Intramolecular Cyclization of 2-Biarylsulfonyl Azides

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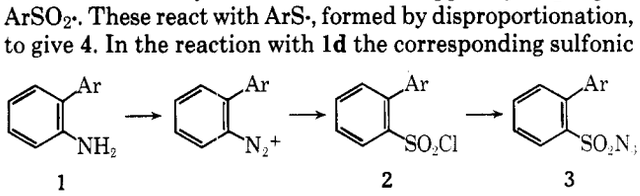
Thermolysis of biphenyl- and 4′-bromobiphenyl-2-sulfonyl azides in various solvents gave the expected sultams (**6**) together with solvent insertion or hydrogen abstraction products, depending on the solvent and reaction conditions. In no case could an *N*-sulfonylazepine be isolated. No rearrangement via a spiro intermediate occurred in the cyclization of 4′-bromobiphenyl-2-sulfonylnitrene, but the bromophenyl nucleus was less reactive than the corresponding phenyl, leading to appreciably more competition by solvent for the nitrene. No cyclization occurred onto sulfur in the thermolysis of 2-*o*-nitrenosulfonylphenylthiophene, thieno[3,2-*c*]-6*H*-benzo[*e*][1,2]thiazine 5,5-dioxide (**25**) being obtained together with solvent insertion product. Photolysis of biphenyl-2-sulfonyl azide and of biphenyl-2-sulfonyliminotriphenylphosphonium ylide did not lead to any sultam, but irradiation of the azide in the presence of di-*tert*-butyl sulfide did produce a small amount of sultam together with 2-biphenyl *tert*-butyl sulfone and 2-biphenyl disulfide.

When this work was initiated[1] it was established that while arylnitrenes could undergo intramolecular aromatic substitution to give five- and six-membered heterocycles readily,[2,3] no examples of their undergoing intermolecular aromatic substitution were known.[3] On the other hand, sulfonylnitrenes do undergo intermolecular aromatic substitution readily.[3,4] It has since been established that if strongly electron-withdrawing substituents are present in the aromatic nucleus making the nitrene more electrophilic then the latter will undergo intermolecular aromatic substitution reactions.[5-8] It seemed likely, therefore, that suitably ortho-substituted arylsulfonylnitrenes would undergo intramolecular cyclization to give cyclic sulfonamides. In this paper, the intramolecular cyclizations of 2-biarylsulfonyl azides are described.

Results and Discussion

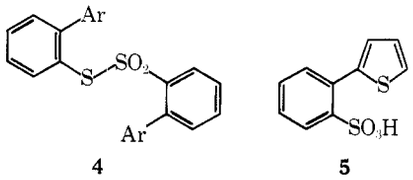
The azides (**3**) were obtained from the corresponding sulfonyl chlorides (**2**) which, in turn, could be prepared from the appropriate diazonium salt via a modified Meerwein synthesis.[9,10] In these latter reactions with both 2-amino- (**1a**) and 2-amino-4′-bromobiphenyl (**1c**), thiosulfonates **4a** (14%) and **4c** (20%) were formed as by-products. This is consistent with the formation of aryl radicals which are trapped by SO_2 to give $ArSO_2\cdot$. These react with ArS·, formed by disproportionation, to give **4**. In the reaction with **1d** the corresponding sulfonic



1 2 3

a, Ar = Ph
b, Ar = 2,4,6-$Me_3C_6H_2$
c, Ar = *p*-BrC_6H_4
d, Ar = 2-thienyl

acid (**5**) was isolated besides the sulfonyl chloride and also probably arises by disproportionation of $ArSO_2\cdot$ to $ArSO_3\cdot$ and subsequent reactions.[11,12]



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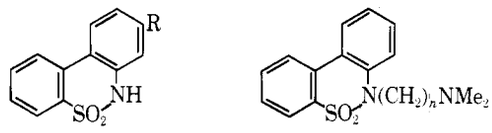
Thermolysis of biphenyl-2-sulfonyl azide (**3a**) in dodecane at 175 °C gave the desired sultam **6a** (73%)[13] which was N-alkylated via the thallium salt to give *N*-2-dimethylaminoethyl- (**7**) and *N*-3-dimethylaminopropyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (**8**). When the thermolysis was carried out at 150 °C, the yield of sultam **6a** was much lower (38%) and



6a, R = H
b, R = Br

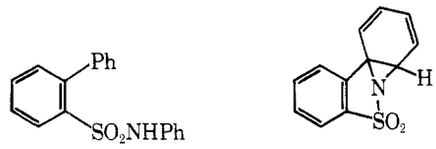
7, *n* = 2
8, *n* = 3

a mixture of (*N*-dodecyl)biphenyl-2-sulfonamides was obtained (15%), resulting from the insertion of the sulfonylnitrene into the solvent.

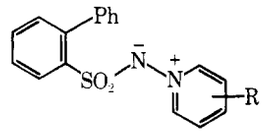
When methanesulfonyl azide is heated in benzene or substituted benzenes an *N*-mesylbenzaziridine is formed which, under kinetic control conditions, ring-expands to an *N*-mesylazepine. Though an azepine cannot be detected as such at 120 °C, it can be trapped by tetracyanoethylene present in the reaction mixture to give the [4 + 2] π adduct. At lower temperatures, the azepine is thermally stable and can be isolated (albeit in very low yield because of low conversion of azide to nitrene at these temperatures).[6] When the thermolysis of **3a** in dodecane was carried out in the presence of TCNE no Diels–Alder adduct could be characterized, though two solids, mp >300 °C, were isolated but could not be purified or identified. On the other hand, no sultam **6a** was formed either. The only products identified were the above mixture of (*N*-dodecyl)biphenyl-2-sulfonamides (12%) and the hydrogen-abstraction product, biphenyl-2-sulfonamide (10%). It would appear that either the sulfonylnitrene is diverted from attacking the adjacent aromatic nucleus by TCNE, which appears somewhat unlikely, or else an *N*-sulfonylazepine is formed and trapped and this then gives rise to the high-melting unidentified products. The TCNE may also catalyze singlet → triplet conversion of the nitrene (though the reason for this is unclear), which would explain the formation of hydrogen-abstraction product.

The best yields of sultam **6a** (80.6%) were obtained when **3a** was heated in cyclohexane at 120 °C. Interestingly, no C–H insertion product, (*N*-cyclohexyl)biphenyl-2-sulfonamide, could be detected in this reaction. An attempt to isolate a possible fused *N*-sulfonylazepine by carrying out the thermolysis at 81 °C for 35 days gave only a small yield of sultam together with some tar. Thermolysis in benzene at 120 °C gave a mixture of sultam (36.8%) and intermolecular substitution product, biphenyl-2-sulfonanilide (**9**) (21.8%). This suggests

that the transition state leading to intermediate **10** is sufficiently strained that competition from intermolecular attack



9 10

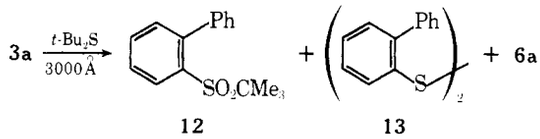


11, R = H, 2-Me, 2,6-Me_2, 2,4,6-Me_3

on benzene becomes appreciable (vide infra). After 35 days at 80 °C in benzene, the azide gave low yields of the sultam **6a** and of **9**, but no azepines could be detected. This contrasts with the behavior of methanesulfonyl azide[6] and ferrocene-1,1′-disulfonyl azide.[14]

As expected,[15] decomposition of **3a** in cyclohexane occurred at room temperature in the presence of diiron nonacarbonyl and did not lead to any products of intramolecular cyclization, the main product being biphenyl-2-sulfonamide. Copper-catalyzed decomposition in cyclohexane or methanol was much slower but led to the same result. Methanesulfonyl azide was similarly decomposed at 80 °C in benzene in the presence of copper to give methanesulfonamide but no product of addition to benzene, confirming[16] that the reactive species is probably a copper nitrenoid. On the other hand, thermolysis of **3a** in pyridine and some methylpyridines gave the corresponding ylides **11** (18–52%) together with **6a**.

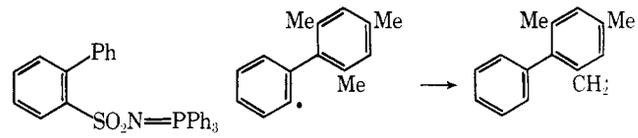
Photolysis of aliphatic and aromatic (except ferrocenyl[17]) sulfonyl azides in nonprotic, nonpolar solvents such as benzene or cyclohexane produces insoluble, high-melting materials that have not been characterized.[6,18,19] Only very small amounts of *N*-mesylazepine were formed in the photolysis of methanesulfonyl azide in benzene.[6] Photolysis (2537 Å) of **3a** in cyclohexane gave a high-melting product which could not be purified, but no azepine or sultam. On the other hand, irradiation of *p*-toluenesulfonyl azide in the presence of 4-butylthiacyclohexane gave a low yield (2–3%) of epimeric sulfimines,[20] while photolysis in the presence of dimethyl sulfide gave the sulfimine in poor yield.[18] Since sulfides seem to assist photolytic generation of singlet[20] sulfonylnitrenes the azide **3a** was photolyzed (3000 Å) in deoxygenated cyclohexane containing di-*tert*-butyl sulfide to give 2-biphenyl *tert*-butyl sulfone (**12**, 4%), 2-biphenyl disulfide (**13**, 20%), and sultam **6a** (3%), together with a tan-colored polymer. Thus, some singlet nitrene seems to be produced under those conditions though a major pathway probably involves formation of $ArSO_2$· radicals.



12 13

Heating biphenyl-2-sulfonamide in dodecane at 150 °C gave unchanged amide as did its attempted oxidation with lead tetraacetate in acetic acid. In neither case was any sultam detected. It has been reported[21] that some *N*-alkylphosphinimines give nitrenes on photolysis. Irradiation of biphenyl-2-sulfonyliminotriphenylphosphonium ylide (**14**) led mainly to recovered starting material.

Thermolysis of 2′,4′,6′-trimethylbiphenyl-2-sulfonyl azide (**3b**) in cyclohexane gave only one product that could be characterized, namely, 2,4-dimethylfluorene (**15**, 35%). This



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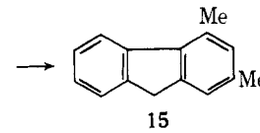

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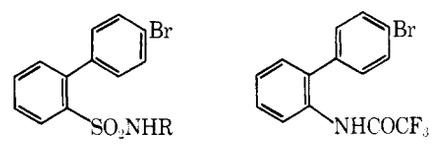
can conceivably arise from the $ArSO_2$· radical, loss of SO_2 to the aryl radical,[1] intramolecular hydrogen abstraction from the adjacent 2′-methyl group, and intramolecular homolytic substitution by the benzyl radical so formed. Other routes are also possible.

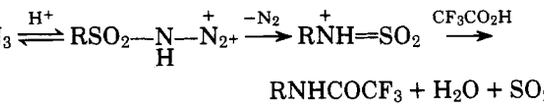
When 4′-bromobiphenyl-2-sulfonyl azide (**3c**) was thermolyzed in cyclohexane, two products were isolated: the sultam **6b** (5%) and the solvent insertion product, 4′-bromo-(*N*-cyclohexyl)biphenyl-2-sulfonamide (**16**, 27%). This is in marked contrast to the behavior of **3a** in the same solvent, when a high yield of **6a** was formed and no solvent insertion product was isolated. This suggests that the bromophenyl group is deactivated compared with phenyl toward intramolecular attack by sulfonylnitrene, allowing solvent to compete effectively with the aromatic nucleus for the nitrene's favors. This can readily be understood when it is remembered that ${}^{Cl}_{H}K = 0.44$ for attack by $MeSO_2\ddot{N}$ on chlorobenzene relative to benzene,[6] though one would perhaps have expected the product ratios to be reversed since a benzene "double bond" has been shown to be approximately eight times more reactive toward a sulfonylnitrene than a C–H bond in cyclohexane.[22] Indeed, when the thermolysis was carried out in benzene at 120 °C, **6b** (27%) and 4′-bromobiphenyl-2-sulfonanilide (**17**, 47%) were obtained. Decomposition of **3c** in chlorobenzene at 130 °C gave the sultam **6b** (24%) and 4′-bromo-(*N*-*o*- (**18**, 10%) and -*p*-chlorophenyl)biphenyl-2-sulfonamide (**19**, 13%), the lower overall yields of **18** and **19** relative to **6b** being expected from the lower reactivity of chlorobenzene than benzene. Interestingly, when **3c** in benzene was heated with trifluoroacetic acid, the sultam **6b** (25%), the anilide **17**, and 4′-bromo-2-trifluoroacetamidobiphenyl (**20**, 4%) were obtained.



16, R = C_6H_{11}
17, R = C_6H_5
18, R = C_6H_4-*o*-Cl
19, R = C_6H_4-*p*-Cl

20

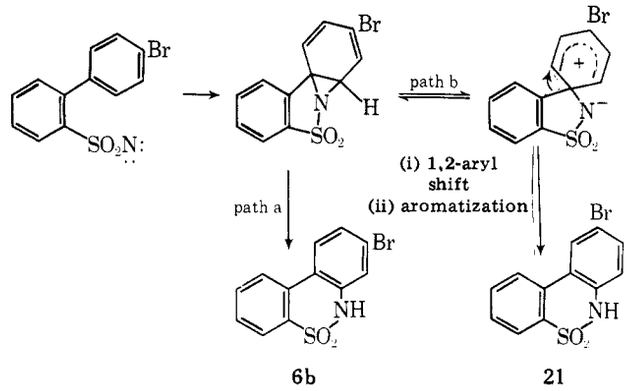
The latter undoubtedly arises by an acid-catalyzed Curtius-type rearrangement of the sulfonyl azide to give the sulfonylamine which is solvolyzed by the trifluoroacetic acid.



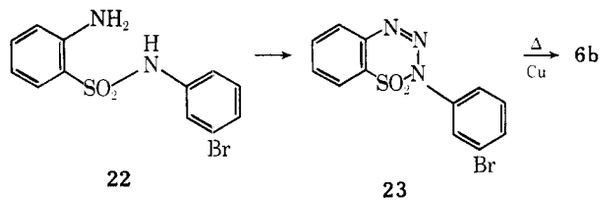
$$RNHCOCF_3 + H_2O + SO_2$$

An interesting point to be determined was the location of the bromine atom in the sultam. It was known[23] that intramolecular cyclization of some arylnitrenes leads to rearranged products via proposed spiro intermediates, and it was conceivable that the isomeric 9-bromosultam (**21**) could be

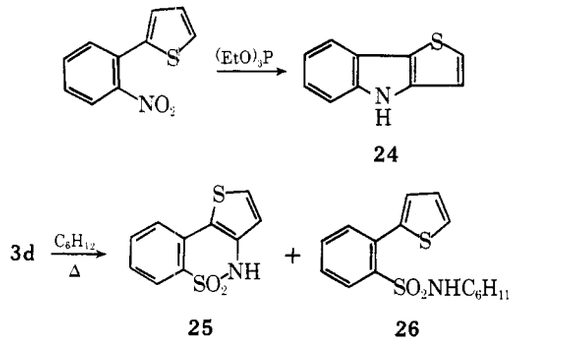
Scheme I



formed from the cyclization of **3c** (Scheme I). In the event, an authentic sample of **6b** was synthesized from 2-amino-*N*-(*m*-bromophenyl)benzenesulfonamide (**22**) via the thiatriazine (**23**) which, on heating with copper, gave the desired **6b**, identical with the product obtained from the sulfonylnitrene. Path a in Scheme I thus appears to be followed without any rearrangement according to path b.



Thermolysis of diphenyl sulfide 2-sulfonyl azide gave 3-phenylbenzo-1,3,2-dithiazole 1,1-dioxide resulting from cyclization at divalent sulfur.[1] On the other hand, cyclization of 2-azidophenylthiophene gave only 4*H*-thieno[3,2-*b*]indole (**24**), no cyclization at sulfur being observed,[24] an observation we have now confirmed. Similarly, thermolysis of **3d** in cyclohexane gave thieno[3,2-*c*]-6*H*-benzo[*e*]-1,2-thiazine 5,5-dioxide (**25**) in good yield, together with *N*-cyclohexyl-*o*-(2-thienyl)benzenesulfonamide (**26**), but no product of cyclization at the thiophene sulfur atom. Again, contrary to the behavior of 2-*o*-nitrophenylpyridine, which on deoxygenation with ferrous oxalate[25] or triethyl phosphite[26] gives mainly attack of the arylnitrene at the pyridine nitrogen atom rather than at a ring carbon, deoxygenation of 2-*o*-nitrophenylthiophene gave only **24**.



Experimental Section

Melting points are uncorrected.

Biphenyl-2-sulfonyl Azide. Biphenyl-2-sulfonyl chloride[10] (2.65 g) in ice-cold acetone (25 mL) was treated with a cold solution of sodium azide (1 g) in water (5 mL) portionwise. The solution was stirred for 1 h and diluted with water (50 mL), and the sulfonyl azide which separated as an oil solidified on stirring (2.53 g, 93%): mp 60–61 °C (from methanol); IR (KBr) 2120 (s) (N_3), 1360, 1160 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_9N_3O_2S$: C, 55.58; H, 3.50; N, 16.20. Found: C, 55.49; H, 3.28; N, 15.91.

Thermolysis of Biphenyl-2-sulfonyl Azide. A. In Dodecane. (a) The azide (0.4 g, 0.002 mol) was suspended in *n*-dodecane (18 mL, 0.2 mol), and the system was degassed and then covered with oxygen-free dry nitrogen. The mixture was heated slowly and stirred until the bath temperature reached 175 °C when nitrogen evolution had ceased. The cooled dark solution deposited 6*H*-dibenzo[*c*,*e*][1,2]thiazine 5,5-dioxide (0.26 g, 72.9%), mp 198–200.5 °C, which was purified by chromatography on a column of alumina and recrystallized from benzene: mp 197–199 °C (lit.[13] mp 196 °C); IR (KBr) 3200 (m) (NH), 1300 (s), 1150 cm^{-1} (s) (SO_2).

Anal. Calcd for $C_{12}H_9NO_2S$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.61; H, 4.22, N, 5.88.

(b) When the thermolysis of the azide (2.59 g) in *n*-dodecane (25 mL) was repeated at 150 °C for 21 h and the reaction mixture was chromatographed on alumina, elution with ether–light petroleum (1:1 v/v) gave a yellow gum (0.58 g) which appears to be a mixture of isomeric (***N*-dodecyl)biphenyl-2-sulfonamides** (15%): IR (film) 3370–3290 (NH), 3060, 3030, 2950, 2920, 2850, 1320, 1175 cm^{-1} (SO_2); NMR (CCl_4) δ 8.04 (m, 1 H, aromatic), 7.53–7.15 (m, 8 H, aromatic), 4.70 (br, NH, exchangeable with D_2O), 3.08 (br s, CH), 1.40–0.60 (m, 24 H).

Anal. Calcd for $C_{24}H_{35}NO_2S$: C, 71.88; H, 8.80. Found: C, 71.95; H, 8.62.

Elution with ether–methanol (4:1 v/v) gave a light brown solid (1.95 g) which, on recrystallization from benzene, gave the above sultam (0.88 g, 38%), mp 200–202 °C.

(c) The thermolysis of the azide (1.29 g) in *n*-dodecane (25 mL) at 150 °C for 20.5 h was repeated in the presence of tetracyanoethylene (0.67 g) and the products were chromatographed on a column of neutral alumina (160 g). Elution with ether–light petroleum (1:1 v/v) gave the mixture of (*N*-dodecyl)biphenyl-2-sulfonamides (0.237 g, 12%). Elution with ether–methanol (2:3 v/v) gave a dark gum (0.317 g) which, on repeated recrystallization from ethanol, gave a light brown solid (0.022 g), mp >300 °C, which could not be characterized. Elution with methanol gave a dark solid (0.36 g) which, after recrystallization from ether–ethanol, gave a buff solid (0.27 g): mp >300 °C; IR (KBr) 3450 (NH), 3070, 1600, 1330, 1310, 1215, 1160, 1145, 1118, 1085, 705 cm^{-1}; no band due to C≡N was observed and the product could not be characterized further.

If the crude reaction mixture was chromatographed on a column of basic alumina, elution with methanol gave biphenyl-2-sulfonamide (10%), identical with an authentic sample (see below).

B. In the Absence of Solvent. The azide (0.29 g) was heated under nitrogen in a sealed tube at 120 °C for 48 h, and the product then chromatographed on neutral alumina (20 g) to give the sultam (0.17 g, 61%), mp 198–200 °C.

C. In Cyclohexane at 120 °C. The azide (1 g) in cyclohexane (20 mL) was heated under nitrogen in a sealed tube at 120 °C for 72 h. Chromatography of the products on a column of silica gel (70 g) gave recovered azide (0.15 g, 15%), the sultam (0.65 g, 80.8%), and an unidentified dark brown solid (0.038 g), mp >300 °C (insoluble in most common solvents). No (*N*-cyclohexyl)biphenyl-2-sulfonamide was detected (for authentic sample, see below).

D. In Cyclohexane at 81 °C. The azide (1 g) in cyclohexane (100 mL) was heated at 81 °C for 35 days under dry nitrogen. A brownish-black intractable solid deposited on the sides of the reaction vessel. Workup as above gave starting azide (0.78 g, 78%) and the sultam (0.06 g, 30.5%), but no azepine derivative.

E. In Benzene at 120 °C. The azide (0.8 g) in benzene (12 mL) was heated in a glass-lined bomb at 120 °C for 72 h. A black, intractable solid was formed on the sides of the vessel. The solution was evaporated and the residue chromatographed on a column of silica gel (60 g). Elution with benzene gave starting azide (0.11 g, 13.75%). Elution with benzene–ether (1:1 v/v) gave **biphenyl-2-sulfonanilide** (0.18 g, 21.8%): mp 135–136 °C (dilute EtOH); IR (KBr) 3375 (s) (NH), 1340, 1178 (SO_2), 770 (s), 760 (s), 742 (m), 708 cm^{-1} (m), identical with that of the authentic sample prepared below; *m/e* 309 ($M^{+\cdot}$).

Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.87; H, 4.89. Found: c, 69.68; H, 5.07.

Further elution with benzene–ether (1:1 v/v) gave the sultam (0.24 g, 36.8%), mp 198–200 °C.

F. In Benzene at 80 °C. This was carried out for 35 days as for the reaction in cyclohexane to give biphenyl-2-sulfonanilide (2.2%), the sultam (23.5%), and starting azide (81%).

G. In Cyclohexane with Diiron Nonacarbonyl at 25 °C. The azide (1 g) in cyclohexane (80 mL) was stirred at room temperature for 2 days with $Fe_2(CO)_9$ (0.73 g) under N_2. The mixture was filtered, the solid was washed with acetone, and the combined filtrates were evaporated and chromatographed on a column of silica gel (40 g) to give biphenyl-2-sulfonamide (81.5%), mp 118–119 °C, identical with

an authentic sample. The residue, mp >300 °C, did not show any SO_2 or CO absorptions in the infrared.

H. In Cyclohexane with Gatterman Copper at 81 °C. The azide (1 g) in cyclohexane (80 mL) was heated under N_2 with freshly prepared Gatterman copper for 10 days. Workup gave unchanged azide (0.42 g, 42%) and biphenyl-2-sulfonamide (0.41 g, 78.6%).

When methanesulfonyl azide was heated in benzene at 80 °C for 84 h in the presence of copper powder 62% was recovered unchanged and methanesulfonamide (67%, based on azide consumed) was isolated.

I. In Pyridines. The azide (3 g) in dry pyridine (80 mL) was boiled under reflux under N_2 for 48 h. The solvent was evaporated and the residue chromatographed on a column of silica gel (60 g). Elution with light petroleum (bp 30–60 °C) gave starting azide (0.6 g, 26.4%). Elution with methanol gave ***N*-(biphenyl-2-sulfonylimino)pyridinium ylide** (1.5 g, 52.2%): mp 213–214 °C (from MeOH); IR (KBr) 1295 (s), 1162 (s) (SO_2), 765 (s), 697 cm^{-1} (s); *m/e* 310 ($M^{+\cdot}$).

Anal. Calcd for $C_{17}H_{14}N_2O_2S$: C, 65.78; H, 4.55. Found: C, 65.93; H, 4.60.

The same thermolysis was repeated but in 2-picoline at 115–120 °C for 48 h to give starting azide (10%), sultam (54.8%), and ***N*-(biphenyl-2-sulfonylimino)-2-picolinium ylide** (32.5%): mp 164–165 °C (from benzene–light petroleum); IR (KBr) 1285, (s), 1145 (s), (SO_2), 760 (m), 695 cm^{-1} (m); *m/e* 324 ($M^{+\cdot}$).

Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 66.64; H, 4.97. Found: C, 66.66; H, 5.06.

The thermolysis in 2,6-lutidine gave starting azide (6.7%), sultam (44%), and ***N*-(biphenyl-2-sulfonylimino)-2,6-dimethylpyridinium ylide** (22%): mp 179–180 °C (from benzene–light petroleum); *m/e* 338 ($M^{+\cdot}$).

Anal. Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.43; H, 5.36. Found: C, 67.50; H, 5.42.

The thermolysis in 2,4,6-collidine gave starting azide (10%), sultam (54%), and ***N*-(biphenyl-2-sulfonylimino)-2,4,6-trimethylpyridinium ylide** (17.7%), mp 184–186 °C (from benzene–light petroleum), identical with the authentic sample prepared as described below.

J. In Methanol with Copper. A solution of the azide (1 g) in methanol (50 mL) was stirred with copper (freshly precipitated) and boiled under reflux for 16 h. The solution gradually turned blue. Workup and chromatography on silica gel gave starting azide (0.01 g, 1%), biphenyl-2-sulfonamide (0.8 g, 89.8%), mp 118–119 °C, and a blue, crystalline solid (0.02 g), mp >300 °C [from benzene–light petroleum (bp 30–60 °C)]; IR (KBr) 3050 (w), 2925 (w), 1575 (w), 1450 (m), 1270 (s), (SO_2), 1120 (s), 985 (m), 850 (w), 755 (s), 700 cm^{-1} (m).

Anal. Found: C, 56.90; H, 4.13.

No structure can be assigned to this product at the present time.

Photolysis of Biphenyl-2-sulfonyl Azide. A. In Cyclohexane. The azide (1 g) in cyclohexane (200 mL) was irradiated in a quartz vessel at 26 °C for 19 h using 2537-Å light. The solution turned orange and an orange-brown pasty mass formed on the sides of the vessel. The reaction mixture was chromatographed on a column of basic alumina to give starting azide (0.15 g, 15%) and a product (0.65 g), mp 266–268 °C (from benzene–acetone), which could not be obtained sufficiently pure for analysis. When the irradiation was carried out for only 4 h, starting azide was recovered (92%).

B. In Cyclohexane and Di-*tert*-butyl Sulfide. The azide (0.286 g) in cyclohexane (50 mL) containing di-*tert*-butyl sulfide (0.21 mL) was deoxygenated and then photolyzed under dry N_2 for 2 h at 32 °C in a Rayonet reactor using 3000-Å lamps. A tan precipitate formed which showed no resolved bands in its infrared spectrum. The whole suspension was evaporated to dryness and subjected to preparative TLC on silica gel [cyclohexane–benzene (9:1 v/v) as developer] to give **2-biphenyl *tert*-butyl sulfone** as a colorless oil (8 mg, 4%): R_f 0.72; IR (KBr) 1360 (m), 1170 cm^{-1} (SO_2); NMR (CCl_4) δ 7.80 (m, 1, H ortho to SO_2), 7.2 (m, 8, ArH), 1.15 (s, 9, *t*-Bu); mass spectrum (70 eV) *m/e* (rel intensity) 274 (20, $M^{+\cdot}$), 218 (60, $M^{+\cdot} - C_4H_8$), 185 (100, $M^{+\cdot} - C_4H_9S$ or $M^{+\cdot} - C_4H_9O_2$).

Anal. Calcd for $C_{16}H_{18}O_2S$: C, 70.07; H, 6.57. Found: C, 69.80; H, 6.41.

2-Biphenyl disulfide (44 mg, 20%); R_f 0.5; mp 113.5–114 °C (EtOH) (lit.[27] mp 114 °C), undepressed on admixture with an authentic sample; mass spectrum (70 eV) *m/e* (rel intensity) 370 (76, $M^{+\cdot}$), 185 (93, $M^{+\cdot} - 185$), 184 (100, $M^{+\cdot} - 186$).

Recovered azide (140 mg, 49%), R_f 0.02.

Dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (4 mg, 3%), R_f 0.05, identical with samples of the sultam obtained above.

The photolysis was repeated using equivalent amounts of azide and di-*tert*-butyl sulfide but in acetonitrile solution. Only a trace of sultam was isolated, together with 2-biphenyl disulfide (4%) and 2-biphenyl *tert*-butyl sulfone (10%). Photolysis of the azide in neat di-*tert*-butyl sulfide similarly yielded a trace of sultam, disulfide (17%), and sulfone (15%).

Biphenyl-2-sulfonamide. Biphenyl-2-sulfonyl chloride (5.05 g) in concentrated ammonium hydroxide solution (200 mL) was stirred at room temperature for 24 h. The solution was filtered, the filtrate acidified, and the amide (4.36 g, 94%), mp 121–122 °C (from aqueous EtOH), filtered: IR (KBr) 3340, 3280 (NH_2), 1330, 1170 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.80; H, 4.72. Found: C, 62.20; H, 4.91.

Biphenyl-2-sulfonanilide. It was prepared in 71.4% yield from biphenyl-2-sulfonyl chloride and aniline in hot benzene, mp 135–136 °C (dilute EtOH), identical with the sample obtained above.

***N*-Cyclohexylbiphenyl-2-sulfonamide** (60%) was prepared from biphenyl-2-sulfonyl chloride and cyclohexylamine in boiling benzene and had mp 96–97 °C (dilute EtOH).

Anal. Calcd for $C_{18}H_{21}NO_2S$: C, 68.57; H, 6.71. Found: C, 68.23; H, 6.69.

***N*-(Biphenyl-2-sulfonylimino)-2,4,6-trimethylpyridinium Ylide.** 2,4,6-Trimethylpyrylium perchlorate (2.23 g) and biphenyl-2-sulfonyl hydrazide (2.48 g) [from biphenyl-2-sulfonyl chloride and 50% hydrazine hydrate in benzene at <20 °C (96%); mp 121 °C dec (MeOH); IR (KBr) 3480 (s), 3230 (s), 1340 (s), 1150 cm^{-1} (s); *m/e* 248 ($M^{+\cdot}$). Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.04; H, 4.87. Found: C, 58.40; H, 4.96] were boiled under reflux in absolute ethanol (150 mL) for 10 h and filtered hot to give recovered pyrylium salt (0.28 g, 13%). The filtrate was concentrated to about 30 mL and treated with 30% KOH solution (2 mL) at 0–5 °C. $KClO_4$ (1.04 g, 75%) separated and was filtered. The solution was evaporated to dryness onto basic alumina (10 g) and the residue chromatographed on a column of basic alumina (2.5 × 40 cm). Elution with ether and then with $CHCl_3$ gave the ylide (1.25 g, 36%): mp 184–185 °C (from benzene–cyclohexane), identical with the sample prepared above; mass spectrum *m/e* (rel intensity) 354 ($M^{+\cdot}$ + 2, 6), 353 ($M^{+\cdot}$ + 1, 25), 352 ($M^{+\cdot}$, 6.7), 288 (22), 135 (100), 121 (42), 107 (64), 106 (42), 79 (22); NMR ($CDCl_3$) δ 7.94 (m, 1, ortho to SO_2), 7.62 (m, 2), 7.35 (m, 6), 7.13 (s, 2, pyridine β protons), 2.49 (s, 6, 2,6-Me_2), 2.35 (s, 3, 4-Me).

Anal. Calcd for $C_{20}H_{20}N_2O_2S$: C, 68.15; H, 5.72. Found: C, 68.32; H, 5.80.

Thermolysis of Biphenyl-2-sulfonamide. The amide (0.466 g) in *n*-dodecane (10 mL) was heated and stirred at 150 °C for 14 h. The products were chromatographed on a column of neutral alumina (150 g). Elution with ether–light petroleum (1:1 v/v) gave a yellow liquid (68 mg) not characterized further. Elution with ether–methanol (19:1 v/v) gave unchanged amide (0.358 g), mp 119–120 °C.

Reaction of Biphenyl-2-sulfonamide with $Pb(OCOCH_3)_4$. The amide (0.405 g) in acetic acid (25 mL) was heated at 80 °C with stirring with lead tetraacetate (1.520 g) for 4 h. Starting amide (0.352 g, 87%) was recovered. TLC indicated the absence of sultam **6a**. A similar result was obtained when the reaction was carried out at 120 °C. Amide (67%) was recovered together with some black solid, mp >300 °C.

No sultam was obtained when the amide (2.5 mmol) in trifluoroacetic acid (25 g) was heated at 20 °C for 5 h with lead tetra(trifluoroacetate) (5.0 mmol). Amide (70%) was recovered, together with two other very minor products (detected by TLC), but no sultam.

When the oxidation was attempted with $Pb(OCOCH_3)_4$ in boiling benzene, amide (61%) was again recovered.

Biphenyl-2-sulfonyliminotriphenylphosphonium Ylide. Biphenyl-2-sulfonyl azide (3 g) and triphenylphosphine (3 g) were heated in benzene for 1 h and the solvent was evaporated to give the ylide (5 g, 87%), mp 226–228 °C (from benzene).

Anal. Calcd for $C_{30}H_{24}NO_2PS$: C, 73.00; H, 4.90. Found: C, 72.84; H, 5.01.

Attempted Photolysis of Phosphonium Ylide. The ylide (0.5 g) in acetonitrile (400 mL) was photolyzed at 35–40 °C using 3000-Å lamps for 24 h. Starting material was recovered.

When the photolysis was carried out for 24 h at 26 °C in a quartz vessel using 2537-Å lamps the solution turned pale yellow. Chromatography on a column of silica gel gave starting ylide (0.42 g, 84%), together with a light brown solid, mp >300 °C, which could not be purified further.

2′,4′,6′-Trimethylbiphenyl-2-sulfonyl Azide. 2-Amino-2′,4′,6′-trimethylbiphenyl[2c] (1 g) in acetic acid (8 mL) containing concentrated HCl (3 mL) was treated with sodium nitrite (0.5 g) in water (2 mL) at 0 °C, and the diazonium salt solution was added to a mixture of a 30% solution of SO_2 in acetic acid (11 mL), benzene (10 mL), and $CuCl_2 \cdot 2H_2O$ (0.5 g). The mixture was stirred for 1 h at 0 °C, 1 h at

room temperature, and 0.5 h at 40 °C, diluted with water (200 mL), and extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and evaporated and the residue recrystallized from benzene to give the sulfonyl chloride (0.6 g, 56%), mp 100–103 °C dec.

Without further purification this was treated as above with sodium azide in aqueous acetone to give the sulfonyl azide (70%), mp 69–70 °C (EtOH), *m/e* 269 ($M^{+\cdot}$).

Anal. Calcd for $C_{15}H_{15}N_3O_2S$: C, 59.78; H, 5.02. Found: C, 59.83; H, 5.07.

Thermolysis of 2′,4′,6′-Trimethylbiphenyl-2-sulfonyl Azide. The azide (0.52 g) in cyclohexane (30 mL) was heated under nitrogen at 135 °C for 2 days. The reaction mixture was concentrated and resolved by preparative TLC on silica gel [benzene–light petroleum (1:1 v/v) as developer] to give two main bands and four minor ones. The fastest moving band was extracted to give 2,4-dimethylfluorene (0.09 g, 35%): mp 64–65 °C (EtOH) (lit.[28] mp 67–67.5 °C); NMR (CCl_4) δ 7.40 (m, 4, ArH), 6.86 (s, 2, ArH), 3.70 (s, 2, CH_2), 2.60 (s, 3, CH_3), 2.31 (s, 3, CH_3); *m/e* 194 ($M^{+\cdot}$). The second band was due to recovered azide (0.133 g, 26%). Other products were not identified.

4′-Bromobiphenyl-2-sulfonyl Chloride. 2-Amino-4′-bromobiphenyl[29] (7.4 g) was diazotized at 0 °C in acetic acid (40 mL) and concentrated HCl (7 mL) with sodium nitrite (3.1 g) in water (5 mL). The diazonium salt solution was poured into a saturated solution of SO_2 in acetic acid (80 mL) and benzene (80 mL) containing $CuCl_2 \cdot 2H_2O$ (1.0 g). After stirring for 6 h the solution was poured into ice water (600 mL) and extracted with $CHCl_3$ (100 mL), and the extract was washed with water (2 × 25 ml), dried ($MgSO_4$), and evaporated to give an oil (8 g). On trituration with ethanol **bis-4′-bromobiphenyl 2-disulfide *S,S*-oxide** (1.6 g, 20%) precipitated: mp 175–176 °C; IR (KBr) 1455 (m), 1320 (s), 1145 cm^{-1} (s).

Anal. Calcd for $C_{24}H_{16}Br_2O_2S_2$: C, 51.44; H, 2.88. Found: C, 51.50; H, 2.88.

The ethanolic filtrate gave **4′-bromobiphenyl-2-sulfonyl chloride** (4 g, 46%): mp 93–94 °C (EtOH); IR (KBr) 1375 (s), 1180 cm^{-1} (s) (SO_2); NMR (CCl_4) δ 8.25 (m, 1, H ortho to SO_2), 7.5 (m, 7, an AB pattern is visible within the multiplet, J = 9 Hz).

Anal. Calcd for $C_{12}H_8BrClO_2S$: C, 43.46; H, 4.43. Found: C, 43.52; H, 2.41.

4′-Bromobiphenyl-2-sulfonyl Azide. The sulfonyl chloride (2 g) in acetone (50 mL) was treated with NaN_3 (2.2 g) in water (10 mL) at 0 °C. The solution was stirred for 6 h at room temperature and poured into ice water (200 mL) to precipitate the azide (1.5 g, 60%): mp 82–83 °C (EtOH); IR (KBr) 2110 (s), 1365 (s), 1160 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 344 [10, $(M + 2)^{+\cdot}$], 342 (10, $M^{+\cdot}$), 264 (99), 262 (100), 234 (80), 232 (80).

Anal. Calcd for $C_{12}H_8BrN_3O_2S$: C, 42.62; H, 2.38. Found: C, 42.53; H, 2.48.

4′-Bromobiphenyl-2-sulfonamide. Ammonia was bubbled through a solution of 4′-bromobiphenyl-2-sulfonyl chloride (0.1 g) in benzene (15 mL) for 2 h at room temperature. The precipitated NH_4Cl was filtered and the filtrate concentrated to give the sulfonamide (0.033 g, 35%): mp 194–195 °C (EtOH); IR (KBr) 3350 (s), 3250 (s), 1320 (s), 1170 cm^{-1} (s); NMR (acetone-d_6) δ 8.2 (m, 1, ortho to SO_2), 7.5 (m, 7, ArH), 6.1 (br s, 2, exchangeable with D_2O, NH_2); mass spectrum (70 eV) *m/e* (rel intensity) 313 (13, $M^{+\cdot}$ + 2), 311 (13, $M^{+\cdot}$).

Anal. Calcd for $C_{12}H_{10}BrNO_2S$: C, 46.16; H, 3.23. Found: C, 46.30; H, 3.30.

4′-Bromobiphenyl-2-sulfonanilide. Prepared from the sulfonyl chloride and aniline it was obtained in 41% yield: mp 151–152 °C (EtOH); IR (KBr) 3220 (s), 1330 (s), 1150 cm^{-1} (s); NMR [$CDCl_3$/$(CD_3)_2CO$] δ 8.2 (m, 1, ortho to SO_2), 8.1 (br s, exchanges with D_2O, NH), 7.3 (m, 7, ArH); *m/e* 390 (12, $M^{+\cdot}$ + 2), 338 (12, $M^{+\cdot}$).

Anal. Calcd for $C_{18}H_{14}BrNO_2S$: C, 55.68; H, 3.63. Found: C, 55.85; H, 3.68.

4′-Bromo-*N*-cyclohexylbiphenyl-2-sulfonamide. Prepared from cyclohexylamine and the sulfonyl chloride in benzene at 90 °C, the amide (55%) had mp 106–107 °C (EtOH); IR (KBr) 3240 (s), 1320 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 8.2 (m, 1, ortho to SO_2), 7.5 (m, 7, ArH), 3.8 (d, 1, exchangeable, NH), 2.9 (br, 1, C–H of cyclohexyl), 1.3 (br m, 10, cyclohexyl).

Anal. Calcd for $C_{18}H_{20}BrNO_2S$: C, 54.83; H, 5.11. Found: C, 54.94; H, 5.21.

4′-Bromo-*N*-(*o*-chlorophenyl)biphenyl-2-sulfonamide (50%), mp 105–106 °C (EtOH). Anal. Calcd for $C_{18}H_{13}BrClNO_2S$: C, 51.14; H, 3.10. Found: C, 51.18; H, 3.12.

4′-Bromo-*N*-(*p*-chlorophenyl)biphenyl-2-sulfonamide (50%), mp 135–137 °C (EtOH).

Anal. Calcd for $C_{18}H_{13}BrClNO_2S$: C, 51.15; H, 3.10. Found: C, 51.14; H, 3.34.

4′-Bromo-2-trifluoroacetamidobiphenyl (50%), mp 97 °C (hexane), was prepared from 2-amino-4′-bromobiphenyl in $CHCl_3$ and trifluoroacetic anhydride: IR (KBr) 3200 (br s), 1700 (s), 1520 (s), 1470 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 7.5 (m).

Anal. Calcd for $C_{14}H_9BrF_3NO$: C, 48.86; H, 2.64. Found: C, 49.09; H, 2.70.

Thermolysis of 4′-Bromobiphenyl-2-sulfonyl Azide. A. In Cyclohexane. The azide (0.5 g) in cyclohexane (30 mL) was heated under dry N_2 at 120–130 °C for 2 days. The cyclohexane was evaporated and the residue was resolved by preparative TLC on silica gel (1.5 mm thick, benzene as developer) to give recovered azide (53 mg, 10%), R_f 0.8, mp 83–84 °C, and 4′-bromo-*N*-cyclohexylbiphenyl-2-sulfonamide (144 mg, 27%), R_f 0.5, mp 106–107 °C, identical with authentic material. Also obtained was **8-bromodibenzo[*c,e*][1,2]thiazine 5,5-dioxide** (22 mg, 5%): R_f 0.1; mp 224–226 °C (EtOH); identical with an authentic sample prepared as described below; IR (KBr) 3150 (br s), 1290 (s), 1150 cm^{-1} (s); NMR (acetone-d_6) δ 7.9 (m); *m/e* 311 (32, $M^{+\cdot}$ + 2), 309 (31, $M^{+\cdot}$).

Anal. Calcd for $C_{12}H_8BrNO_2S$: C, 46.47; H, 2.60. Found: C, 46.37; H, 2.66.

B. In Benzene. The azide (0.5 g) in benzene (50 mL) was heated as described above and the products were resolved by preparative TLC to give recovered azide (182 mg, 36%); 4′-bromobiphenyl-2-sulfonanilide (170 mg, 47%), mp 149–150 °C, identical with an authentic sample; and the 8-bromosultam (77 mg, 27%), mp 224 °C, identical with an authentic sample.

C. In Chlorobenzene. The azide (2.76 g) in chlorobenzene (140 mL) was heated at 130 °C for 3 days, and the products were resolved by preparative TLC to give 4′-bromo-*N*-(*o*-chlorophenyl)biphenyl-2-sulfonamide (366 mg, 10%), mp 106–108 °C; 4′-bromo-*N*-(*p*-chlorophenyl)biphenyl-2-sulfonamide (423 mg, 13%), mp 136–137 °C; and the 8-bromosultam (353 mg, 24%), mp 225–229 °C, all identical with authentic samples.

D. In Benzene Containing Trifluoroacetic Acid. The azide (2.0 g) in benzene (100 mL) and CF_3CO_2H (5.3 mL) was heated at 130 °C for 2 days. The solution was washed with 5% aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated. The residue was resolved by preparative TLC to give starting azide (323 mg, 16%); 4′-bromo-2-trifluoroacetamidobiphenyl (37 mg, 4%), mp 98 °C; 4′-bromobiphenyl-2-sulfonanilide (316 mg, 34%), mp 151–152 °C; and 8-bromosultam (147 mg, 25%), mp 226–227 °C, all identical with authentic samples.

***N*-(*m*-Bromophenyl)-2-nitrobenzenesulfonamide.** *o*-Nitrobenzenesulfonyl chloride (20 g) and *m*-bromoaniline (30.9 g) in benzene (30 mL) were stirred at room temperature for 6 h. The solution was washed with cold 5% HCl (2 × 15 mL), dried ($MgSO_4$), and concentrated to give the sulfonamide (23 g, 70%): mp 128–129 °C; IR (KBr) 3300 (s), 1530 (s), 1355 (s), 1330 (s), 1170 cm^{-1} (s); NMR (acetone-d_6) δ 9.25 (br s, 1, exchangeable, NH), 7.6 (m, ArH).

Anal. Calcd for $C_{12}H_9BrN_2O_4S$: C, 40.35; H, 2.54. Found: C, 40.40; H, 2.60.

2-Amino-*N*-(*m*-bromophenyl)benzenesulfonamide. The nitro compound (10 g), zinc powder (5.7 g), and calcium chloride (2.5 g) in 78% ethanol (50 mL) were boiled under reflux for 3 h and then poured onto ice. The amine (6.5 g, 71%) had mp 114–115 °C (from CCl_4); IR (KBr) 3400 (m), 3320 (m), 3140 (m), 1320 (s), 1150 cm^{-1} (s).

Anal. Calcd for $C_{12}H_{11}BrN_2O_2S$: C, 44.05; H, 3.39; N, 8.56. Found: C, 43.74; H, 3.40; N, 8.60.

8-Bromodibenzo[*c,e*][1,2]thiazine 5,5-Dioxide. *N*-(*m*-Bromophenyl)-2-aminobenzenesulfonamide (3.28 g), sodium hydroxide (0.5 g), and sodium nitrite (0.7 g) were dissolved in water (25 mL) and added to cold concentrated HCl (5 mL) and water (25 mL). After 15 min the solution was filtered and diluted to 150 mL and sodium acetate (6 g) was added. 2-(*m*-Bromophenyl)benzo[*e*]-1,2,3,4-thiatriazine 1,1-dioxide separated as a tan powder (1.6 g, 47%) which was immediately dissolved in EtOH (30 mL) and decomposed with Gatterman copper at room temperature. After a rapid gas evolution (15 min) the solution was heated to 80 °C for 30 min. The copper was filtered and the filtrate was evaporated to dryness to give a red oil. This was chromatographed on silica gel. Elution with $CHCl_3$ gave the 8-bromosultam (0.77 g, 25%), mp 224–226 °C (EtOH), identical with the sample prepared above.

2-*o*-Chlorosulfonylphenylthiophene. 2-*o*-Aminophenylthiophene[7] (1.3 g) in 20% HCl (10 mL) was diazotized at 0 °C with sodium nitrite (1 g) in water (10 mL) and the solution was stirred into acetic acid (20 mL) saturated with SO_2 mixed with benzene (20 mL) and $CuCl_2 \cdot 2H_2O$ (0.25 g) at 5–10 °C. After 1 h at that temperature the stirred mixture was warmed at 40 °C for 40 min and then poured into water (200 mL). The mixture was extracted with ether, and the extract was dried ($MgSO_4$) and evaporated. The residual brown oil (1 g) was heated with light petroleum (bp 30–60 °C) (20 mL) for 5 min, the

cooled light petroleum was decanted, and benzene (3 mL) was added to give the solid sulfonyl chloride (0.78 g, 40.7%), mp 82–83 °C (light petroleum), *m/e* 258 ($M^{+\cdot}$ ^{35}Cl).

Anal. Calcd for $C_{10}H_7ClO_2S_2$: C, 46.43; H, 2.73. Found: C, 46.15; H, 2.88.

Some sulfonic acid, mp 87–88 °C, *m/e* 240 ($M^{+\cdot}$), was also isolated in some cases by chromatography of the reaction mixture on a column of silica gel.

2-*o*-Azidosulfonylphenylthiophene. The sulfonyl chloride (0.65 g) in acetone (30 mL) at 0–5 °C was treated with sodium azide (0.75 g) in water (5 mL). The solution was stirred at 0–5 °C for 1 h, diluted with water (75 mL), and extracted with ether. The dried ($MgSO_4$) extract was evaporated to give the azide (0.54 g, 80.8%) as an oil. Chromatography through a column of silica gel (20 g) and elution with benzene gave an oil with solidified: mp 70–71 °C (dilute MeOH); IR (film) 2330 (w), 2130 (s), (N_3), 1360 (s), 1350 (s), 1165 cm^{-1} (br s).

Anal. Calcd for $C_{10}H_7N_3O_2S_2$: C, 45.29; H, 2.66. Found: C, 45.45; H, 2.82.

Thermolysis of 2-*o*-Azidosulfonylphenylthiophene. A. In Cyclohexane. The azide (0.5 g) in freshly distilled cyclohexane (20 mL) was heated under dry N_2 in a glass bomb at 120 °C for 72 h. The solvent was evaporated and the residue was chromatographed on a column of silica gel (40 g). Elution with light petroleum (bp 30–60 °C)-benzene (1:1 v/v) gave starting azide (0.15 g, 30%). Elution with benzene gave ***N*-cyclohexyl-*o*-(2-thienyl)benzenesulfonamide** (0.15 g, 35.4% based on azide consumed): mp 97–98 °C (dilute EtOH); IR (KBr) 3340 (s), 1310 (s), 1160 cm^{-1} (s); *m/e* 321 ($M^{+\cdot}$); identical with an authentic sample prepared (72%) from the sulfonyl chloride and cyclohexylamine.

Anal. Calcd for $C_{16}H_{19}NO_2S_2$: C, 59.78; H, 5.96. Found: C, 59.85; H, 6.10.

Elution with benzene–ether (1:1 v/v) gave **thieno[3,2-*c*]-6*H*-benzo[*e*][1,2]thiazine 5,5-dioxide** (0.19 g, 60.7% based on azide consumed): mp 204–205 °C (dilute EtOH); IR (KBr) 3200 (m), 1315 (s), 1180 cm^{-1} (s).

Anal. Calcd for $C_{10}H_7NO_2S_2$: C, 50.61; H, 2.97. Found: C, 50.75; H, 3.12.

B. With Cu in Benzene. The azide (0.5 g) in benzene (80 mL) containing copper powder (0.2 g) was heated at 80 °C for 84 h. The filtered solution was evaporated and the residue chromatographed on a column of silica gel (40 g) to give recovered azide (0.4 g, 80%) and ***o*-(2-thienyl)benzenesulfonamide** (0.06 g, 66.6%): mp 144–146 °C (dilute EtOH); IR (KBr) 3370 (s), 3270 (s), 1320 (s), 1160 cm^{-1} (s); *m/e* 239 ($M^{+\cdot}$); identical with an authentic sample prepared in 76% yield from the sulfonyl chloride and ammonia.

Anal. Calcd for $C_{10}H_9NO_2S_2$: C, 50.19; H, 3.79. Found: C, 50.44; H, 3.97.

***N*-2-Dimethylaminoethyl-6*H*-dibenzo[*c,e*][1,2]thiazine 5,5-Dioxide.** 6*H*-Dibenzo[*c,e*][1,2]thiazine 5,5-dioxide (0.46 g) in ethanol (20 mL) was treated with thallous ethoxide (0.5 g) to give a precipitate of the thallium salt (0.84 g, 97%). A well-stirred suspension of β-dimethylaminoethyl chloride hydrochloride (0.37 g) in toluene (10 mL) was treated with 50% aqueous KOH (5 mL), the mixture was stirred for 15 min, the aqueous layer was extracted with toluene (2 × 5 mL), and the combined toluene solutions were dried (Na_2CO_3). They were added to a boiling suspension of the thallium salt (0.87 g) in toluene (25 mL) and the mixture boiled under reflux for 22 h. It was then filtered and the solvent evaporated to give the product (0.24 g, 39%), mp 102–103 ° (from light petroleum).

Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.50; H, 6.00. Found: C, 63.60; H, 6.16.

***N*-3-Dimethylaminopropyl-6*H*-dibenzo[*c,e*][1,2]thiazine 5,5-dioxide** (48%), mp 94–95 °C, was prepared similarly.

Anal. Calcd for $C_{17}H_{20}N_2O_2S$: C, 64.53; H, 6.37. Found: C, 64.63; H, 6.44.

Deoxygenation of 2-*o*-Nitrophenylthiophene with Triethyl Phosphite. The nitro compound (1 g) and triethyl phosphite (3.5 g) were boiled under reflux under N_2 for 9 h. The excess phosphite was distilled in vacuo and the residue was chromatographed on a column of silica gel (50 g). Elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave 4*H*-thieno[3,2-*b*]indole (0.4 g, 47.4%), mp 174–175 °C (dilute EtOH), identical with the product obtained from the thermolysis of 2-*o*-azidophenylthiophene in decalin.[7]

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Registry No.—**1b,** 25627-20-7; **1c,** 62532-98-3; **1d,** 62532-99-4; **2a,** 2688-90-6; **2b,** 62533-00-0; **2c,** 62533-01-1; **2d,** 62533-02-2; **3a,** 40182-14-7; **3b,** 62533-03-3; **3c,** 62533-04-4; **3d,** 62533-05-5; **6a,** 1864-33-1; **6b,** 62533-06-6; **7,** 14858-84-5; **8,** 14858-85-6; **9,** 40182-08-9; **11** (R = H), 40949-59-5; **11** (R = 2-Me), 62562-59-8; **11** (R = 2,6-Me_2), 62533-07-7; **11** (R = 2,4,6-Me_3), 40949-60-8; **12,** 62533-08-8; **13,** 19813-97-9; **14,** 62533-09-9; **15,** 2928-44-1; **16,** 62533-10-2; **17,** 62533-11-3; **18,** 62533-12-4; **19,** 62533-13-5; **20,** 62533-14-6; **22,** 62533-15-7; **23,** 62533-16-8; **25,** 62533-17-9; **26,** 62533-18-0; sodium azide, 12136-89-9; *n*-dodecane, 112-40-3; (*n*-dodecyl)biphenyl-2-sulfonamide, 62533-19-1; benzene, 71-43-2; pyridine, 110-86-1; 2-picoline, 109-06-8; 2,6-lutidine, 108-48-5; biphenyl-2-sulfonamide, 40182-06-7; di-*tert*-butyl sulfide, 107-47-1; aniline, 62-53-3; *n*-cyclohexylbiphenyl-2-sulfonamide, 62533-20-4; cyclohexylamine, 108-91-8; 2,4,6-trimethylpyridinium perchlorate, 61244-34-6; biphenyl-2-sulfonyl hydrazide, 62533-21-5; triphenylphosphine, 603-35-0; cyclohexane, 110-82-7; bis-4′-bromobiphenyl 2-disulfide *S,S*-oxide, 62533-22-6; 4′-bromobiphenyl-2-sulfonamide, 62533-23-7; 2-amino-4′-bromobiphenyl, 62532-98-3; chlorobenzene, 108-90-7; *n*-(*m*-bromophenyl)-2-nitrobenzenesulfonamide, 62533-24-8; *o*-nitrobenzenesulfonyl chloride, 1694-92-4; *m*-bromoaniline, 591-19-5; *o*-(2-thienyl)benzenesulfonic acid, 62533-25-9; *o*-(2-thienyl)benzenesulfonamide, 62533-26-0; β-dimethylaminoethyl chloride hydrochloride, 4584-46-7.

References and Notes

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