 Hz), 2.88 (1 H, dd, J = 17, 4 Hz), 2.63 (1 H, m), 2.37 (3 H, s), 1.99 (3 H, s), 1.13 (3 H, d, J = 7 Hz); exact mass, m/e 202.0496 (calcd for $C_9H_{14}OS_2$ 202.0486).

2-Acetyl-3,6-dihydro-3,5-dimethyl-2*H*-thiopyran (17). Triphenylphosphine Method.[10] A solution of 2-acetyl-3,6-dihydro-3,5-dimethyl-2-(methylthio)-2*H*-thiopyran (22.2 g, 103 mmol), **15**, in absolute ethanol (250 mL) was stirred with triphenylphosphine (84.0 g, 321 mmol) and acetic acid (7.4 mL, 130 mmol). The reaction flask was vented through a bubbler containing bleach solution to absorb methanethiol, and the mixture was refluxed for 5 days. After the solution was cooled to room temperature, methyl iodide (20 mL, 320 mmol) was added to consume the remaining triphenylphosphine. Water (100 mL) was added and the mixture was extracted with hexane (5 × 100 mL). The hexane layer was dried (Na_2SO_4) and the solvent was removed (rotary evaporator). Bulb-to-bulb distillation (at 0.05 mm, 50–60 °C) afforded the product **17** (14.8 g, 85%) as a colorless oil, mixture of diastereomers: IR (neat) 1715 cm^{-1}; 270-MHz NMR ($CDCl_3$) of major diastereomer δ 5.43 (1 H, m), 3.19 (1 H, d, J = 4 Hz), 2.89 (1 H, J = 17 Hz), 2.75 (1 H, d, J = 17 Hz), 2.63 (1 H, m), 2.33 (3 H, s), 1.72 (3 H, br s), 1.10 (3 H, d, J = 7 Hz); 270-MHz NMR of minor diastereomer δ 5.43 (1 H, m), 3.69 (1 H, d, J = 4.4 Hz), 3.02 (1 H, d, J = 17 Hz), 2.87 (1 H, d, J = 17 Hz), 2.63 (1 H, m), 2.25 (3 H, s), 1.74 (3 H, br s), 1.03 (3 H, d, J = 7 Hz); exact mass, m/e 170.0768 (calcd for $C_9H_{14}OS$ 170.0766).

Preparation of 17 Using Sodium *p*-Toluenethiolate.[10] A solution of *p*-toluenethiol (0.062 g) was stirred with sodium hydride (0.004 g, hexane washed) and DMF (1 mL, distilled from CaH_2) until H_2 evolution ceased. A solution of **15** (0.065 g) in minimal DMF was added and the mixture was stirred for 4 h at 20 °C. The product was partitioned between water–hexane, and the hexane layer was dried ($MgSO_4$) and evaporated to give an oily residue. Separation by PLC (silica gel, 30% ether–hexane) gave three zones: R_f 0.8, *p*-$CH_3C_6H_4SSCH_3$, R_f 0.5, recovered **15** (0.004 g), and R_f 0.4, **17** (0.040 g, 78%). The product **17** was identical with material prepared by the triphenylphosphine method.

2-Acetyl-3,6-dihydro-3-methyl-2*H*-thiopyran (18). The same triphenylphosphine procedure was used as described for **17** (82% yield). The product was obtained as a mixture of diastereomers: colorless oil; IR (neat) 1715 cm^{-1}; NMR ($CDCl_3$) of major diastereomer δ 5.77 (2 H, unresolved br s), 3.26 (1 H, d, J = 4 Hz), 2.3–3.2 (3 H, unresolved), 2.35 (3 H, s), 1.14 (3 H, d, J = 7 Hz); NMR ($CDCl_3$) of minor diastereomer δ 5.77 (2 H, unresolved br s), 3.75 (1 H, d, J = 5 Hz), 2.3–3.2 (3 H, unresolved), 2.28 (3 H, s), 1.05 (3 H, d, J = 7 Hz); exact mass, m/e 156.0608 (calcd for $C_8H_{12}OS$ 156.06088).

4-Ethoxy-3,6-dihydro-2*H*-thiopyran-2-carbonitrile (19). A solution of 2-ethoxybutadiene (4 g, 40 mmol) in DMF (20 mL, distilled from CaH_2) was heated to 50 °C. Dibromoacetonitrile (0.5 g, 2.5 mmol) was added. A solution of 0.8 g of $K^+{}^-S_2COC_2H_5$ in DMF (20 mL) was then added dropwise over 10 min. The mixture was stirred at 50 °C for 15 min and was then cooled to 20 °C. Partition between water (50 mL) and pentane (100 mL) gave an organic layer which was dried ($MgSO_4$). Removal of pentane by distillation through a Vigreux column gave a residue which was distilled under aspirator vacuum to recover ethoxybutadiene. The yellow residual oil was purified by high-performance LC (Waters Porasil A, 4 ft × $^3/_8$ in., 3% ethyl acetate/hexane, 8 mL/min). The product **19** was obtained as a white solid (0.06 g, 15%), recrystallized from pentane: mp 53–55 °C; IR (CCl_4) 2230, 1670 cm^{-1}; NMR ($CDCl_3$) δ 4.68 (1 H, br s), 3.72 (2 H, m), 3.58 (2 H, AB q, J = 17.5 Hz), 2.7 (2 H, br s), 1.29 (3 H, t, J = 7 Hz); exact mass, m/e 169.0564 (calcd for $C_8H_{11}NOS$ 169.05305).

Acknowledgment. This work was supported by a grant from the National Institute of Health (CA 17918).

Registry No. **5**, 73496-44-3; **6**, 73496-45-4; **7**, 73496-46-5; **10a**, 33406-25-6; **10b**, 21504-08-5; **11a**, 73496-48-7; **11b**, 73496-50-1; **12a**, 73496-51-2; **12b**, 66739-97-7; **13**, 73496-52-3; **14**, 73496-53-4; **15**, 73496-54-5; **16**, 73496-55-6; *cis*-**17**, 73496-56-7; *trans*-**17**, 73496-57-8; *cis*-**18**, 73496-58-9; *trans*-**18**, 73496-59-0; **19**, 73496-60-3; 1,3-dithiolane-2-carboxylic acid, 5616-65-9; 2-[((trimethylsilyl)oxy)-carbonyl]-1,3-dithiolane, 73496-61-4; 2-(carboethoxy)-1,3-dithiolane, 20461-99-8; methyl fluorosulfonate, 421-20-5; 2,3-dimethylbutadiene, 513-81-5; 2-methyl-1,3-pentadiene, 1118-58-7; 1,3-pentadiene, 504-60-9; 2-ethoxybutadiene, 4747-05-1; $K^+{}^-S_2COC_2H_5$, 140-89-6; dibromoacetonitrile, 3252-43-5.

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

Bruce B. Jarvis* and G. Patrick Stahly

Department of Chemistry, University of Maryland, College Park, Maryland 20742

Received February 4, 1980

A series of nucleophiles was allowed to react with 2,3-diphenylthiirene 1,1-dioxide (**1**) in dipolar aprotic solvents to produce a variety of derivatives. Fluoride ion gave diphenylacetylene and (*E*)-1,2-diphenylvinylsulfonyl fluoride (**2**); thiophenoxide gave (*E*)-1,2-diphenyl-2-(thiophenoxyl)vinylsulfinate which gave the corresponding methyl sulfone **5** on treatment with methyl iodide. Azide ion gave a variety of products including diphenylvinyl azides **12** and **13**, 2,3-diphenylazirine (**14**), 2,6-diphenyl-4-[(*E*)-diphenylvinyl]-1,3,4,5-thiatriazine 1,1-dioxide (**15**), benzil (**16**), 4,5-diphenyltriazole (**17**), 2,4,5-triphenylimidazole (**18**), and (*Z*)-1,2-diphenyl-2-azidovinylsulfinate which gave the corresponding methyl sulfone **22** on treatment with methyl iodide. The diphenylvinyl group was removed from the new heterocycle **15** by ozonolysis followed by mild base hydrolysis to yield the thiatriazine 1,1-dioxide **20**. Compound **20** undergoes thermolysis at 40 °C to give stilbenes, and **20** also undergoes a facile base-catalyzed extrusion of sulfur dioxide to give imidazole **18**.

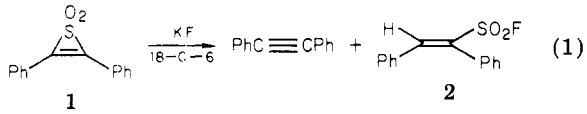
The reactions of 2,3-diphenylthiirene 1,1-dioxide (**1**) with nucleophiles have provided a variety of new and interesting compounds.[1] In general, it has been found that strongly basic nucleophiles attack the sulfonyl sulfur atom of **1**

0022-3263/80/1945-2604$01.00/0

while less basic nucleophiles attack a ring carbon atom.[2] In certain cases, intermediates are produced which can undergo rearrangements to give olefinic or heterocyclic compounds containing sulfur and elements of the nucleophile.[1] Previous work indicated that 1 undergoes interesting reactions with amines, phosphines, and sodium benzenesulfinate,[2] and the following describes our findings concerning the reactions of 1 with a variety of other nucleophiles.

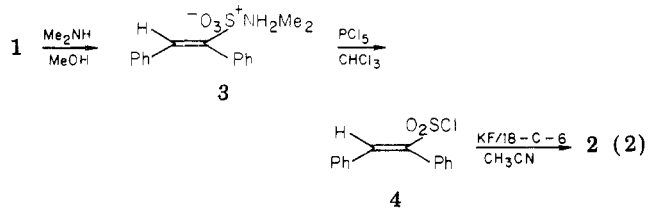
Results and Discussion

The advent of phase-transfer catalysis has allowed the use of halides and other salts in organic media, particularly via crown ether mediated solid–liquid transfer.[3] Under these conditions, fluoride ion was shown to be the most nucleophilic member of the halide family.[4] Treatment of 1 with potassium fluoride and 18-crown-6 (18-C-6) in acetonitrile at room temperature afforded two products (eq 1). Diphenylacetylene was isolated in 35% yield, and



1 2 (1)

the sulfonyl fluoride 2 was found in 23% yield. The structure of 2 was suggested by the infrared absorptions of the sulfonyl group and by analogy to products formed by the reactions of 1 with such nucleophiles as ethoxide and hydroxide, which attack the sulfur atom to give diphenylacetylene and a sulfonate ester and sulfonic acid, respectively.[2,5] To prove the structural assignment, we synthesized 2 (eq 2) by an alternate route involving halide

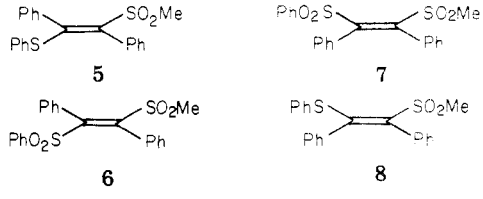


exchange[6] of (*E*)-1,2-diphenylvinylsulfonyl chloride (4), prepared earlier.[2] The configuration of 2 was inferred from its relationship to 3, whose configuration has been assigned.[2]

The softer, less basic halides bromide and iodide proved unreactive toward 1 under a variety of conditions. TLC analyses indicated the inertness of 1 toward potassium iodide and 18-crown-6 in acetonitrile or dichloromethane–water and toward the preformed 1:1 complex of potassium bromide and dicyclohexyl-18-crown-6[7] in acetonitrile, acetone, or benzene at ambient temperatures. The use of elevated temperatures is generally not helpful in reactions of 1 due to the ease of sulfur dioxide extrusion from 1, which occurs in ca. 2 h in refluxing benzene. Indeed, treatment of 1 with potassium iodide and 18-crown-6 in acetonitrile at 70 °C or with a saturated solution of sodium iodide in refluxing acetone resulted only in the production of diphenylacetylene.

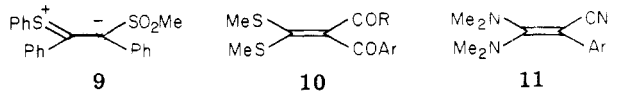
Potent nucleophiles other than halides may be derived by the interaction of crown ethers with many kinds of alkali metal salts.[3] Treatment of 1 with several of these was to no avail. No reaction could be detected by TLC when 1 was exposed to potassium thiocyanate or selenocyanate and a catalytic amount of 18-crown-6 in acetonitrile at room temperature. Similar results were obtained on treatment of 1 with the preformed 1:1 complex of potassium thiocyanate and dibenzo-18-crown-6[7] in benzene. Also, potassium nitrite and 18-crown-6 in acetonitrile or benzene had no effect on 1 at ambient temperature.

Thiophenoxide ion is a common nucleophile that has proven useful in sulfide synthesis.[8] Potassium thiophenoxide and 1 reacted in DMF at room temperature to produce a very polar compound which was difficult to isolate. This was presumably a vinylsulfinate which would be expected to arise by attack of thiophenoxide at a ring carbon in aprotic media.[2] Indeed, addition of methyl iodide to the reaction mixture resulted in isolation of a methyl vinyl sulfone that was shown to be sulfone 5.



Oxidation of 5 gave disulfone 6 which upon photoisomerization gave the known isomeric disulfone 7.[2] On the other hand thermolysis of the *Z* disulfone 7 at 140 °C produced *E* disulfone 6. These data clearly establish the *E* configuration for disulfone 6.[9] It is noteworthy that physical data also support these assignments. Melting points have been shown to correlate well with configuration in similar compounds,[10] with the more stable (sulfonyl groups trans) isomers having the higher melting points. The melting points of 7 (172–173 °C) and 6 (207–208 °C) suggest that 6 has the *E* configuration. In addition, 7 is more polar than 6 as judged by their TLC R_f values on silica gel.

All tetrasubstituted olefins previously obtained by additions of nucleophiles to 1 have been assigned configurations in which the phenyl groups are cis.[2,5] This stereoselectivity has been explained based on application of the principle of least motion to the ring opening of intermediate carbanions to the olefins.[2] Isolation of the *E* isomer 5 was therefore quite unexpected. It seems likely that 5 arises via isomerization, under the reaction conditions, of *Z* isomer 8, which should be formed initially. The double bond in 8 probably has a lowered barrier to rotation due to polarization as illustrated by structure 9. Similar compounds such as 10 and 11 have low barriers to rotation at room temperature.[11]



(1) (a) Rosen, M. H.; Blatter, H. M. U.S. Patent 3 706 769, 1972; *Chem. Abstr.* **1976**, *78*, P97475. (b) Potts, K. T.; Elliott, A. G.; Sorm, M. *J. Org. Chem.* **1972**, *37*, 3838. (c) Matsukubo, H.; Kojima, M.; Kato, H. *Chem. Lett.* **1975**, 1153. (d) Hayasi, Y.; Nakamura, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 667. (e) Rosen, M. H.; Bonet, G. *J. Org. Chem.* **1974**, *39*, 3805. (f) Jarvis, B. B.; Tong, W. P. *Synthesis* **1975**, 102.

(2) Jarvis, B. B.; Tong, W. P.; Ammon, H. L. *J. Org. Chem.* **1975**, *40*, 3189.

(3) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977.

(4) Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250.

(5) Carpino, L. A.; McAdams, L. V., III; Rynbrandt, R. H.; Spiewak, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 476.

(6) Bianchi, T. A.; Cate, L. A. *J. Org. Chem.* **1977**, *42*, 2031.

(7) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386. (b) Sam, D. J., Simmons, H. E. *Ibid.* **1974**, *96*, 2252.

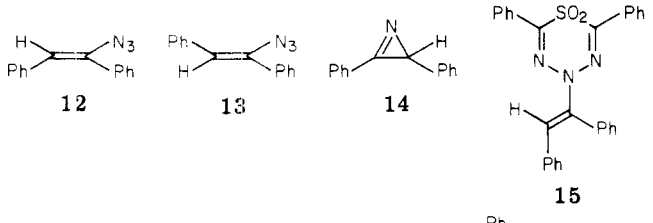
(8) March, J. "Advanced Organic Chemistry"; McGraw-Hill: New York, 1977; p 597.

(9) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 341.

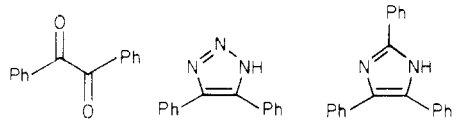
(10) Truce, W. E.; McManimie, R. J. *J. Am. Chem. Soc.* **1954**, *76*, 5745.

In view of the heterocycles obtained by the reactions of 1 with ylides[1d] or with mesoionic compounds,[1b,c] we anticipated that nucleophiles incorporating potential electrophilic centers would provide cyclic compounds containing elements of the nucleophile. In particular, we felt that azide ion would react with 1 to give an anionic intermediate(s) which might undergo ring closures to generate interesting heterocycles containing sulfur and one or two more nitrogen atoms. A cyclization process of this type has been observed in the base-promoted conversion of vinyl azides bearing an acidic terminal proton to triazoles.[12]

When finely ground lithium azide was added to a solution of 1 in acetonitrile, an immediate reaction ensued, as evidenced by the appearance of a bright yellow color in the heterogeneous mixture. After 20 h, TLC analysis indicated all of the starting material had reacted. Removal of the solids by filtration and chromatography of the acetonitrile soluble fraction provided several products[13] (12–18).



12 13 14 15



16 17 18

The vinyl azides 12 and 13 and azirine 14 are known compounds and were identified by comparison with samples synthesized by the methods of Fowler, Hassner, and Levy.[14] Azirine 14 presumably arises by cyclization of 12 and 13, a very facile, thermally induced process. The *E* isomer 12 is particularly prone to undergo this reaction.[14]

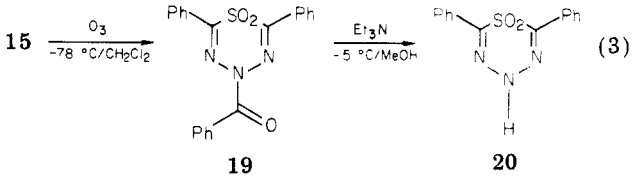
Recovery of 12 and 14 from the reaction mixture was found to be dependent on the amount of lithium azide used and the scale at which the experiment was carried out. Preliminary experiments using 250 mg of 1 and approximately 1.1 equiv of lithium azide afforded, after 20 h, 12, 13, 14, and unreacted 1. When 1.0 g of 1 was treated with 5 equiv of lithium azide for 20 h, the product mixture was found to contain 13, but no 12, 14, or 1 was observed even though an NMR spectrum of the crude reaction mixture after 2 h indicated the presence of 12, 13, and 14. Occasionally, however, a small amount of 14 was found in small-scale reactions using 5 equiv of lithium azide.[13] Control experiments showed that under the reaction conditions 12 and 13 do not isomerize but are converted to 14.

These results indicate that 12 and 14 undergo further reaction under the reaction conditions. It is likely that 12 is simply cyclized to 14, but the fate of azirine 14 has not been determined. No effort was made to discern the factors responsible for the production and fate of 12, 13, and 14. In most experiments the column fraction containing 12 and 13 was dissolved in hexane and heated at reflux for 3 h so that only 14 was isolated (ca. 11% yield).

Other easily identified, acetonitrile-soluble products were benzil (16, isolated in 1% yield), 4,5-diphenyltriazole (17), isolated in 8% yield), and 2,4,5-triphenylimidazole (isolated in 6% yield). The structures were established by comparison with authentic samples. Both 16 and 18 are commercially available, and 17 was synthesized by the addition of sodium azide to diphenylacetylene.[15]

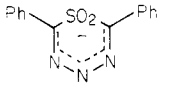
Purification of the material responsible for the color of the reaction mixture gave a bright yellow, crystalline sulfone in 10% yield. Aside from the presence of the sulfonyl group, structural features were not readily apparent in the physical, spectral, or chemical properties of this compound. However, crystals of the sulfone obtained by slow evaporation of an isooctane solution proved amenable to X-ray crystallographic analysis. By this method, the compound was identified as 2,6-diphenyl-4-[(*E*)-1,2-diphenylvinyl]-1,3,4,5-thiatriazine 1,1-dioxide (15).[13,16]

The vinyl substituent could be removed from 15 via ozonolysis followed by amide hydrolysis (eq 3). The oxidation was unusual in that no ozonide cleavage procedure was required; 19 could be crystallized directly from a solution of 15 in dichloromethane that had been treated with excess ozone. Cleavage of 19 was accomplished under very mild conditions, indicating the relative stability of the anion 21. However, treatment of 20 with 0.1 M triethylamine in methanol at room temperature gave a yellow solution which turned colorless after ca. 10 min. The resulting solution was found to contain only triazole 17. Apparently the easily generated anion 21 undergoes a rapid six-electron electrocyclic ring contraction followed by loss of sulfur dioxide[17] (eq 4).

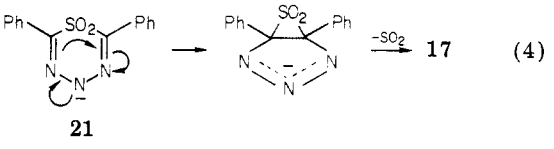


(3)

19 20



21



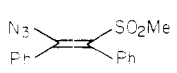
(4)

21

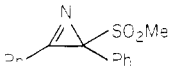
Other reactions of thiatriazine 20 proved interesting. If a solution of 20 in dichloromethane was heated at reflux for 8 h, *cis*- and *trans*-stilbenes were isolated. Although recovery was not good in this reaction (55%), no other UV absorbing products were detected by TLC analysis of the reaction mixture. Treatment of 20 with lithium azide in acetonitrile on a small scale indicated, via TLC analysis, that *cis*- and *trans*-stilbenes and triazole 17 were produced. The origin of stilbenes under these conditions is not clear at the present time.

(11) Kalinowski, H.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295.
(12) Beck, G.; Gunter, D. *Chem. Ber.* **1973**, *106*, 2758.
(13) A preliminary account of this work has appeared: Jarvis, B. B.; Stahly, G. P.; Ammon, H. L. *Tetrahedron Lett.* **1978**, 3781.
(14) Fowler, F. W.; Hassner, A.; Levy, L. A. *J. Am. Chem. Soc.* **1967**, *89*, 2077.
(15) Woerner, F. P.; Reimlinger, H. *Chem. Ber.* **1970**, *103*, 1908.
(16) Stahly, G. P.; Ammon, H. L.; Jarvis, B. B., submitted for publication in *Acta Crystallogr.*
(17) In a similar fashion, 1,3,5-thiadiazines (Giordano, C.; Cassar, L.; Panossian, S.; Belli, A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 939) and 1,3,4-thiadiazines (Bulka, V. E.; Pfeiffer, W. D. *J. Prakt. Chem.* **1976**, *318*, 971) undergo base-initiated extrusion of sulfur to give imidazoles and pyrazoles, respectively.

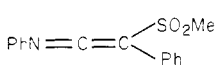
The acetonitrile-insoluble fraction from the reaction of **1** with lithium azide was found to contain, in addition to unreacted lithium azide, a very polar, water-soluble product. Dissolution of the solids in DMF followed by addition of methyl iodide produced an ether-soluble fraction from which was obtained, by crystallization, the azido sulfone **22** in 7% yield. The stereochemical assignment of **22** was not established with certainty but was inferred as *Z* from the configurations of the majority of other products that arise under similar conditions.[2]



22



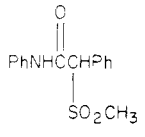
23



24

The mother liquor left after crystallization of **22** was found to contain azirine **23** and ketenimine **24**. These compounds result from the thermally induced rearrangement of **22**, a reaction which occurs to some extent even at 0 °C. Simply heating pure **22** to the melting point causes complete thermolysis. The production of azirines via thermolysis is a well-known process,[14] and in some cases ketenimines have been obtained as side products.[18] Thus, identification of **23** and **24**, vide infra, provides supporting evidence for the structure assignment of **22**.

Sulfonylazirine **23** is a stable, crystalline compound that was characterized by the usual methods. Ketenimine **24**, which was obtained as a pale yellow oil after chromatography, exhibits an infrared band (2040 cm^{-1}) characteristic of a heterocumulated bond. Although **24** appeared thermally stable, it underwent partial reaction on exposure to moisture. This reaction occurred quickly and completely if **24** was treated with aqueous acid and provided sulfonyl amide **25** as the major product. Since ketenimines, which



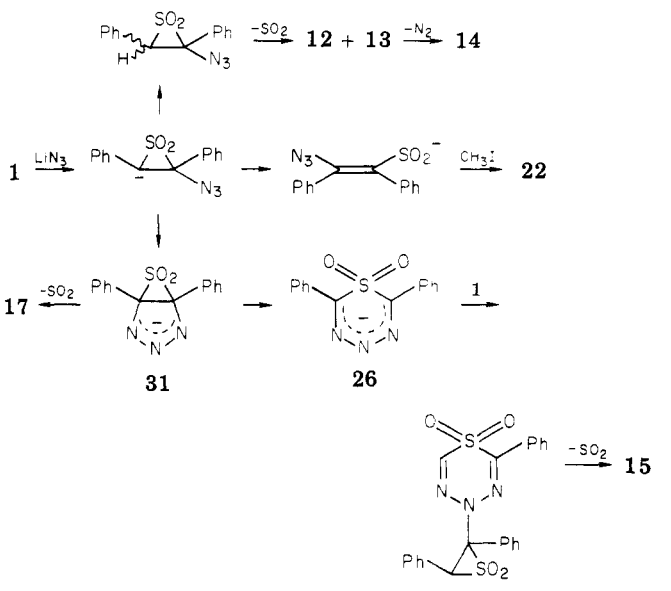
25

are a well-known class of compounds,[19] are known to produce amides on acid-catalyzed hydrolysis, only spectral data were obtained to support the structural assignment of the relatively unstable **24** while amide **25** derived from it was completely characterized. It was also possible to produce **25** by thermolysis of **22** in the presence of aqueous hydrochloric acid.

Most of the products obtained from the reaction of **1** with lithium azide may be accounted for by a mechanism involving attack at carbon (Scheme I). Although recovery of vinyl azide **13** seems inconsistent with earlier results,[2] it is possible that under these conditions proton transfer is competitive with carbanion inversion. Triazole **17** and thiatriazine **15** are conveniently explained via intermediate **26**. The formation of **26** may be rationalized by either a two-step process as shown in Scheme I or by a concerted cycloaddition. Recovery of **12**, **13**, and **22** supports a two-step mechanism, but cycloaddition may be competitive with nucleophilic attack.

The mechanisms for the formation of benzil (**16**) and imidazole **18** are not as straightforward. In particular, **18** cannot be easily accounted for via any intermediate of the proposed mechanistic scheme. It should be realized that **18** contains three benzyl units, which presumably come

Scheme I



from 1.5 molecules of **1**. However, all other products isolated contain only 14 or 28 carbons. Thus, the fate of the remaining seven-carbon unit is undetermined. It was felt that **18** might arise via further reaction of one of the other products. Azirine **14** was particularly suspect due to the inconsistent recovery of **14** discussed earlier. It has also been reported that photolysis of **17** produces **18**.[20] However, if a mixture of **1** and **14** was treated with lithium azide, the only effect was the absence of **17** in the product mixture. All other products were isolated in yields similar to those found in the absence of **14**, and unreacted **14** was recovered in high yield. Therefore, the mechanism of formation of **18** remains obscure.

The reactions of **1** with fluoride, thiophenoxide, and azide ions follow courses similar to those found for other nucleophiles.[1,2] Regiospecificity of the attacking nucleophile has been explained on the basis of the basicity of the nucleophile, both in reaction of **1**[2] and in reactions of other alkyl, aryl, and vinylsulfonyl compounds.[21] The weakly basic thiophenoxide and azide ions, which attack a carbon atom of **1**, behave in a manner consistent with this explanation. Fluoride ion, on the other hand, attacks the sulfonyl sulfur atom of **1**. This would not have been predicted by a consideration of basicity alone because fluoride ion is less basic than other nucleophiles which are known to attack a ring carbon (e.g., thiophenoxide, secondary amines[2]) although the basicities of anions are certainly increased under the influence of crown ethers. It therefore seems reasonable to consider both the basicity and the polarizability of the nucleophile (as in HSAB theory[22]) when explaining the regiospecificity of attack on **1**.

Experimental Section

General Methods. Melting points were determined on a Fisher-Johns hot-stage melting point apparatus and are uncorrected. Infrared spectra were determined in chloroform or potassium bromide on a Perkin-Elmer 281 recording spectrophotometer. The polystyrene absorption at 1601.8 cm^{-1} was used for

(18) (a) Smolinsky, G. *J. Org. Chem.* **1962**, *27*, 3557. (b) Harvey, G. R.; Ratts, K. W. *Ibid.* **1966**, *31*, 3907. (c) Friedrich, K. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 959.

(19) Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435.

(20) Selvarajan, R.; Boyer, J. H. *J. Heterocycl. Chem.* **1972**, *9*, 87.

(21) (a) Ferns, J.; Lapworth, A. *J. Chem. Soc.* **1912**, *101*, 273. (b) Bordwell, F. G.; Pitts, B. M.; Knell, M. *J. Am. Chem. Soc.* **1951**, *73*, 5004. (c) Potter, H. *Ibid.* **1954**, *76*, 5472. (d) Bunnet, J. F.; Bassett, J. Y., Jr. *Ibid.* **1959**, *81*, 2104.

(22) Pearson, R. G. "Hard and Soft Acids and Bases"; B. Dowden, Hutchinson, and Ross, Inc.: Stroudsburg, PA, 1973.

calibration of the infrared spectra. Nuclear magnetic resonance spectra were determined in deuteriochloroform on a Varian EM-360 or XL-100 spectrometer with tretramethylsilane as an internal standard. Ultraviolet–visible spectra were determined on a Cary 15 spectrophotometer. Microanalyses were carried out by Dr. Franz Kasler of the University of Maryland or by Galbraith Laboratories. Petroleum ether refers to the fraction of boiling point 35–60 °C. Benzene and DMF were dried by distillation from calcium hydride and stored over 3 Å molecular sieves. Crown ethers were obtained from Parrish Chemical Co. Thin-layer chromatography was carried out on prepared plates (E. Merck or Analtech), and visualization was effected with short-wavelength ultraviolet light. 2,3-Diphenylthiirene 1,1-dioxide (1) was prepared from α,α-dichlorodibenzyl sulfone[5] by the method of Philips et al.[23]

Reaction of 1 with Potassium Fluoride. To a solution of 100 mg (0.41 mmol) of 1 and 11 mg (0.042 mmol) of 18-crown-6 in 2 mL of acetonitrile was added 120 mg (2.1 mmol) of anhydrous potassium fluoride. This heterogeneous mixture was stirred at room temperature for 20 h. The solids were removed by filtration, and the filtrate was concentrated in vacuo. The resulting residue was subjected to preparative TLC on silica gel (one 1-mm plate) with 25% dichloromethane in petroleum ether as eluent to give two fractions. Crystallization of the less polar fraction from ethanol–water yielded 26 mg (35%) of diphenylacetylene, while crystallization of the more polar fraction from hexane afforded 25 mg (23%) of (*E*)-1,2-diphenylvinylsulfonyl fluoride (**2**): mp 130–132 °C; IR ($CHCl_3$) 1630 (C=C), 1405 and 1200 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 7.0–7.5 (m, 10 H, aromatic), 7.9 (s, 1 H, olefinic); ^{19}F NMR ($CDCl_3$, external standard CF_3CO_2H) δ 131.9.

Anal. Calcd for $C_{14}H_{11}FO_2S$: C, 64.10; H, 4.23. Found: C, 63.93; H, 4.10.

Preparation of (*E*)-1,2-Diphenylvinylsulfonyl Fluoride (2). To a solution of 25 mg (0.09 mmol) of (*E*)-1,2-diphenylvinylsulfonyl chloride (**4**)[2] and 5.0 mg (0.02 mmol) of 18-crown-6 in 1.0 mL of acetonitrile was added 55 mg (0.95 mmol) of anhydrous potassium fluoride. The heterogeneous mixture was stirred at room temperature for 100 min, poured into 10 mL of water, and extracted with two 10-mL portions of dichloromethane. The combined organic layers were dried (magnesium sulfate) and concentrated in vacuo to give a residue which was subjected to preparative TLC on silica gel (one 0.5-mm plate) with 50% dichloromethane in petroleum ether as eluent. Recrystallization of the major band from hexane provided 14 mg (61%) of **2**, which was identical (TLC behavior, mixture melting point, NMR and IR spectra) with the sample from the previous experiment.

Preparation of Potassium Thiophenoxide. A mixture of 5.0 g (0.05 mol) of thiophenol and 2.2 g (0.04 mol) of potassium hydroxide (pellets) in 50 mL of benzene was heated at reflux under a Dean–Stark trap for 5 h. The resulting white percipitate was collected by filtration, washed with pentane, and dried in vacuo to give 5.0 g (86%) of potassium thiophenoxide.[24]

Reaction of 1 with Potassium Thiophenoxide. To a solution of 100 mg (0.41 mmol) of 1 in 3 mL of dry DMF was added 65 mg (0.44 mmol) of potassium thiophenoxide. After being allowed to stand for 30 min at room temperature, the mixture was warmed to 40 °C, and 0.2 mL of methyl iodide was added. After 1 h the reaction mixture was poured into 20 mL of water and extracted with three 10-mL portions of diethyl ether. The combined organic layers were dried (magnesium sulfate), concentrated in vacuo, and crystallized from dichloromethane–hexane to give 128 mg (85%) of (*E*)-1,2-diphenyl-2-(thiophenoxy)vinyl methyl sulfone (**5**): mp 148–148.5 °C; IR (KBr) 2920 (CH_3), 1305 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.58 (s, 3 H, methyl), 6.9–7.7 (m, 15 H, aromatic).

Anal. Calcd for $C_{21}H_{18}O_2S_2$: C, 68.82; H, 4.95. Found: C, 68.55; H, 4.77.

Preparation of (*E*)-1,2-Diphenyl-2-(methylsulfonyl)vinyl Phenyl Sulfone (6). To a solution of 40 mg (0.11 mmol) of (*E*)-1,2-diphenyl-2-(thiophenoxy)vinyl methyl sulfone (**5**) in 10 mL of chloroform was added 50 mg (0.46 mmol) of 85% *m*-chloroperbenzoic acid (Aldrich). After being allowed to stand for 24 h at room temperature, the mixture was washed with two 10-mL portions of 5% sodium bicarbonate, dried (magnesium sulfate), concentrated in vacuo, and crystallized from dichloromethane–hexane to give 39 mg (91%) of **6**: mp 207–208 °C; IR (KBr) 2930 (CH_3), 1320 and 1140 cm^{-1} (br 2 SO_2's); ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H, methyl), 7.1–7.6 (m, 15 H, aromatic).

Anal. Calcd for $C_{21}H_{18}O_4S_2$: C, 63.29; H, 4.55. Found: C, 63.00; H, 4.26.

Isomerization of (*E*)-1,2-Diphenyl-2-(methylsulfonyl)vinyl Phenyl Sulfone (6). A solution of 20 mg of **6** in 1.0 mL of acetonitrile was irradiated in a quartz tube for 1 h with a mercury resonance lamp (254 nm). The reaction mixture was then concentrated in vacuo and subjected to preparative TLC on silica gel (one 0.5-mm plate) with 1% methanol in dichloromethane as eluent to give 15 mg of unchanged **6** and 4 mg (20%) of (*Z*)-1,2-diphenyl-2-(methylsulfonyl)vinyl phenyl sulfone (**7**), which was identified by comparison (TLC behavior, mixture melting point, IR and NMR spectra) with an authentic sample.[2]

Isomerization of (*Z*)-1,2-Diphenyl-2-(methylsulfonyl)vinyl Phenyl Sulfone (7). A solution of 26 mg of **7** in 1.0 mL of DMF was heated at 140 °C (oil bath) for 46 h. The mixture was then poured into 10 mL of water, and the resulting white precipitate was removed by filtration. Preparative TLC of the filter cake on silica gel (one 0.5-mm plate) with 1% methanol in dichloromethane as eluent gave 2 mg of unchanged **7** and 16 mg (62%) of (*E*)-1,2-diphenyl-2-(methylsulfonyl)vinyl phenyl sulfone (**6**).

Reaction of 1 with Lithium Azide. To a solution of 1.00 g (4.13 mmol) of 1 in 20 mL of acetonitrile was added 1.00 g (20.4 mmol) of finely ground lithium azide. The heterogeneous mixture was stirred vigorously at room temperature for 20 h. Filtration removed the insoluble materials, which were washed with 50 mL of dichloromethane to give 1.18 g of white solid (fraction A). Concentration of the combined filtrate and washings in vacuo afforded a yellow oil which was adsorbed on 4 g of silica gel and chromatographed on 70 g of silica gel with petroleum ether containing increasing amounts of dichloromethane as eluent. Elution with 30% dichloromethane in petroleum ether provided fractions B (143 mg) and C (159 mg), elution with 0.5% methanol in dichloromethane provided fraction D (68 mg), and elution with 1% methanol in dichloromethane provided fraction E (98 mg).

Fraction A was dissolved in 10 mL of DMF, and 1.0 mL of methyl iodide was added. After being allowed to stand at room temperature for 2 h, the mixture was poured into 50 mL of water and extracted with three 25-mL portions of diethyl ether. The combined organic layers were dried (magnesium sulfate) and concentrated in vacuo to give an oily residue (352 mg) which was chromatographed on 50 g of silica gel with dichloromethane as eluent and crystallized from dichloromethane–hexane to afford 89 mg (7.2%) of (*Z*)-1,2-diphenyl-2-azidovinyl methyl sulfone (**22**): mp 101–103 °C (with gas evolution); IR ($CHCl_3$) 2110 (N_3), 1620 (C=C), 1317 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.61 (s, 3 H, methyl), 7.3–7.6 (m, 10 H, aromatic).

The mother liquor from the above crystallization was subjected to preparative TLC on silica gel (one 2-mm plate) with 25% ethyl acetate in petroleum ether as eluent (three developments) to give 56 mg of a mixture of **22** and **23** and 57 mg (5.1%) of (methylsulfonyl)phenylketene *N*-phenylimine (**24**): IR ($CHCl_3$) 2020 (C=C=N), 1317 and 1135 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.07 (s, 3 H, methyl), 7.3–7.8 (m, 10 H, aromatic).

Fraction B was dissolved in 6 mL of hexane and heated at reflux for 3 h. Concentration of the mixture in vacuo and cooling induced crystallization of 89 mg (11%) of 2,3-diphenylazirine (**14**).

Recrystallization of fraction C from dichloromethane–hexane afforded 58 mg of 2,6-diphenyl-4-[(*E*)-diphenylvinyl]-1,3,4,5-thiatriazine 1,1-dioxide (**15**). The mother liquor was subjected to preparative TLC on silica gel (one 1-mm plate) with 25% dichloromethane in petroleum ether as eluent (three developments) to give 9 mg (1.0%) of benzil (**16**) and, following recrystallization from dichloromethane–hexane, an additional 40 mg of **15** (total of 98 mg, 10%): mp 181.5–182 °C; IR (KBr) 1305, 1290, and 1125 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 6.9–8.0 (m, aromatic); UV (CH_3OH) λ_{max} 230 nm (ϵ 43000), 275 (sh), 330 (44000), 375 (sh).

Anal. Calcd for $C_{28}H_{21}N_3O_2S$: C, 72.57; H, 4.54; N, 9.07; S, 6.91. Found: C, 72.58; H, 4.55; N, 8.92; S, 6.89.

(23) Philips, J. C.; Swisher, J. V.; Haidukewych, D.; Morales, O. *Chem. Commun.*, **1971**, 22.
(24) Campbell, J. R. *J. Org. Chem.* **1964**, *29*, 1830.
(25) Commercially available (Aldrich Chemical Co.).

Fraction D was recrystallized from acetonitrile to give 36 mg (5.9%) of 2,4,5-triphenylimidazole (**18**), and recrystallization of fraction E from dichloromethane–hexane yielded 70 mg (7.7%) of 4,5-diphenyltriazole (**17**).

Compounds **14**,[14] **16**,[25] **17**,[15] and **18**[25] were identified by comparison (TLC behavior, mixture melting point, IR and NMR spectra) with authentic samples.

Preparation of 2,6-Diphenyl-4-benzoyl-1,3,4,5-thiatriazine 1,1-Dioxide (19). An oxygen–ozone stream was bubbled through a cooled (−78 °C) solution of 218 mg of 2,6-diphenyl-4-[(*E*)-diphenylvinyl]-1,3,4,5-thiatriazine 1,1-dioxide (**15**) in 5 mL of dichloromethane until the solution turned blue (ca. 5 min). Warming of the reaction mixture followed by addition of hexane resulted in the crystallization of 136 mg (74%) of **19**: mp 180–182 °C; IR ($CHCl_3$) 1738 (C=O), 1295 and 1130 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 7.3–8.1 (m, aromatic).

Anal. Calcd for $C_{21}H_{15}N_3O_3S$: C, 64.76; H, 3.88; N, 10.79. Found: C, 64.48; H, 3.72; N, 10.44.

Preparation of 4*H*-2,6-Diphenyl-1,3,4,5-thiatriazine 1,1-Dioxide (20). To a cooled (−10 °C), heterogeneous mixture of 150 mg of 2,6-diphenyl-4-benzoyl-1,3,4,5-triatriazine 1,1-dioxide (**19**) in 3.0 mL of THF and 1.8 mL of methanol was added 1.2 mL of a cold (0 °C) solution of 0.5 M triethylamine in methanol. After being stirred for 70 min at −5 to −10 °C, the yellow reaction mixture became homogeneous. The reaction was allowed to continue an additional 10 min, and the solvents were removed in vacuo at a temperature below 40 °C. The resulting residue was purified via preparative TLC on silica gel (two 1-mm plates) with 2% methanol in dichloromethane as eluent followed by crystallization from dichloromethane–hexane to give 70 mg (64%) of **20**: mp 113–114 °C (with gas evolution); IR (KBr) 3270 (NH), 1282 and 1135 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 7.3–8.1 (m, 10 H, aromatic), 10.15 (br s, 1 H, amino).

Anal. Calcd for $C_{14}H_{11}N_3O_2S$: C, 58.93; H, 3.89; N, 14.73. Found: C, 58.53; H, 3.70; N, 14.98.

Reaction of 4*H*-2,6-Diphenyl-1,3,4,5-thiatriazine 1,1-Dioxide (20) with Triethylamine. A solution of 20 mg of **20** in 1.0 mL of 0.1 M triethylamine in methanol was allowed to stand at room temperature overnight. Removal of the solvent in vacuo and crystallization of the residue from dichloromethane–hexane gave 11 mg (69%) of 4,5-diphenyltriazole (**17**), which was identified by comparison with an authentic sample.[15]

Thermolysis of 4*H*-2,6-Diphenyl-1,3,4,5-thiatriazine 1,1-Dioxide (20). A solution of 30 mg of **20** in 2 mL of dichloromethane was heated at reflux for 8 h. Preparative TLC of the reaction mixture on silica gel (one 0.5-mm plate) with 5% dichloromethane in petroleum ether as eluent afforded 6 mg (33%) of *trans*-stilbene and 4 mg (22%) of *cis*-stilbene. The stilbenes were identified by comparison (TLC behavior, IR spectra) with authentic samples.[25]

Thermolysis of (*Z*)-1,2-Diphenyl-2-azidovinyl Methyl Sulfone (22). Crystals of **22** (69 mg) were heated in an open Pyrex tube to 130 °C by using an oil bath. Melting and gas evolution occurred at ca. 100 °C. Preparative TLC of the resulting oil on silica gel (one 1-mm plate) with 25% ethyl acetate in petroleum ether as eluent (three developments) provided 30 mg (48%) of (methylsulfonyl)phenylketene *N*-phenylimine (**24**) and 24 mg (41%) of 2,3-diphenyl-3-(methylsulfonyl)azirine (**23**): mp 120–122 °C; IR ($CHCl_3$) 1758 (C=N), 1315 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.90 (s, 3 H, methyl), 7.2–8.1 (m, 10 H, aromatic).

Anal. Calcd for $C_{15}H_{13}NO_2S$ (**28**): C, 66.39; H, 4.83; N, 5.16. Found: C, 66.60; H, 4.82; N, 5.15.

Hydrolysis of (Methylsulfonyl)phenylketene *N*-Phenylimine (24). To a solution of 19 mg of **24** in 0.25 mL of methanol was added 1 drop of 5% hydrochloric acid. After 15 min, the mixture was poured into 10 mL of saturated sodium bicarbonate and extracted with two 10-mL portions of dichloromethane. The organic layers were combined, dried (magnesium sulfate), concentrated in vacuo, and subjected to preparative TLC on silica gel (one 0.5-mm plate) with dichloromethane as eluent to give 10 mg (50%) of *N*-phenyl-2-(methylsulfonyl)-2-phenylacetamide (**25**): mp 174–175 °C; IR (KBr) 3350 (NH), 1670 (C=O), 1320 and 1135 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 3.09 (s, 3 H, methyl), 5.20 (s, 1 H, methine), 7.0–7.9 (m, 10 H, aromatic), 8.52 (br s, 1 H, NH).

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.34; H, 5.29; N, 4.76.

Thermolysis of (*Z*)-1,2-Diphenyl-2-azidovinyl Methyl Sulfone (22) in the Presence of Hydrochloric Acid. A solution of 50 mg of **22** and 2 drops of 37% hydrochloric acid in 2 mL of 95% ethanol was heated at reflux for 8 h. The mixture was then poured into 10 mL of saturated sodium bicarbonate and extracted with three 10-mL portions of dichloromethane. The organic layers were combined, dried (magnesium sulfate), concentrated in vacuo, and subjected to preparative TLC on silica gel (one 0.5-mm plate) with dichloromethane as eluent to give 22 mg (52%) of *N*-phenyl-2-(methylsulfonyl)-2-phenylacetamide (**25**).

Acknowledgment. G.P.S. wishes to thank the Gillette Corp. for a fellowship.

Registry No. **1**, 5162-99-2; **2**, 73558-54-0; **4**, 56437-49-1; **5**, 73558-55-1; **6**, 73558-56-2; **7**, 56437-46-8; **14**, 16483-98-0; **15**, 69754-64-9; **16**, 134-81-6; **17**, 5533-73-3; **18**, 484-47-9; **19**, 73558-57-3; **20**, 73558-58-4; **22**, 73558-59-5; **23**, 73558-60-8; **24**, 73558-61-9; **25**, 73558-62-0; potassium thiophenoxide, 3111-52-2; thiophenol, 108-98-5; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.