Intramolecular Cyclizations of Diphenyl Ether, Benzophenone, and Related 2-Sulfonylnitrenes[1a]

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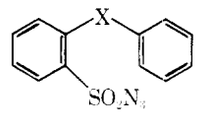
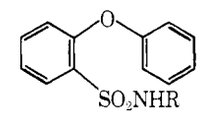
Thermolysis of 2-phenoxybenzenesulfonyl azide gave 6*H*-dibenzo[*b*,*f*][1,4,5]oxathiazepine 5,5-oxide (**4**) (the first seven-membered ring compound formed by intramolecular aromatic cyclization of a sulfonylnitrene) and other nitrene-derived products. On the other hand, diphenyl sulfide 2-sulfonyl azide (**1b**) gave some 3-phenylbenzo[1,3,2]-dithiazolium ylide 1,1-dioxide (**10**), but no seven-membered ring compound. Thermolysis of diphenyl sulfone 2-sulfonyl azide gave only small amounts of products derived from the aryl radical **16**, but no nitrene-derived compounds. Decomposition of 2-azidosulfonylbenzophenones gave the desired seven-membered sultams without rearrangement, together with an array of other products. Some of these are formed from the sulfonylnitrene, while it is proposed that the others result from ring–chain tautomerization of some undecomposed sulfonyl azide to 3-aryl-3-azidobenzo[*d*][2,1]oxathioles (**34**). Decomposition of the latter to the alkylnitrene and 1,2-aryl shifts would account for the products observed.

In earlier papers, the intramolecular cyclization of 2-biarylsulfonyl azides[2] and the intramolecular insertion of arylsulfonylnitrenes into aliphatic side chains[3] were described. A variety of five- and six-membered sultams was obtained and a number of important side reactions were noted and discussed. The present paper describes work aimed at synthesizing seven-membered sultams by intramolecular cyclization of appropriate ortho-substituted arylsulfonylnitrenes and discusses the scope and limitations of some of these reactions. At the time this work was initiated direct intramolecular cyclization of a nitrene to a seven-membered ring was unprecedented. Since then a number of examples (rings formed indirectly, however) have been recorded.[4]

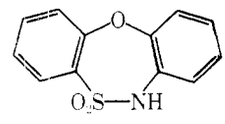
A. Decomposition of 2-Phenoxybenzenesulfonyl Azide (1a). The azide was thermolyzed in *n*-dodecane at 130–135 °C to give *N*-dodecyl-2-phenoxybenzenesulfonamide (**2**) (1%;



1a, X = O
b, X = S
c, X = SO_2
d, X = $NCOCH_3$; 4,4′-Me_2
e, X = CO



2, R = $C_{12}H_{25}$
3, R = H



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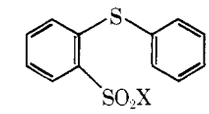
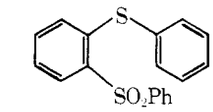
a mixture of isomers resulting from insertion of the nitrene into the solvent) and the hydrogen-abstraction product **3** (4%), together with the desired cyclization products 6*H*-dibenzo[*b*,*f*][1,4,5]oxathiazepine 5,5-dioxide (**4**) (15%). A better yield of **4** was obtained (38%) by carrying out the thermolysis in the absence of solvent.

B. Decomposition of Diphenyl sulfide 2-Sulfonyl Azide (1b). This azide was prepared as usual from the corresponding sulfonyl chloride **5.** When benzene was used as the solvent in the synthesis of **5** from the primary amine and the reaction mixture was warmed to 40 °C instead of being kept at room temperature, acylation of the solvent occurred and 2-phenyl thiodiphenyl sulfone (**6**) was isolated. No seven-membered ring product was isolated on thermolysis of **1b** in *n*-dodecane at 150 °C. Instead there were obtained the solvent insertion (**7**) and hydrogen-abstraction (**8**) products, together with some



5, X = Cl
7, X = $NHC_{12}H_{25}$
8, X = NH_2



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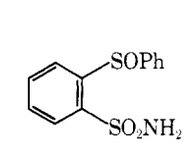
(4%) diphenyl sulfoxide 2-sulfonamide (**9**) and 3-phenylbenzo[1,3,2]dithiazolium ylide 1,1-dioxide (**10**) (10%). Again,



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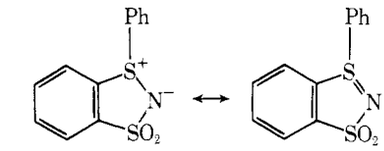

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a better yield (28%) of **10** was obtained when the reaction was carried out in the absence of solvent. The sulfoxide **9** undoubtedly arises by hydrolysis of **10** during workup and, indeed, chromatography of **10** on neutral alumina gave **9,** as did basic hydrolysis of **10.** Authentic **10** could be prepared from **8** and bromine in aqueous methanol, with or without added base. On the other hand, bromination of **8** in chloroform at room temperature gave a mixture of 2- and 4-bromodiphenyl sulfide 2′-sulfonamide (**11**). Treatment of **10** with dimethyl sulfate and KOH gave diphenyl sulfide 2-*N*,*N*-dimethylsulfonamide (**12**), also obtained by the methylation of **8.**

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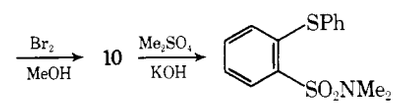

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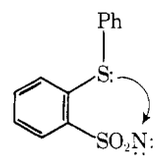
In view of the fact that both C–H insertion and hydrogen-abstraction products were obtained, indicating the intermediacy of a free sulfonylnitrene in these reactions, it seems likely that **10** is formed by nucleophilic trapping of the sul-



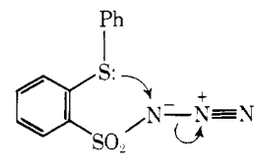


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Table I. Thermolysis Products of 1a–d

Registry no.	Compd	Temp, °C	Time, h	Solvent	Yield of products (%)
40182-15-8	**1a**	130–135	30	*n*-Dodecane	**2** (11%), **3** (4%), **4** (15%)
	1a	165	12		**3** (59.9%), **4** (37.9%)
64939-38-4	**1b**	150	61	*n*-Dodecane	**7** (8.8%), **8** (19%), **9** (4%), **10** (10%)
	1b	160–170	3		**9** (26%), **10** (27%)
64939-39-5	**1c**	150	16	*n*-Dodecane	**13** (27%), **14** (9%)
	1c	150	16	*n*-Dodecane/S_8	**13** (19%), **14** (19%)
	1c	160	18	Freon E-4	**14** (1.9%), **15** (2.6%)

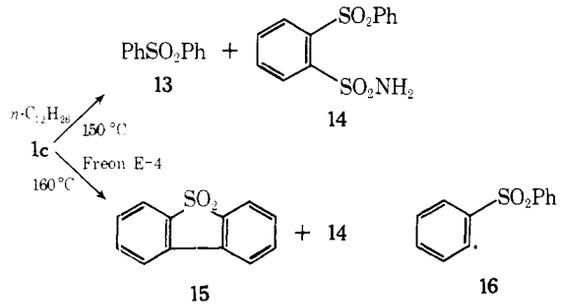
Table II. Thermolysis Products of Benzophenone-2-Sulfonyl Azides

					% yield of Products[a]								
Registry no.	Compd	Temp, C°	Time, h	Solvent	Starting azide	**17**	**18**	**19**	**20**	**21**	**25**	**26**	**27**
63113-42-8	**1e**	100	120	Freon 113	35	3.5	15	1	1	1			
	1e	140	48	Freon 113		3		2	1				
	1e	150	48	C_6H_5Cl		7		2		4			
	1e	100	120	EtOH	40	3		20					
63113-43-9	**23**	100	120	Freon 113	43	5	35	2	3	2			26
	23	140	10	Freon 113	15	6		4	4	trace	33		
63113-44-0	**24**	140	18	Freon 113		6				1		40	

[a] Corrected for recovered azide.

fonylnitrene by the sulfur atom rather than by participation of the latter in the nitrogen elimination.[5]

C. Decomposition of Diphenyl Sulfone 2-Sulfonyl Azide (1c). In order to prevent this nucleophilic attack by sulfur on nitrogen, the decomposition of **1c** was studied. In this case, again no seven-membered ring product was detected. Thermolysis in *n*-dodecane at 150 °C gave diphenyl sulfone (**13**) (27%) and diphenyl sulfone 2-sulfonamide (**14**) (9%), both identical with authentic samples. Decomposition in Freon E-4 at 160 °C gave dibenzothiophene 5,5-dioxide (**15**) and **14**, both in very low yields. Much tar was formed. While the hydrogen-abstraction product (**14**) probably arises from the triplet nitrene we propose that both **13** and **15** are formed from the corresponding aryl radical **16**. Evidence for the formation of



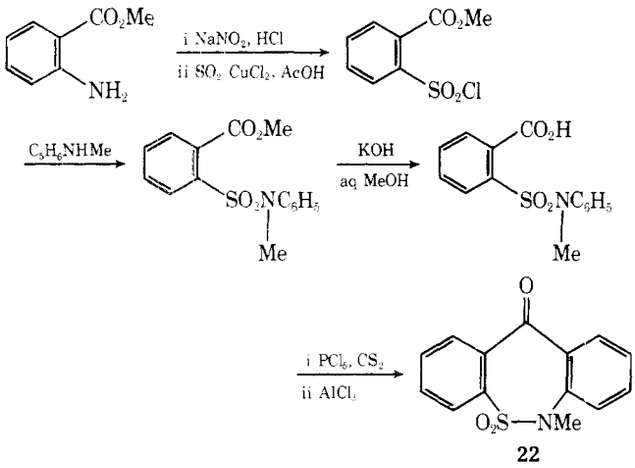
alkyl and aryl radicals in the thermolysis of some sulfonyl azides has been summarized.[6] For example, it has been shown that a small amount of *n*-pentane was formed in the decomposition of *n*-pentanesulfonyl azide in mineral oil and that aromatic sulfonyl azides can undergo free-radical thermal decomposition if a source of radicals is provided.[2,5,7] Diphenyl sulfone (**13**) would result from **16** by hydrogen abstraction from solvent, while in Freon E-4 where hydrogen atoms are not available Pschorr-type cyclization occurs to give **15**. That no seven-membered ring product is formed from **1c** might be due to a rapid intersystem crossing of singlet to triplet nitrene in this instance, or to an unfavorable geometry imposed by the relatively large SO_2 bridging group. The ease of Pschorr-type cyclizations in related systems has similarly been attributed to the internuclear separation between the rings involved as determined by the nature of the bridging group.[8]

A similar attempt to effect the cyclization of *N*-acetyldi-*p*-tolylamine 2-sulfonyl azide (**1d**) in dodecane did not yield any of the desired product; only the thermally unstable solvent insertion products were isolated. The results of the thermolyses of azides **1a–d** are summarized in Table I.

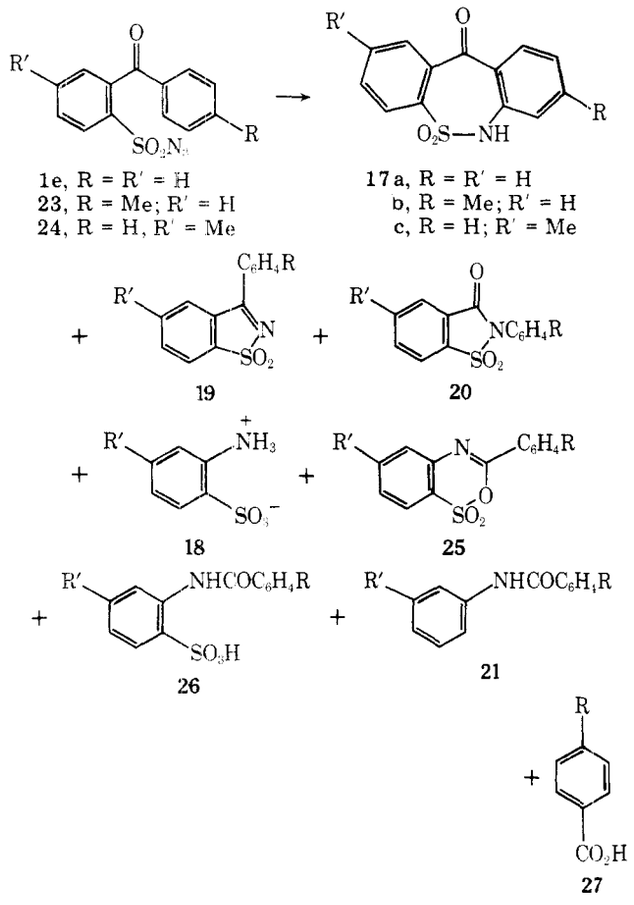
D. Decomposition of 2-Azidosulfonylbenzophenones. The decomposition of 2-azidosulfonylbenzophenone (**1e**) was much more productive. A low yield of the desired sultam **17a** was obtained (3.5%) together with some orthanilic acid (**18a**) (15%) and small amounts of 3-phenylbenzisothiazole 1,1-dioxide (**19a**), 2-phenylbenzisothiazolin-3-one 1,1-dioxide (**20a**), and benzanilide (**21**). The structure of the sultam **17a** was supported by its infrared spectrum (ν_{NH} 3200, $\nu_{C=O}$ 1640, ν_{SO_2} 1350, 1180 cm^{-1}) and by the synthesis of an authentic sample of its *N*-methyl derivative **22** from methyl anthranilate (Scheme I). Sultam **22** was identical with the product obtained on methylation of **17a** with sodium hydride and dimethyl sulfate. The benzisothiazole **19a** was identical with an authentic sample.[9] The isothiazolinone **20a** [IR 1730 (CO), 1335, 1185 cm^{-1} (SO_2)] could be synthesized from the *N*,2-dilithio derivative of benzenesulfonanilide by carbonation.[10]

In order to determine whether or not any rearrangements via a spiro intermediate[11] had occurred and to throw light on the formation of **21a**, the decompositions of 4′-methylbenzophenone-2-sulfonyl azide (**23**) and 5-methylbenzophenone-2-sulfonyl azide (**24**) were investigated. The results are summarized in Table II, and the nature of the products obtained is outlined in Scheme II. The sultam **17b** from the decomposition of **23** was *N*-ethylated to give **28**. If a rearrangement via a spiro intermediate in the cyclization step had occurred (Scheme III) then sultam **29** could have resulted. The *N*-ethyl derivative of the latter was prepared as described in Scheme I except that *N*-ethyl-*p*-toluidine was used in lieu of *N*-methylaniline. The product obtained was different from

Scheme I



Scheme II

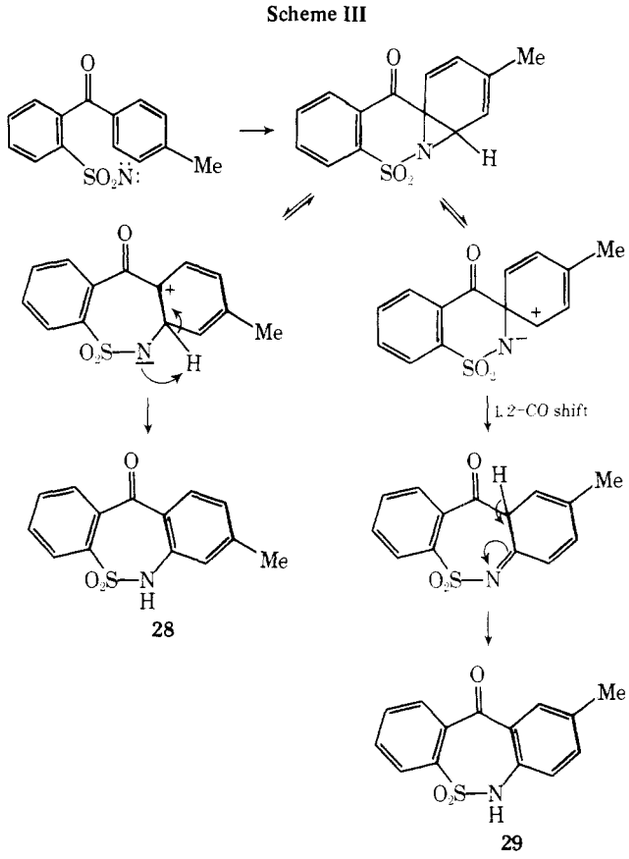


that formed on *N*-ethylation of **23**, showing that no rearrangement had occurred.

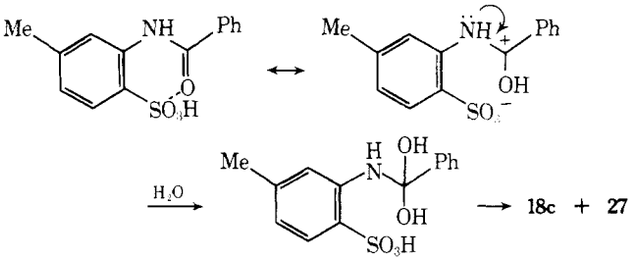
3-*p*-Tolylbenzisothiazole 1,1-dioxide (**19b**) was prepared either from saccharin and *p*-tolylmagnesium bromide[9] or from ammonium 4'-methylbenzophenone-2-sulfonic acid (synthesized from *o*-sulfobenzoic anhydride and toluene with aluminum chloride; only one product isolated) and $SOCl_2$ or PCl_5, and was identical with the product obtained from the azide. Authentic **20b** was prepared from *o*-sulfobenzoic anhydride and *p*-toluidine and then $SOCl_2$ as described,[12] while **20c** was made analogously to **20a**.

The thermolysis of 5-methylbenzophenone-2-sulfonyl azide (**24**) was studied to determine the origin of **18, 21,** and **26.** It gave some 2-benzamido-4-methylbenzenesulfonic acid (**26**) as the major product, identical with an authentic sample. This

Scheme III



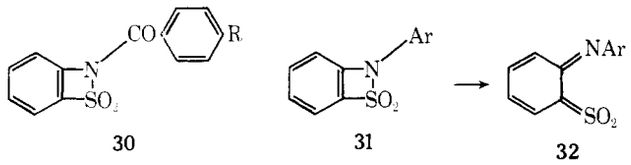
underwent hydrolysis with remarkable ease: for example, attempted recrystallization from 95% ethanol gave 4-methylorthanilic acid (**18c**). Thus, the orthanilic acids obtained in those reactions arise from **26.** This ease of hydrolysis is to be contrasted, say, with the hydrolysis of *N,N*-dicyclohexylbenzanilide-2-carboxamide in 1 M sulfuric acid at 80 °C for 6 h, which gave 2-benzamidobenzoic acid,[13] indicating the stability of the latter *o*-carboxyamide under these much more drastic conditions. It seems likely that intramolecular acid catalysis is responsible for the facile hydrolysis of **26c.** Support for this comes from the observation of a broad carbonyl stretching band at 1615 cm^{-1}, indicating strong hydrogen bonding between the sulfonic acid and the ortho amide group.



A small amount of *N*-benzoyl-*m*-toluidide (**21,** R = H; R' = Me) was also isolated in the thermolyses. Formation of these products indicates that the amino group occupies the position originally bearing the carbonyl group ortho to the sulfonyl azide function. The usual small yield (6%) of seven-membered sultam **17c** was also obtained.

In the thermolysis of 4'-methylbenzophenone-2-sulfonyl azide (**23**) at 140 °C in Freon 113, the main product (33%) obtained on careful workup was 3-(*p*-tolyl)benzo[*c*][2,1,4]-oxathiazine 1,1-dioxide (**25,** R' = H). It exhibited a band at 1633 cm^{-1} consistent with an imidate C=N group,[14] and bands at 1360 and 1190 cm^{-1} (SO_2). It underwent solvolysis

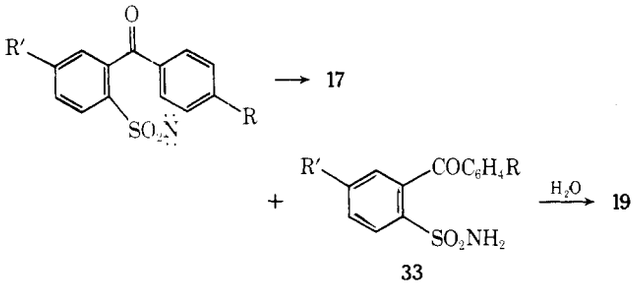
in ethanol readily to give orthanilic acid and ethyl *p*-methylbenzoate. An alternate structure considered for this product could be that of a β-sultam (**30**, R = CH_3). Some β-sultams (**31**) similar to **30** have been postulated, but only one has been



30 **31** **32**

characterized.[15] They are reported to cleave easily to the sulfene **32** and only when Ar is bulky can **31** be isolated. If, therefore, **30** were initially formed it would most likely rearrange to **25** (R′ = H) via the sulfene corresponding to **32.** Formation of **30** would, however, probably require insertion of a sulfonylnitrene into a position ortho to it and this has never been observed. Also, the frequency of the band observed at 1633 cm^{-1} is somewhat lower than that observed for a tertiary aromatic amide, particularly when it is considered that the electron-withdrawing SO_2 group on nitrogen is expected to raise the C=O stretching frequency by destabilizing the contributing structure $-SO_2N^+=C(-O^-)Ar$.

Assuming then that the compound has structure **25,** it is possible to explain the array of products formed in these reactions by postulating two competing processes. Thermolysis with loss of nitrogen to give the sulfonylnitrene would account for the intramolecular cyclization products **17** and the 3-arylbenzisothiazole 1,1-dioxides (**19**); the latter arising by dehydration of the hydrogen abstraction products (**33**).[10] It is



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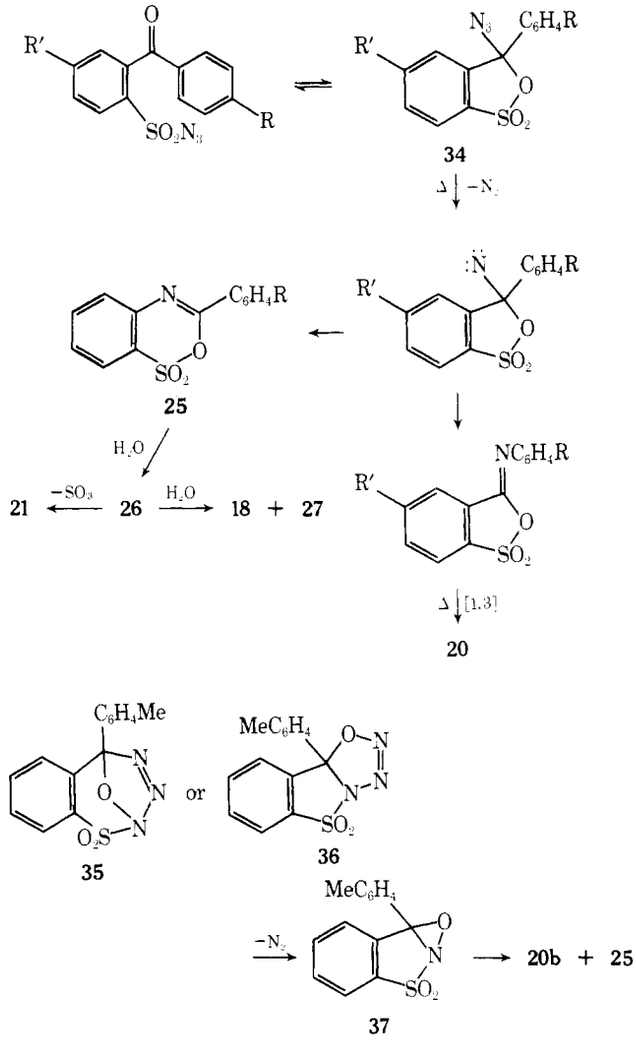
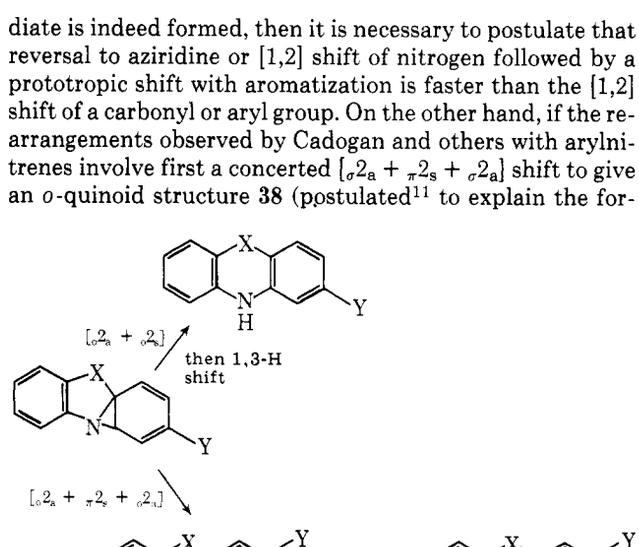
suggested that the other products arise by ring–chain tautomerization of some undecomposed sulfonyl azide (**1c, 23, 24**) to 3-aryl-3-azidobenzo[*d*][2,1]oxathioles (**34**). Decomposition of the latter to the alkylnitrene and 1,2-aryl shifts would give the observed products (Scheme IV), though a concerted nitrogen elimination aryl shift cannot be discounted.[16] Other mechanisms for the formation of the products are possible (e.g., 1,3-dipolar cycloaddition of the azide to the carbonyl group[17,18] to give **35** or **36** which, following cheletropic nitrogen elimination, would yield the oxaziridine **36** and thence on to the observed product[19]), but are considered less likely since they would predict the product ratios to be inverted.

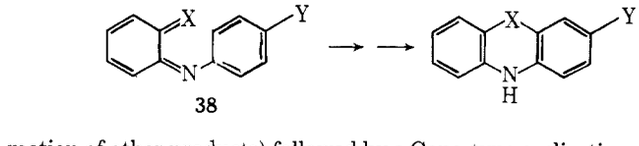
Ring–chain tautomerism analogous to that proposed in Scheme IV has been reported often. Some examples include the tautomerization of *o*-benzoylbenzamide to aminophenylbenzo[*c*]oxoline,[20] of *o*-formylbenzoyl chloride to 3-chlorophthalide,[21] of *o*-formylbenzenesulfonyl chloride to 3-chlorobenzoxathiazoline,[22] of *o*-formylbenzenesulfonic acid to 3-hydroxybenzoxathiole,[23] and of benzophenone-2-sulfonamides to 3-hydroxy-3-phenyl-2,3-dihydrobenzisothiazole 1,1-dioxide.[24]

The fact that no rearrangement was observed in the intramolecular cyclization here or in that of 4′-bromobiphenyl-2-sulfonyl azide[2] deserves some comment. Had spiro intermediates been involved in the formation of the final sultams then one might have expected to observe at least some rearranged products, which was not the case. If a spiro intermediate is indeed formed, then it is necessary to postulate that reversal to aziridine or [1,2] shift of nitrogen followed by a prototropic shift with aromatization is faster than the [1,2] shift of a carbonyl or aryl group. On the other hand, if the rearrangements observed by Cadogan and others with arylnitrenes involve first a concerted $[_\sigma2_a + _\pi2_s + _\sigma2_a]$ shift to give an *o*-quinoid structure **38** (postulated[11] to explain the formation of other products) followed by a Cope-type cyclization, then the absence of rearrangements in the cases now under consideration is understandable, since concerted electrocyclic ring opening to an *o*-quinoid system is not possible in **39** and **40,** and the only option available is ring opening to the unrearranged products.

Scheme IV







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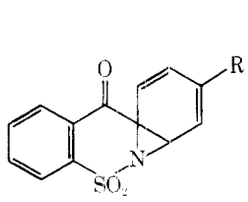
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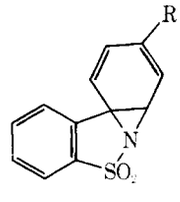
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Experimental Section

2-Phenoxybenzenesulfonyl Azide (1a). Sodium azide (3.25 g) in water (25 mL) was added to a stirred solution of 2-phenoxybenzenesulfonyl chloride (13.4 g) in acetone (125 mL) and the solution was stirred at room temperature for a further 27 h. It was evaporated in vacuo to about one-third of its volume and water (500 mL) was added. The precipitate (10.9 g, 79%) was filtered, washed with water (2 × 30 mL), and dried and had: mp 79–79.5 °C (from aqueous EtOH); IR (KBr) 2130, 1360, 1168 cm^{-1}.

Anal. Calcd for $C_{12}H_9N_3O_3S$: C, 52.35; H, 3.30; N, 15.26. Found: C, 52.26; H, 3.46; N, 15.41.

Thermolysis of 2-Phenoxybenzenesulfonyl Azide. A. In *n*-Dodecane. A suspension of the azide (4.125 g) in *n*-dodecane (25 mL) was heated with stirring at 130–135 °C for 30 h. The mixture was cooled to room temperature, the dodecane solution was decanted onto a column of neutral alumina (150 g) and the black tarry residue was extracted with boiling methanol (4 × 25 mL), and the extracts were evaporated, concentrated to 2 mL, and added to the alumina column. Elution with light petroleum gave *n*-dodecane. Elution with ether gave an almost colorless gum (0.972 g) which was distilled (some decomposition) to give slightly impure ***N*-dodecyl-2-phenoxybenzenesulfonamide (2)** as a yellow viscous liquid (0.696 g, 11%): bp 208 °C (0.2 mm); IR 3300, 1340, 1165 cm^{-1}; NMR (CCl_4) δ 7.90–6.66 (m, ArH), 4.88 (d, 1, NH, exchangeable), 3.20 (m, 1, CH), 1.40–0.70 (m, 24); mass spectrum *m/e* 417 ($M^{+\cdot}$) (calcd for $C_{24}H_{35}NO_3S$: $M^{+\cdot}$ 417). Elution with ether–methanol (95:5 v/v) gave **2-phenoxybenzenesulfonamide (3)** (0.134 g, 4%) [mp 113–114 °C (from benzene–light petroleum); IR (KBr) 3340, 3240, 1335, 1165 cm^{-1}] identical with an authentic sample prepared (76%) from sulfonyl chloride and ammonium hydroxide at room temperature.

Anal. Calcd for $C_{12}H_{11}NO_3S$: C, 57.84; H, 4.42; N, 5.62. Found: C, 57.72; H, 4.40; N, 5.59.

Elution with methanol gave a brown gum which, on crystallization from benzene, gave **6*H*-dibenzo[*b,f*][1,4,5]oxathiazepine 5,5-dioxide (4)** (0.571 g, 15%): mp 142–144 °C (aqueous EtOH); λ_{max} 279 mm; IR (KBr) 3180, 1335, 1172 cm^{-1}; mass spectrum *m/e* 247 ($M^{+\cdot}$).

Anal. Calcd for $C_{12}H_9NO_3S$: C, 58.29; H, 3.67; N, 5.67. Found: C, 58.32; H, 3.66; N, 5.75.

B. In Absence of Solvent. The azide (0.70 g) was heated at 165 °C for 12 h. The tarry products were chromatographed on a column of neutral alumina (30 g). Elution with light petroleum (bp 40–60 °C) gave 2-phenoxybenzenesulfonamide (0.19 g, 59.5% based on 2 mol of azide/mol of amide): mp 113–114 °C. Elution with methanol gave 6*H*-dibenzo[*b,f*][1,4,5]oxathiazepine 5,5-dioxide (0.24 g, 37.9%): mp 136–139 °C.

Diphenyl Sulfide 2-Sulfonyl Chloride (5). To a solution of 2-aminodiphenyl sulfide (20.1 g) in glacial acetic acid (140 mL) and concentrated HCl (44 mL) at 0 °C was added a solution of sodium nitrite (8.0 g) in water (20 mL) at 0 °C. The diazonium salt solution of SO_2 in glacial acetic acid (61 mL), ether (61 mL), and cupric chloride (5.0 g) was stirred at room temperature for 22 h. The solution was poured into ice-cold water (1500 mL) and the resulting yellow-orange solid was collected, washed with ice cold water (3 × 60 mL), and dried to give the sulfonyl chloride (17.4 g, 61%): mp 54–54 °C (lit.[25] mp 53–55 °C).

If benzene was used in the above reaction instead of ether and the reaction mixture was warmed at 40 °C for 30 h instead of being kept at room temperature for 22 h an oil mixed with needle-shaped crystals was obtained on pouring the mixture into water. The crystals (6 g) could be separated by taking advantage of their slight solubility in acetone. Recrystallization from benzene–methanol (1:1 v/v) gave **2-phenyl thiodiphenyl sulfone (6):** mp 123.5–125.5 °C; IR (KBr) 1445 (s), 1075 cm^{-1} (m); mass spectrum *m/e* 326 ($M^{+\cdot}$).

Anal. Calcd for $C_{18}H_{14}O_2S_2$: C, 66.27; H, 4.29. Found: C, 66.50; H, 4.42.

Diphenyl Sulfide 2-Sulfonyl Azide (1b). Sodium azide (0.65 g) in water (5.0 mL) was added to a stirred solution of diphenyl sulfide 2-sulfonyl chloride (2.85 g) in acetone (25 mL) at room temperature and stirring was continued for 46 h. The mixture was concentrated with ether (3 × 25 mL), the combined extracts were dried (Na_2SO_4), and the solvent was evaporated to give the azide (2.91 g, 100%) which, on attempted distillation, decomposed; IR (film) 2130 (s) (N_3), 1360, 1165 (s) cm^{-1} (SO_2).

Thermolysis of Diphenyl Sulfide 2-Sulfonyl Azide. A. In *n*-Dodecane. An emulsion of the azide (2.91 g) in *n*-dodecane (25 mL) was heated with stirring at 150 °C for 61 h. The mixture was cooled, the dodecane was decanted onto a column of neutral alumina (140 g), and the residual black tar was extracted with boiling MeOH (4 × 25 mL). The combined extracts were concentrated to 2 mL and added to the above alumina column. Elution with light petroleum gave *n*-dodecane. Elution with ether–light petroleum (1:1 v/v) gave a mixture of ***N*-dodecyldiphenyl sulfide 2-sulfonamides (7)** (0.397 g) as a yellow gum: IR (film) 3300, 3060, 2950, 2920, 2850, 1320, 1175 cm^{-1}; NMR ($CDCl_3$) δ 8–6.90 (m, 9, ArH), 5.55 (m, 1, exchangeable, NH), 3.18 (m, 1, CH), 1.40–0.7 (m, 24); mass spectrum *m/e* 433 ($M^{+\cdot}$). Elution with ether–methanol (19:1 v/v) gave a yellow gum (0.875 g) which crystallized from ethanol–light petroleum to give **diphenyl sulfide 2-sulfonamide (8)** (0.504 g, 19%) [mp 111–112 °C; IR (KBr) 3380, 3270, 1340, 1170 cm^{-1}] identical with a sample prepared (76% yield) from the sulfonyl chloride and ammonia.

Anal. Calcd for $C_{12}H_{11}NO_2S_2$: C, 54.34; H, 4.15. Found: C, 54.60; H, 4.20.

Further elution with the same solvent gave a yellow gum (0.176 g) which crystallized from ethanol to give **diphenyl sulfoxide 2-sulfonamide (9)** (0.101 g, 4%): mp 155.5–156.5 °C; IR (KBr) 3310, 3170, 1360, 1184 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}NO_3S_2$: C, 51.25; H, 3.91. Found: C, 51.10; H, 4.00.

Continued elution with ether–methanol gave a yellow gum (0.558 g) which crystallized from ethanol to give **3-phenylbenzo[1,3,2]-dithiazolium ylide 1,1-dioxide (10)** (0.274 g, 10%): mp 191–193 °C; IR (KBr) 1293 (s), 1160 cm^{-1} (s); λ_{max} (95% EtOH) 277.5, 270, 265, 230 nm (ε 4632, 3242, 3367, 14690); mass spectrum *m/e* 263 ($M^{+\cdot}$).

Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.71; H, 3.45. Found: C, 54.79; H, 3.78.

B. In the Absence of Solvent. The azide (3.0 g) was heated under dry nitrogen at 160–170 °C for 3 h. The dark product was chromatographed on a column of neutral alumina (90 g). Elution with benzene gave 3-phenylbenzo[1,3,2]dithiazolium ylide 1,1-dioxide (0.75 g, 27%) (mp 191–193 °C) identical with the sample obtained above and with an authentic sample (vide infra). Elution with methanol gave diphenyl sulfide 2-sulfonamide (0.36 g, 26%), identical with the product obtained above.

3-Phenylbenzo[1,3,2]dithiazolium Ylide 1,1-Dioxide (10). A. To a stirred solution of diphenyl sulfide 2-sulfonamide (1.325 g) in methanol (6 mL) and water (2 mL) was slowly added a solution of bromine (0.80 g) in methanol (2 mL) at room temperature. The solution was stirred for a further 20 min and poured into water (75 mL). The precipitated solid was filtered, washed with water, dried, and recrystallized from ethanol to give the ylide (1.034 g, 79%): mp 189–192 °C, undepressed on admixture with the above sample. The same product was obtained (69%; mp 191–192 °C) when the sulfonamide in 5 N NaOH was treated at 0 °C with a solution of bromine in methanol.

B. Bromine (0.80 g) in $CHCl_3$ (5 mL) was added slowly to a stirred solution of the sulfonamide (1.325 g) in $CHCl_3$ (15 mL) and the mixture was stirred at room temperature for 75 h. The solution was washed with water (2 × 20 mL), dried (Na_2SO_4), and evaporated to give an orange-red gum (1.71 g) which was chromatographed on a column of neutral alumina. Elution with ether gave a colorless gum (1.58 g) which crystallized from benzene to give what appears to be a mixture of 2- and 4-bromodiphenyl sulfide 2′-sulfonamide (11) [mp 91–94 °C; IR (KBr) 3420, 3360, 3290, 3250, 1330, 1175, 1170 cm^{-1}; mass spectrum *m/e* ($M^{+\cdot}$, ^{81}Br), 343 ($M^{+\cdot}$, ^{79}Br)] which could not be resolved.

Diphenyl Sulfoxide 2-Sulfonamide (9). A. 3-Phenylbenzo[1,3,2]dithiazolium ylide 1,1-dioxide (0.526 g) in ethanol (25 mL) and 20% aqueous NaOH (25 mL) was boiled under reflux for 13 h. The mixture was cooled, water (100 mL) was added, and the solution was acidified with concentrated HCl and kept at room temperature overnight. The solid was collected, washed with water (3 × 15 mL), dried, and recrystallized from ethanol to give the sulfoxide (0.313 g, 56%) (mp 155–157 °C) identical with the product obtained from the sulfonyl azide thermolysis.

B. The ylide (0.526 g) in the minimum volume of $CHCl_3$ was chromatographed on a column of neutral alumina (150 g). The column was eluted with light petroleum and then allowed to stand for 3 days. Elution with ether–methanol (19:1 v/v) gave unchanged ylide (0.266

g): mp 191.5–193 °C. Elution with MeOH gave the sulfoxide (0.139 g, 26%) [mp 155–156 °C (EtOH)], identical with the above sample.

Diphenyl Sulfone 2-Sulfonamide (14). Diphenyl sulfoxide 2-sulfonamide (**9**) (0.281 g) in glacial acetic acid (2.0 mL) and 30% hydrogen peroxide (1.0 mL) was heated at 100 °C for 21 h. The cooled solution was poured into water (50 mL) and the solid which precipitated was recrystallized from ethanol to give **diphenyl sulfone 2-sulfonamide** (0.151 g, 51%) (mp 162–163 °C) identical with a sample prepared from the sulfonyl chloride (see below) and ammonia: IR (KBr) 3360, 3270, 1345, 1145 cm^{-1}.

Anal. Calcd for $C_{12}H_{11}NO_4S_2$: C, 48.48; H, 3.70. Found: C, 48.61; H, 3.82.

Diphenyl Sulfide 2-*N,N*-Dimethylsulfonamide (12). A. 3-Phenylbenzo[1.3,2]dithiazolium ylide 1,1-dioxide (**10**) (0.5 g) in absolute ethanol (5 mL) containing saturated aqueous KOH (15 mL) was stirred at 60 °C as dimethyl sulfate (6 mL) was added dropwise. The mixture was then boiled under reflux for 6 h, cooled, and diluted with water until the white precipitate formed initially almost completely dissolved. The mixture was kept overnight and the **diphenyl sulfide 2-*N,N*-dimethylsulfonamide** which separated was recrystallized from a benzene–hexane mixture (1:4 v/v) (0.48 g, 81.7%): mp 118–119 °C; mass spectrum *m/e* 309 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{15}NO_2S_2$: C, 54.33; H, 4.89; N, 4.53. Found: C, 54.38; H, 4.70; N, 4.47.

B. To a solution of diphenyl sulfide 2-sulfonamide (0.56 g) in EtOH (5 mL) containing 20% aqueous NaOH (15 mL) was added slowly with shaking dimethyl sulfate (6 mL) and the solution was boiled under reflux for 13 h. Workup as above gave the *N,N*-dimethyl derivative (0.34 g, 55%): mp 121–122 °C.

Diphenyl Sulfone 2-*N,N*-Dimethylsulfonamide. The sulfoxide (0.31 g) in glacial acetic acid (2.0 mL) and 30% H_2O_2 (1.0 mL) was heated at 100 °C for 17.5 h. The mixture was cooled and poured into water (50 mL). The precipitated solid was filtered, washed with water (3 × 10 mL), and recrystallized from benzene–light petroleum to give the sulfone (0.20 g, 63%) [mp 148–149 °C (EtOH)] identical with a sample prepared (55%) from the sulfonyl chloride and dimethylamine: IR (KBr) 1320, 1310, 1170, 1160 cm^{-1}.

Anal. Calcd for $C_{14}H_{15}NO_4S_2$: C, 51.69; H, 4.62. Found: C, 15.91; H, 4.61.

Diphenyl Sulfone 2-Sulfonyl Chloride. A solution of 2-aminodiphenyl sulfone[26] (2.33 g) in glacial acetic acid (7.0 mL) and concentrated HCl (2.2 mL) at 0 °C was treated with sodium nitrite (0.8 g) in water (2.0 mL). The diazonium salt solution was poured into an ice cold mixture of a saturated solution of SO_2 in glacial acetic acid (6.1 mL), benzene (6.1 mL), and cupric chloride (0.5 g), and the mixture was stirred at room temperature for 16 h. It was poured into water and the yellow solid which precipitated was filtered, washed with water, dried, and recrystallized from ethyl acetate–light petroleum to give the sulfonyl chloride (2.68 g, 85%): mp 137–138 °C; IR (KBr) 1370, 1310, 1150 cm^{-1}.

Anal. Calcd for $C_{12}H_9ClO_4S_2$: C, 45.50; H, 2.84. Found: C, 45.81; H, 2.90.

Diphenyl Sulfone 2-Sulfonyl Azide (1c). Sodium azide (1.30 g) in water (10 mL) was added to a stirred solution of diphenyl sulfone 2-sulfonyl chloride (8.31 g) in acetone (50 mL) at room temperature and stirring was continued for 16 h. The solution was concentrated in vacuo down to 15 mL to give the azide as an oil which solidified (6.34 g, 85%): mp 99.5–100 °C (ethanol–light petroleum); IR (KBr) 2150, 1340, 1205, 1180 cm^{-1}.

Anal. Calcd for $C_{12}H_9N_3O_4S_2$: C, 44.56; H, 2.79. Found: C, 44.62; H, 2.91.

Thermolysis of Diphenyl Sulfone 2-Sulfonyl Azide. A. In *n*-Dodecane. A suspension of diphenyl sulfone 2-sulfonyl azide (1.615 g) in *n*-dodecane (25 mL) was heated with stirring at 150 °C for 16 h. The reaction mixture was cooled and worked up as in the above cases. Elution of the alumina column with light petroleum gave first *n*-dodecane and then diphenyl sulfone (**13**) (0.297 g, 27%) (mp 125 °C) identical (mixture melting point and infrared spectrum) with an authentic sample. Elution with MeOH gave a dark brown gum (0.381 g) which was extracted with benzene (10 mL), filtered, and concentrated down to ~1 mL to give diphenyl sulfone 2-sulfonamide (**14**) (0.138 g, 9%) (mp 159–160 °C) identical with an authentic sample.

When this thermolysis was repeated but in the presence of sulfur (0.128 g), diphenyl sulfone (0.203 g, 19%) and diphenyl sulfone 2-sulfonamide (0.287 g, 19%) were isolated.

B. In Freon E-4. A suspension of the azide (0.969 g) in Freon E-4 (15 mL) was heated with stirring at 160 °C for 18 h. The cooled mixture was worked up as usual. Elution of the column with ether gave a brown gum (0.062 g) which gave dibenzothiophene *S,S*-dioxide (**15**) as colorless needles (0.002 g) [mp 232–233 °C from EtOH; IR (KBr) 1295, 1170, 1160 cm^{-1}] identical with an authentic sample.[27] Elution with methanol gave diphenyl sulfone 2-sulfonamide (**14**) (0.002 g), identical with an authentic sample.

***N*-Acetyldi-*p*-tolylamine 2-Sulfonyl Chloride.** *N*-Acetyldi-*p*-tolylamine (1 g) (mp 84–85 °C) was dissolved in $CHCl_3$ (5 mL) and the solution cooled in ice. Chlorosulfonic acid (5 mL) was added dropwise with stirring and the solution was kept at room temperature for 1 h. It was then poured onto crushed ice and the $CHCl_3$ layer was separated, washed with cold water, dried ($MgSO_4$), and evaporated to give the sulfonyl chloride (1.09 g, 77.2%): mp 133.5–134.5 °C (from light petroleum containing a few drops of $CHCl_3$); IR (KBr) 1665 (s), 1365 (s), 1170 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{16}ClNO_3S$: C, 56.85; H, 4.78. Found: C, 56.43; H, 4.84.

***N*-Acetyldi-*p*-tolylamine 2-Sulfonyl Azide (1d).** The sulfonyl chloride (0.14 g) in acetone (20 mL) was treated at 0 °C with a solution of sodium azide (0.5 g) in the minimum amount of water. After stirring the solution at 0 °C for 1 h it was diluted with water (200 mL) and the precipitated azide (0.13 g, 91.1%) was recrystallized from *n*-hexane to give colorless crystals: mp 94–95 °C; IR (KBr) 2118 (s), 1670 (s), 1170 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{16}N_4O_3S$: C, 55.77; H, 4.69. Found: C, 55.79; H, 4.93.

Thermolysis of *N*-Acetyldi-*p*-tolylamine 2-Sulfonyl Azide in *n*-Dodecane. The azide (1.0 g) in degassed *n*-dodecane (10 mL) was heated at 160–170 °C for 6 h with stirring. Workup as usual and chromatography on neutral alumina gave, on elution with light petroleum (bp 40–60 °C), a mixture of the ***N*-acetyldi-*p*-tolylamine *N'*-dodecyl-2-sulfonamides** as a brown oil (0.3 g) which could not be crystallized or distilled without decomposition: IR (film) 3280 (NH), 1650 (CO), 1315, 1150 cm^{-1} (SO_2); mass spectrum *m/e* (rel intensity) 486 ($M^{+\cdot}$, 8), 239 ($M^{+\cdot} - SO_2NHC_{12}H_{25}$, 36), 197 ($C_{14}H_{15}N^+$, 100).

Benzophenone-2-sulfonyl Azide (1e). This was prepared (0.4 g, 70%) from the sulfonyl chloride[28] (0.6 g) in acetone (25 mL) with sodium azide (1 g) in water (6 mL): mp 120–121 °C (hexane); IR (KBr) 2140, 1660, 1375, 1190 cm^{-1}.

Anal. Calcd for $C_{13}H_9N_3O_3S$: C, 54.35; H, 3.16; N, 14.63. Found: C, 54.28; H, 3.32; N, 14.89.

Thermolysis of Benzophenone-2-sulfonyl Azide. A. In Chlorobenzene. The azide (1 g) in chlorobenzene (50 mL) was heated at 150 °C for 2 days. The black residue on evaporation of the solvent was resolved by preparative TLC (silica gel, benzene developer) to give: (i) 3-phenylbenzoisothiazole 1,1-dioxide (**19**, R = R' = H) (19 mg, 2%) [mp 167 °C, mass spectrum *m/e* 243 ($M^{+\cdot}$)] identical (mmp and IR) with an authentic sample;[9] (ii) benzanilide (**21**, R = R' = H) (30 mg, 4%) (mp 160–161 °C) identical with an authentic sample; (iii) **11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (17a)** (60 mg, 7%) [mp 214–215 °C; IR (KBr) 3200, 1635, 1345, 1290, 1180 cm^{-1}; mass spectrum *m/e* 259 ($M^{+\cdot}$)].

Anal. Calcd for $C_{13}H_9NO_3S$: C, 60.22; H. 3.50. Found: C, 60.12; H, 3.50.

This (20 mg) was treated with sodium hydride (10 mg) in THF (1 mL) and dimethyl sulfate (0.3 mL) was added. After 12 h at room temperature the mixture was filtered and the solvent was evaporated to give 6-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (**22**) (20 mg, 90%) [mp 159–160 °C (absolute EtOH)] identical with authentic material (vide infra).

B. In Freon 133 at 100 °C. The azide (1.0 g) in Freon 113 (50 mL) was heated for 5 days at 100 °C in a sealed tube. The solvent was evaporated and ethanol (10 mL) was added to precipitate orthanilic acid (60 mg, 15%) (mp > 250 °C dec), identical (IR) with authentic material. The ethanol was evaporated and the residue was resolved by preparative TLC (silica gel, benzene developer) to give: (i) recovered azide (332 mg, 35%); (ii) 2-phenylbenzoisothiazolin-3-one 1,1-dioxide (4 mg, 1%) [mp 186–187 °C (EtOH); IR (KBr) 1735, 1725, 1340, 1300, 1185 cm^{-1}; mass spectrum *m/e* 259 ($M^{+\cdot}$)] identical with an authentic sample;[10] (iii) 3-phenylbenzoisothiazole 1,1-dioxide (5 mg, 1%) (mp 165–167 °C) identical with an authentic sample; (iv) 11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (32 mg, 3.5%) (mp 213–214 °C); (v) benzanilide (7 mg, 1%) (mp 160°161 °C).

C. In Freon 113 at 140 °C. Thermolysis of the azide (2.0 g) in Freon 113 at 140 °C for 2 days gave: (i) 2-phenylbenzoisothiazolin-3-one 1,1-dioxide (**20**) (14 mg, 1%); (ii) 3-phenylbenzoisothiazole 1,1-dioxide (40 mg, 2%); (iii) 11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (54 mg, 3%).

D. In Absolute Ethanol. The azide (0.8 g) in absolute ethanol (50 mL) was heated at 100 °C for 5 days to give recovered azide (0.39 g, 40%), 3-phenylbenzoisothiazole 1,1-dioxide (82 mg, 20%), and 11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (17 mg, 3%).

Methyl Benzoate 2-*N*-Methylsulfonanilide. Methyl benzoate 2-sulfonyl chloride[29] (11 g) and *N*-methylaniline (5 mL) in pyridine (16 mL) were kept at room temperature for 30 min and water (50 mL) was then added. The precipitate was filtered and washed with 3% HCl (50 mL) and then with water (3 × 50 mL) to give the anilide (12.2 g, 90%): mp 93–94 °C (MeOH); IR (KBr) 1720, 1340, 1170 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 9), 3.8 (s, 3, OCH_3), 3.3 (s, 3, NCH_3); mass spectrum *m/e* 305 ($M^{+\cdot}$).

Anal. Calcd for $C_{15}H_{15}NO_4S$: C, 59.00; H, 4.95. Found: C, 58.98; H, 4.95.

6-Methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-Dioxide (22). The above anilide (12.1 g) was saponified with 30% aqueous methanolic (130 mL) KOH (4.6 g). After 3 h at 40 °C the mixture became homogeneous. Concentration afforded a white solid, a portion (6.2 g) of which was treated with PCl_5 (5 g) in carbon disulfide (200 mL) at 50 °C for 1 h, and then with anhydrous aluminum chloride (3.5 g) in nitromethane (6 mL). Heating was continued for 1 h, the CS_2 was decanted, and the red residue was treated with ice water (50 mL). The organic material was extracted with methylene chloride (100 mL), washed with 5% aqueous KOH (2 × 25 mL) and water (2 × 25 mL), and dried ($MgSO_4$). Evaporation of the solvent gave the 6-methyl compound (2 g, 30%): mp 158–159 °C (absolute EtOH); IR (KBr) 1630, 1350, 1180 cm^{-1}; NMR ($CDCl_3$) δ 8.25 (m, 1, ortho to SO_2), 7.65 (m, 7), 3.36 (s, 3, CH_3); mass spectrum *m/e* 273 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06. Found: C, 61.53; H, 4.07.

4-Methylbenzophenone-2-sulfonic Acid. A. 2-Amino-4′-methylbenzophenone[30] (7.2 g) in acetic acid (20 mL) and concentrated HCl (10 mL) was treated with sodium nitrite (2.8 g) at 0 °C and the diazonium salt solution poured all at once into a cold saturated solution of SO_2 in acetic acid (30 mL) and benzene (70 mL) containing copper(II) chloride dihydrate (3 g). After 25 min at 25–30 °C (negative β-naphthol test) the dark green solution was poured into ice water (280 mL). The benzene layer was separated, the aqueous layer was extracted with ether (2 × 50 mL), and the combined organic layers were washed with water (3 × 50 mL), dried ($MgSO_4$), and concentrated to give an orange oil (10.1 g). This was treated with KOH (4 g) in water (100 mL) at 60 °C for 1 h. The aqueous phase was decanted and extracted with toluene (20 mL). Acidification and concentration of the water layer gave a semisolid which was treated with ethanol. The potassium chloride was filtered and the ethanol concentrated to give 4′-methylbenzophenone-2-sulfonic acid (5 g, 53%) as an oil: NMR (D_2O) δ 8.2 (dd, 1, ortho to SO_2), 7.5 (m, 7), 2.4 (s, 3, CH_3). The acid was treated with KOH (5 g) in water (20 mL) to give potassium 4′-methylbenzophenone-2-sulfonate (4 g, 50%): mp 249–253 °C (lit.[31] mp 248 °C).

The alkali insoluble residue from the above reaction (3.9 g) was triturated with EtOH to give **bis(4′-methyl-2-benzophenone) disulfide** (1.6 g, 21%): mp 160–162 °C (from CH_3CN); IR (KBr) 1640 cm^{-1}; mass spectrum *m/e* 227 ($M^{+\cdot}/2$); NMR ($CDCl_3$) δ 8.2 (m, 8), 2.4 (s, 3).

Anal. Calcd for $C_{28}H_{22}O_2S_2$: C, 73.97; H, 4.88. Found: C, 73.77; H, 4.95.

The ethanol filtrate gave **bis(4′-methyl-2-benzophenone) disulfide *S,S*-dioxide** (0.25 g, 3%): mp 115–116 °C (toluene); IR (KBr) 1650, 1320, 1280, 1265, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.5 (m, 17), 2.3 (d, 6, 2 CH_3).

Anal. Calcd for $C_{28}H_{22}O_6S_2$: C, 69.11; H, 4.55. Found: C, 69.18; H, 4.46.

B. Aluminum chloride (43 g) in nitromethane (43 mL) was added at room temperature to *o*-sulfobenzoic anhydride[32] (30 g) in toluene (500 mL). A precipitate formed immediately. After 2 h the supernatent liquid was decanted, cold ammonium hydroxide (100 mL) was added to the solid, and the mixture was filtered. The solid was washed with EtOH, the combined filtrates were evaporated, and the residual syrup was treated with KOH (30 g) in water (250 mL) at 40 °C for 1 h. On cooling, potassium 4′-methylbenzophenone-2-sulfonate separated as brownish crystals. Recrystallization from water (70 mL) gave pure sulfonate (30 g, 59%): mp 245–250 °C.

3-*p*-Tolylbenzoisothiazole 1,1-Dioxide (19, R = *p*-Me; R′ = H). A. Ammonium 4′-methylbenzophenone-2-sulfonate (5 g), prepared (syrup) as under B above, was heated with thionyl chloride (15 mL) in toluene (15 mL) at 100 °C for 7 h. Concentration of the solution afforded **3-*p*-tolylbenzoisothiazole 1,1-dioxide** (3.9 g, 61%): mp 179–180 °C (EtOH); IR (KBr) 1335, 1175 cm^{-1}; NMR (CF_3CO_2H) δ 7.9 (m, 6), 7.45 (d, 2, J = 8 Hz, half of an A_2B_2 quartet), 2.5 (s, 3, CH_3); mass spectrum *m/e* 257 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.34; H, 4.31. Found C, 65.24; H, 4.32.

B. To saccharin (1.8 g) in dry THF (200 mL) was added dropwise a THF solution of *p*-tolylmagnesium bromide [from *p*-bromotoluene (6.5 g) and magnesium (1.1 g) in THF (20 mL)]. After 2 days the solvent was evaporated and water was added to the residue. The mixture was filtered and solid was washed with water (25 mL) and then with ethanol–chloroform (1:1 v/v; 3 × 25 mL). Concentration of the organic filtrates gave the product (1 g, 50%): mp 179–180 °C (CH_3CO_2H).

C. 4′-Methylbenzophenone-2-sulfonyl chloride (2 g) in methanol (20 mL) was treated with ammonia for 2 h at room temperature. Evaporation of the methanol, washing the residue with water, and recrystallization from acetic acid gave the desired product (1 g, 60%): mp 179–180 °C.

4′-Methylbenzophenone-2-sulfonyl Azide (23). Potassium 4′-methylbenzophenone-2-sulfonate (33 g) and phosphorus pentachloride (28 g) were heated for 3 h at 100 °C, ice water was added, and the mixture was extracted with methylene chloride (50 mL). The organic layer was washed with water (2 × 20 mL), dried ($MgSO_4$), and treated with tetramethylguanidinium azide (19 g). After 6 h the solution was washed with water (2 × 20 mL), dried ($MgSO_4$), and evaporated to give an orange oil (23 g). This was chromatographed on a column of silica gel (25 × 250 mm) and eluted with toluene (400 mL) to give the azide as an oil which crystallized from ethanol (8.1 g, 25%): mp 72–73 °C; IR (KBr) 2140, 1665, 1360, 1170 cm^{-1}; NMR (CH_3OD) δ 8.1 (m, 1, ortho to SO_2), 7.7 (m, 7), 2.4 (s, CH_3); mass spectrum *m/e* 301 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}N_3O_3S$: C, 55.80; H, 3.68; N, 13.94. Found: C, 56.05; H, 3.78; N, 13.50.

Methyl Benzoate 2-[*N*-Ethyl-*N*-(*p*-tolyl)]sulfonamide. Triethylamine (7.4 g) and *N*-ethyltoluidine (10 g) were added to an ether (200 mL) solution of methyl benzoate 2-sulfonyl chloride (17.0 g). After 12 h, triethylamine hydrochloride (9.8 g, 95%) was filtered. The ether was evaporated and the residue was recrystallized at low temperature from MeOH to give the amide (18 g, 75%): mp 54–56 °C; IR (KBr) 1730, 1330, 1290, 1170, 1150 cm^{-1}; NMR ($CDCl_3$) δ 7.4 (br, s, 4), 7.06 (s, 4), 3.90 (s, 3, OCH_3), 3.74 (q, 2, J = 7 Hz, NCH_2), 2.33 (s, 3, CH_3), 1.08 (t, 3, J = 7 Hz, NCH_2CH_3); mass spectrum *m/e* 333 ($M^{+\cdot}$).

Anal. Calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74. Found: C, 61.27; H, 5.74.

***N*-Ethyl-*N*-*p*-tolylbenzenesulfonamide-2-carboxylic Acid.** The ester (4.8 g) in MeOH (10 mL) was saponified with NaOH (3.2 g) in water (171 mL) at 60 °C for 3 h. The solution was made just acidic with concentrated HCl and the oil which separated was extracted with $CHCl_3$. Evaporation gave the acid (3.0 g, 65%): mp 119–120 °C (CCl_4); IR (KBr) 2600 (br), 1720 (m), 1630 (br s), 1345 (s), 1150 cm^{-1} (s); NMR ($CDCl_3$) δ 11 (br s, 1, CO_2H), 7.5 (m, 4), 7.1 (s, 4), 3.7 (q, 2, J = 7 Hz, CH_2), 2.3 (s, 3, CH_3), 1.1 (t, 3, J = 7 Hz, CH_2CCH_3); mass spectrum *m/e* 319 ($M^{+\cdot}$).

Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.36. Found: C, 60.20; H, 5.33.

6-Ethyl-9-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-Dioxide. The above acid (1.0 g) and phosphorus pentachloride (0.91 g) in CS_2 (20 mL) were boiled under reflux for 1 h, and then anhydrous aluminum chloride (0.3 g) was added. After heating for 1 h more, the solvent was evaporated and concentrated HCl (1 mL) and water (30 mL) were added. The oil was extracted with methylene chloride (60 mL) and the extract was washed with water (2 × 20 mL), dried ($MgSO_4$), and evaporated to give an oil which, on treatment with methanol, gave the thiazepine dioxide (0.30 g, 32%): mp 154–155 °C (MeOH); IR (KBr) 1645, 1345, 1180 cm^{-1}; NMR ($CDCl_3$) δ 7.7 (m, 7), 3.7 (q, 2, J = 7 Hz, NCH_2), 2.3 (s, 3, CH_3), 0.99 (t, 3, J = 7 Hz, CH_2CH_3); mass spectrum *m/e* 301 ($M^{+\cdot}$).

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.75; H, 5.02. Found C, 63.78; H, 5.02.

Evaporation of the methanol mother liquors gave methyl benzoate 2-[*N*-ethyl-*N*-(*p*-tolyl)]sulfonamide (0.50 g, 48%).

Thermolysis of 4′-Methylbenzophenone-2-sulfonyl Azide (23). A. In Freon 113 at 100 °C. The azide (0.643 g) in Freon 113 (40 mL) was heated for 5 days at 100 °C in a sealed tube. The Freon was evaporated and chloroform was added to the black residue to precipitate orthanilic acid (73 mg, 35%) (mp >250 °C) identical (IR) with an authentic sample. The chloroform solution was added to the black residue to precipitate orthanilic acid (73 mg, 35%) (mp >250 °C) identical (IR) with an authentic sample. The chloroform solution was evaporated and the residual mixture was resolved by preparative TLC (silica gel, toluene developer) to give: (i) starting azide (0.278 g, 43%); (ii) 2-(*p*-tolyl)benzoisothiazolin-3-one 1,1-dioxide (**20**, R = *p*-Me; R′ = H) (10 mg, 3%) [mp 198–199 °C; IR (KBr) 1730, 1335, 1305, 1180; mass spectrum *m/e* 273 ($M^{+\cdot}$)] identical with an authentic sample;[12] (iii) 3-*p*-tolylbenzoisothiazole 1,1-dioxide (**19**) (7.5 mg, 2%) (mp 177–179 °C) identical with the sample prepared above; (iv) 4-

methylbenzanilide (**21**, R = Me; R′ = H) (3 mg, 2%) [mp 145 °C; IR (KBr) 3280, 1635 cm^{-1}; mass spectrum *m/e* 211 ($M^{+\cdot}$)] identical with an authentic sample; (v) **8-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]-thiazepine 5,5-dioxide (17b)** (19 mg, 5%) [mp 235–236 °C (toluene); IR (KBr) 3190, 1630, 1340, 1290, 1185, 1175 cm^{-1}; NMR (acetone-d_6) δ 7.95 (d, 1, ortho to SO_2), 7.75 (m, 5), 7.08 (m, 2), 4.7 (br s, 1, exchanges with D_2O, NH), 2.36 (s, 3, CH_3); mass spectrum *m/e* 273 ($M^{+\cdot}$)].

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06. Found: C, 61.53; H, 4.08.

The above sultam (25 g) in THF (1 mL) was treated with sodium hydride (10 mg) and then with diethyl sulfate (30 μL). After 12 h at room temperature the solution was filtered and evaporated to give **6-ethyl-8-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide** (21 mg, 90%) [mp 118–119 °C (toluene–hexane); IR (KBr) 1640, 1355, 1285, 1243, 1178 cm^{-1}; NMR ($CDCl_3$) δ 7.90 (m, 5), 7.24 (m, 2), 3.84 (q, 2, *J* = 7 Hz), 2.45 (s, 3, CH_3), 0.93 (t, 3, *J* = 7 Hz)]; this compound was different from the 6-ethyl-9-methyl derivative prepared above.

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.75; H, 5.02. Found: C, 63.79; H, 5.02.

(vi) *p*-Toluic acid (**27**, R = Me) (40 mg, 26%) (mp 176–178 °C) identical with an authentic sample.

B. In Freon 113 at 140 °C. Thermolysis of the azide (1.67 g) in Freon 113 (40 mL) at 140 °C for 10 h gave a precipitate of 3-(*p*-tolyl)benzo[*c*][2,1,4]oxathiazine 1,1-dioxide (**25**, R = Me; R′ = H) (0.430 g, 33%): mp 144–146 °C (from hexane); IR (KBr) 1633, 1360, 1190; mass spectrum *m/e* 273 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06. Found: C, 61.28; H, 4.21.

Treatment of this compound with ethanol gave orthanilic acid (**18**, R′ = H), identical with an authentic sample, and ethyl *p*-methylbenzoate [the latter was detected in the alcohol mother liquors by GLC on a column of 15% SE 30 on Chromosorb W at 152 °C, and identified by its infrared spectrum (identical with that of an authentic sample)].

The Freon filtrate was evaporated and resolved by TLC (silica gel; toluene developer) to give: (i) recovered sulfonyl azide (0.256 g, 15%); (ii) 2-*p*-tolylbenzoisothiazolin-3-one 1,1-dioxide (45 mg, 4%); (iii) 3-*p*-tolylbenzoisothiazole 1,1-dioxide (44 mg, 4%); (iv) 8-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (80 mg, 6%); (v) a trace of 4-methylbenzanilide.

Rechromatography of the material that had remained on the baseline using $CHCl_3$ as eluent gave an unidentified compound (40 mg): mp 182–183 °C (EtOH); IR (KBr) 3240, 1650, 1340, 1180 cm^{-1}; NMR ($CDCl_3$) δ 7.9 (m, 6), 7.3 (m, 2), 2.7 (s, 3); mass spectrum *m/e* 345 ($M^{+\cdot}$ + 4 for ^{35}Cl), 343 ($M^{+\cdot}$ + 2), 341 ($M^{+\cdot}$, ^{35}Cl) (in the abundance ratio 1.7:6.1:9.0; calcd for 2 Cl 1.0:6.0:9.0), 309, 307 (abundance ratio 1.2:3.0; calcd for 1 Cl 1.0:3.0).

Anal. Found: C, 55.54; H, 3.67.

2-Benzamido-4-methylbenzenesulfonic Acid. Sodium 2-amino-4-methylbenzenesulfonate [from 2-amino-4-methylbenzenesulfonic acid[33] (0.5 g) and an equivalent amount of aqueous NaOH followed by evaporation of the water] and benzoyl chloride (2 mL) were heated for 3 h at 100 °C and then for 30 min under reflux. The excess benzoyl chloride was distilled and the residue was extracted with hot acetonitrile. On cooling the benzamido derivative separated: mp 180–183 °C (from CH_3CN); IR (KBr) 1620, 1325, 1190, 1175 cm^{-1}; mass spectrum *m/e* 273 ($M^{+\cdot}$ − 18).

Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.71; H, 4.50. Found: C, 57.57; H, 4.49.

5-Methylbenzophenone-2-sulfonyl Chloride. 2-Amino-5-methylbenzophenone hydrochloride[34] (19 g) in acetic acid (30 mL) and concentrated HCl (25 mL) was diazotized with sodium nitrite (7 g) in water (10 mL) and then added to a cold saturated solution of SO_2 in benzene (90 mL) and acetic acid (90 mL) containing $CuCl_2$ (5 g). After 5 h at room temperature, the organic layer was separated, washed with water (5 × 50 mL), dried ($MgSO_4$), and evaporated to yield an oil (10.8 g). This was treated with acetic acid (100 mL), concentrated HCl (20 mL), and potassium chlorate (5.8 g) in water (50 mL).[35] After 3 h at room temperature the solvent was evaporated, ethanol was added to the residual oil, and KCl (3.2 g, 91%) was separated. Concentration of the ethanol filtrate give **5-methylbenzophenone-2-sulfonic acid** (7.7 g, 36%) as a lime-colored syrup. The crude sulfonic acid (7.7 g) was heated under reflux with thionyl chloride (20 mL) and DMF (0.5 mL) for 3 h and poured over ice (100 g) to give **5-methylbenzophenone-2-sulfonyl chloride** (6 g, 73%): mp 118–120 °C (EtOH); IR (KBr) 1670, 1360, 1170 cm^{-1}; NMR ($CDCl_3$) δ 8.05 (d, 1, *J* = 8 Hz, ortho to sulfonyl), 7.75 (dd, 2, *J* = 8, 2 Hz, H_3 and H_4), 7.4 (m, 5, Ph), 2.5 (s, 3, CH_3); mass spectrum *m/e* 296 ($M^{+\cdot}$, ^{37}Cl), 294 ($M^{+\cdot}$, ^{35}Cl).

Anal. Calcd For $C_{14}H_{11}ClO_3S$: C, 57.04; H, 3.76. Found: C, 56.91; H, 3.73.

5-Methylbenzophenone-2-sulfonyl Azide (24). This was prepared from the sulfonyl chloride (1.5 g) and tetramethylguanidinium azide (2 g) in $CHCl_3$ (30 mL) at room temperature for 12 h. The azide (0.52 g, 34%) had: mp 97.5–99 °C (from toluene); IR (KBr) 2130, 1675, 1360, 1175 cm^{-1}; NMR ($CDCl_3$) δ 7.95 (d, 1, *J* = 8 Hz, ortho to SO_2), 7.65 (dd, 2, *J* = 8, 2 Hz, H_3 and H_4), 7.4 (m, 5, Ph), 2.45 (s, 3, CH_3); mass spectrum *m/e* 301 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}N_3O_3S$: C, 55.80; H, 3.68. Found: C, 55.82; H, 3.69.

Thermolysis of 5-Methylbenzophenone-2-sulfonyl Azide. The azide (1.17 g) in Freon 113 (60 mL) was heated for 18 h at 140 °C in a sealed tube. The mixture was filtered from 2-benzamido-5-methylbenzenesulfonic acid (**26**, R = H; R′ = Me) (0.42 g, 40%) [mp 183 °C (toluene or CH_3CN)] identical with the authentic sample prepared above. This, on treatment with ethanol, gave 2-amino-5-methylbenzenesulfonic acid (**18**, R′ = Me) identical with authentic material.

The Freon filtrate was resolved by preparative TLC (silica gel, $CHCl_3$ eluent) to give: (i) benz-*m*-toluidide (**21**, R = H; R′ = Me) (20 mg, 1%) (mp 125–126 °C) identical with an authentic sample; (This was shown to be a single isomer under conditions—microslide TLC, silica gel, methylene chloride development—suitable for the resolution of the *m*- and *p*-toluidides.) (ii) **2-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide (17c)** (64 mg, 6%): mp 203–204 °C (toluene); IR (KBr) 3200, 1640, 1350, 1300, 1180, 1140 cm^{-1}; mass spectrum *m/e* 273 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.52; H, 4.06. Found: C, 61.43; H, 4.11.

Treatment of this sultam (21 mg) in THF (1 mL) with sodium hydride (5 mg) and diethyl sulfate (50 μL) in THF (1 mL) for 2 h at 80 °C gave **6-ethyl-2-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiazepine 5,5-dioxide** (20 mg, 90%): mp 140–142 °C (MeOH); IR (KBr) 1655, 1345, 1175 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.75; H, 5.02. Found: C, 63.71; H, 5.02.

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Registry No.—**1d**, 64939-40-8; **2**, 64939-41-9; **3**, 23393-41-1; **4**, 22172-69-6; **5**, 2688-87-1; **6**, 64939-42-0; **7**, 64939-43-1; **8**, 22172-72-1; **9**, 64939-44-2; **10**, 22172-71-0; **11** (2-Br), 64939-45-3; **11** (4-Bu), 64939-46-4; **12**, 22172-73-2; **13**, 127-63-9; **14**, 6462-14-2; **14** *N,N*-dimethyl, 64939-47-5; **17a**, 63113-45-1; **17b**, 63113-46-2; **17** (R = *p*-Me; R′ = H), 38938-54-4; **20** (R, R′ = H), 15449-00-0; **21** (R, R′ = H), 93-98-1; **22**, 26638-46-0; **25**, (12 = *p*-Me; R′ = H), 63113-48-4; sodium azide, 26628-22-8; 2-phenoxybenzenesulfonyl chloride, 2688-85-9; diphenyl sulfone 2-sulfonyl chloride, 6462-15-3; 2-aminodiphenyl sulfone, 4273-98-7; *N*-acetyldi-*p*-tolylamine, 32047-89-5; chlorosulfonic acid, 7790-94-5; *N*-acetyldi-*p*-tolylamine 2-sulfonyl chloride, 64939-29-3; *N*-acetyldi-*p*-tolylamine *N*′-dodecyl-2-sulfonamide, 64939-30-6; dodecane, 112-40-3; benzophenone-2-sulfonyl chloride, 54075-06-8; methyl benzoate 2-*N*-methylsulfonanilide, 26638-44-8; methyl benzoate 2-sulfonyl chloride, 26638-43-7; *N*-methyaniline, 100-61-8; 2-amino-4′-methylbenzophenone, 36192-63-9; 4′-methylbenzophenone-2-sulfonic acid, 64939-31-7; potassium 4′-methylbenzophenone-2-sulfonate, 64939-32-8; bis(4′-methyl-2-benzophenone) disulfide, 64939-33-9; bis(4′-methyl-2-benzophenone) disulfide *S,S*-dioxide, 64939-34-0; *o*-sulfobenzoic anhydride, 64975-68-4; ammonium 4′-methylbenzophenone-2-sulfonate, 64939-35-1; *p*-bromotoluene, 106-38-7; 4′-methylbenzophenone-2-sulfonyl chloride, 64939-36-2; tetramethylguanidinium azide, 64939-37-3; methyl benzoate 2-[*N*-ethyl-*N*-(*p*-tolyl)sulfonamide, 64939-24-8; *N*-ethyltoluidine, 622-57-1; *N*-ethyl-*N*-*p*-tolylbenzenesulfonamide-2-carboxylic acid, 63113-54-2; 6-ethyl-9-methyl-11-oxo-6*H*-dibenzo[*c,f*]-[1,2]thiazepine 5,5-dioxide, 63113-52-0; diethyl sulfate, 64-67-5; 6-ethyl-8-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2[thiazepine 5,5-dioxide, 63113-53-1; 2-benzamido-4-methylbenzenesulfonic acid, 63113-51-9; sodium 2-amino-4-methylbenzenesulfonate, 42876-65-3; benzoyl chloride, 98-88-4; 2-amino-5-methylbenzophenone HCl, 64939-25-9; 5-methylbenzophenone-2-sulfonic acid, 64939-26-0; 5-methylbenzophenone-2-sulfonyl chloride, 64939-27-1; 6-ethyl-2-methyl-11-oxo-6*H*-dibenzo[*c,f*][1,2]thiozepine 5,5-dioxide, 64939-28-2.

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Addition and Annulation Reactions between Indoles and α,β-Unsaturated Ketones

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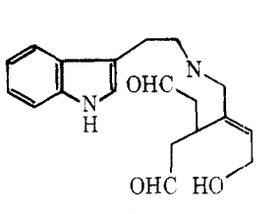
The structure of the addition product formed by acid-catalyzed reaction between 1,3-dimethylindole and mesityl oxide is shown to be **12**. Analogous products are formed with methyl vinyl ketone and benzalacetone as annulating agents. The reactions between methyl vinyl ketone and indole, 1,2-dimethylindole, and 3-methylindole are compared with these and with cyclization steps in the syntheses of the alkaloids villalstonine and vindorosine.

In a planned synthesis of strychnine Robinson and Saxton envisaged[1] the conversion of the dialdehyde **1** by a combination of Mannich and aldol-type condensations into the Wieland–Gumlich aldehyde **2**, already known to be convertible into strychnine. The conversion **1** → **2** would have exemplified the concept of annulation utilizing electrophilic addition reactions of indoles. Subsequently, this concept has been realized in Büchi's synthesis of vindorosine,[2] in which a key step is the cyclization of the *N*-acetylenone **3** with boron trifluoride etherate into the indoline **4**, and by our biomimetic synthesis of villalstonine (**5**) from macroline (**6**) and pleio-



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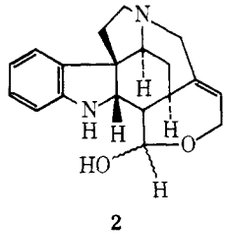

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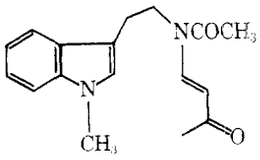

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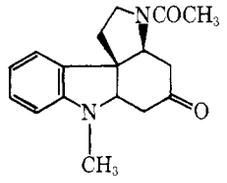

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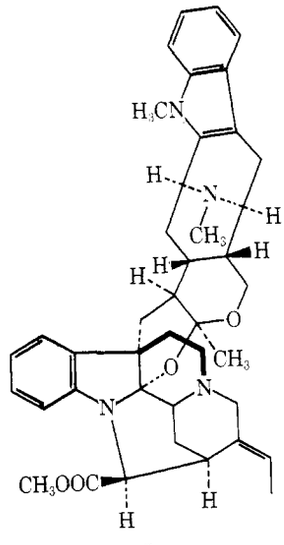

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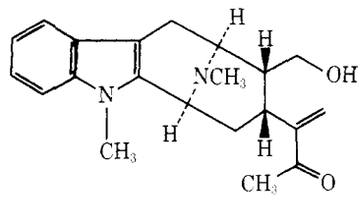

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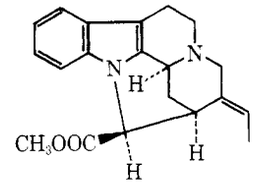

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