Registry No.—**1a**, 53973-62-9; **1b**, 7117-27-3; **1c**, 16753-80-3; **1d**, 16753-81-4; **1e**, 53992-03-3; **1f**, 53992-04-4; **2a**, 53992-05-5; **2b**, 53992-06-6; **1f**, 53992-04-4; **2a**, 53992-05-5; **2b**, 53992-06-6; **2c**, 53992-07-7; **2d**, 53992-08-8; **2e**, 53992-09-9; **2f**, 53992-10-2; **2g**, 53992-11-3; **2h**, 53992-12-4; **2i**, 53992-13-5; **4a**, 53992-14-6; **4b**, 53992-15-7; **4c**, 53992-16-8; **4d**, 53992-17-9; **4e**, 53992-18-0; **4f**, 53992-19-1; **4g**, 53992-20-4; **4h**, 53992-21-5; **4i**, 53992-22-6; **4j**, 53992-23-7; diphenyl malonate, 1969-44-4.

References and Notes

(1) (a) Part II: B. E. Hoogenboom, M. S. El-Faghi, S. C. Fink, E. D. Hoganson, S. E. Lindberg, T. J. Lindell, C. J. Linn, D. J. Nelson, J. O. Olson, L. Rennerfeldt, and K. A. Wellington, *J. Org. Chem.*, **34**, 3414 (1969). (b) Supported by a F. G. Cottrell grant from Research Corporation, Public Health Service Grant GM12153, National Science Foundation Undergraduate Research Participation Grant No. GE-9467, and the Gustavus Adolphus College Research Fund.

(2) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967).

(3) Phenyl carbethoxymethanesulfonate, $PhOSO_2CH_2CO_2C_2H_5$, derived from $ClSO_2CH_2CO_2C_2H_5$ [R. Vieillefosse, *Bull. Soc. Chim. Fr.*, 351 (1947)], reacts with salicylaldehyde under the same conditions to produce the same product, 2a. Phenyl carboxymethanesulfonate, $PhOSO_2CH_2CO_2H$, is not cyclized to **2a** under the same conditions (piperidine in refluxing benzene) but is instead decarboxylated to form $PhOSO_2CH_3$ in 98% yield.[7a] *N*-Phenylsulfamylacetic acid, $PhNHSO_2CH_2CO_2H$,[7a] is less readily decarboxylated, however, and is cyclized under the same conditions or in refluxing pyridine to form the coumarin (**2l**) in 83% yield.

(4) G. Jones, *Org. React.*, **15**, 204 (1967).

(5) R. W. Hein, M. J. Astle, and J. R. Shelton, *J. Org. Chem.*, **26**, 4874 (1961).

(6) Diphenyl malonate reacts with 5-bromosalicylaldehyde in an acetone solvent without the benefit of an added basic agent to form a high yield (91%) of 6-bromo-3-carbophenoxycoumarin (**3b**, Table II).

(7) The parent sultone is referred to in *Chemical Abstracts* as 1,2-benzoxathiin 2,2-dioxide.

(8) In fact, when water is not carefully excluded from the reaction mixture, the product isolated is the hydrolysis product (**8**). Apparently, once the anion of **1f** is formed, the unimolecular dissociation to form a sulfene (**9**) is faster than the bimolecular reaction with an aldehyde to form the Knoevenagel intermediate addition product, $ArCHOHCHAr'SO_2OPh$.

(9) V. Auger, *C. R. Acad. Sci.*, **136**, 556 (1903).

Thermal Decomposition of *o*- and *p*-Benzenedisulfonyl Azides in Benzene, Cyclohexane, Cyclohexene, and Tetracyclone[1]

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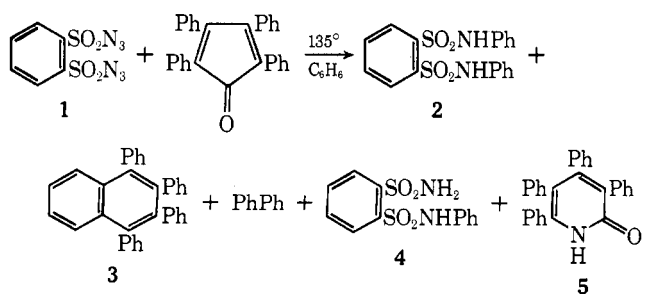
Received October 29, 1974

The thermolysis of *o*-benzenedisulfonyl azide in benzene and cyclohexane gives products which can be rationalized as arising from both benzyne and a singlet sulfonyl nitrene. The former can be trapped with tetracyclone whereas the sulfonyl nitrene undergoes aromatic substitution with benzene, C–H insertion into cyclohexane, and addition to tetracyclone. The termolysis of *p*-benzenedisulfonyl azide in benzene, toluene, and cyclohexane leads only to singlet sulfonyl nitrene. Both *o*- and *p*-benzenedisulfonyl azide react readily with cyclohexene to give a diimine or dienamine as the primary product. In the case of the *o*-diazide, an interesting secondary product was isolated. Formation of the primary product is best explained in terms of a 1,3-dipolar addition mechanism.

The thermal decomposition of monosulfonyl azides in benzene and cyclohexane is known[2] to give singlet sulfonyl nitrene. While disulfonyl azides have been used for the cross-linking of hydrocarbon polymers,[2b] their reactions with aromatic hydrocarbons have not been reported. In this paper we report the thermal decompositions of *o*- and *p*-benzenedisulfonyl azide in benzene, cyclohexane, tetracyclone, and cyclohexene.

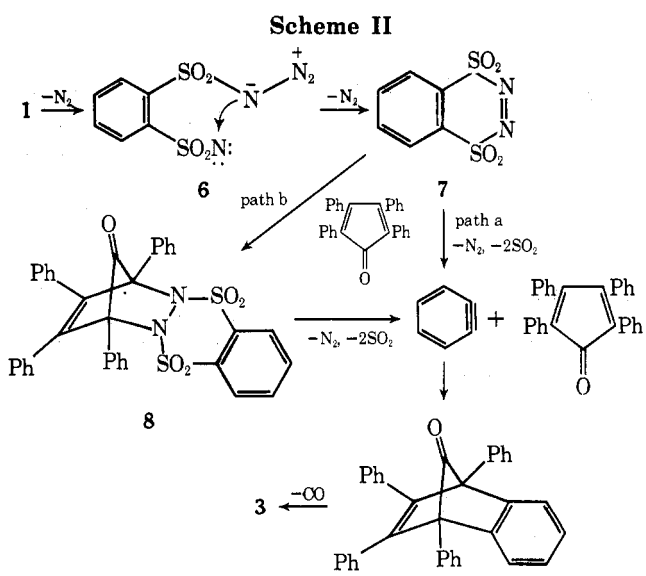
Thermolysis of the *o*-diazide (**1**) in a large excess of benzene at 135° gave the expected nitrene product, *o*-benzenedisulfonylanilide (**2**, 21%) as the only isolable product. When the same reaction was carried out in the presence of tetracyclone (1.1 molar equiv), an interesting array of products was isolated and these are illustrated in Scheme I.

Scheme I

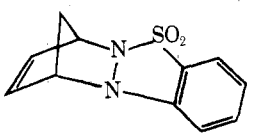


From the nature of the products, it is evident that two different reactive intermediates, likely a benzyne and a sulfonyl nitrene, are being generated from **1** and that at least three mechanisms must be invoked in order to explain the formation of all products. The tetraphenylnaphthalene (**3**, 6%) probably results from the cycloaddition of benzyne to tetracyclone. Possible mechanisms leading to benzyne from **1** are depicted in Scheme II. The electrophilic singlet nitrene (**6**) could cyclize to the unstable cyclic azodisulfone (**7**), which could either eliminate nitrogen and two molecules of sulfur dioxide (path a) or undergo cycloaddition (path b) to tetracyclone to give adduct **8**, and then eliminate nitrogen and sulfur dioxide to give benzyne. Although

Scheme II



the reaction was carried out at 135° and path a would be expected to be a facile process, path b cannot be discounted. It has been observed[3] that 1,2,3-benzothiadiazole 1,1-dioxide reacts with cyclopentadiene to give adduct **9**, which

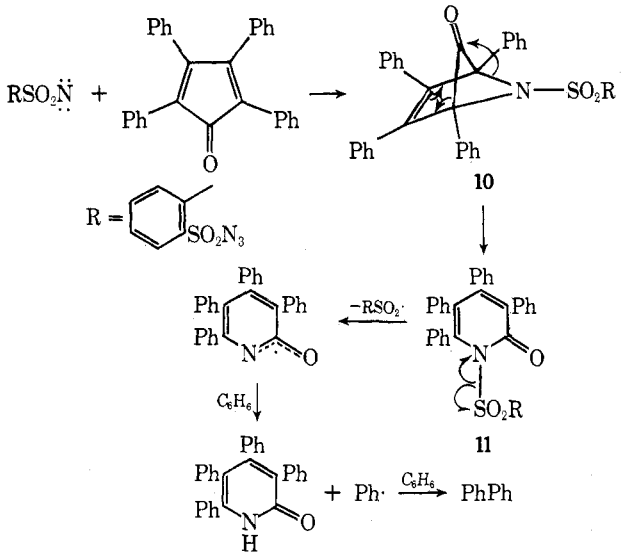


9

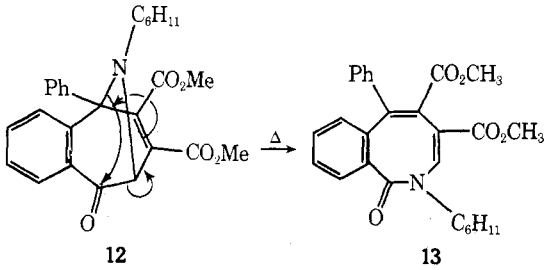
decomposes at 75° to give nitrogen, sulfur dioxide, cyclopentadiene, and benzyne.

o-Benzenedisulfonylanilide (**2**, 9%) and benzenesulfonylanilide-2-sulfonamide (**4**, 5%) are normal aromatic substitution and mixed substitution–hydrogen abstraction products, respectively, of the disulfonyl nitrene. It is not obvious, however, why **4** is formed only in the presence of tetracyclone but not in its absence, but it (or other products or intermediates, e.g., see Scheme III) could probably catalyze the singlet → triplet interconversion in the monosubstituted mononitrene.

Scheme III

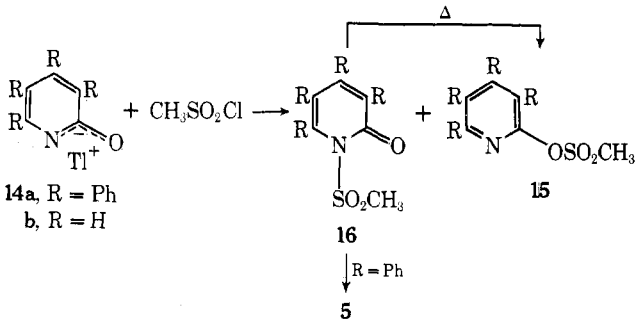


A possible mechanism which could explain the formation of tetraphenyl-2-pyridone (**5**, 13%) and biphenyl is outlined in Scheme III. 1,4-Addition by singlet sulfonyl nitrene to tetracyclone would give the symmetrical intermediate **10** which, on ring expansion, would lead to **11**. Homolytic cleavage of the S–N bond [probably encouraged by the presence of the 6-phenyl substituent in **11** (see below)] followed by hydrogen abstraction from benzene would lead to **5** and a phenyl radical. The latter with benzene would give biphenyl. The ring expansion **10** → **11** has precedent in the known[4] expansion of **12** in boiling toluene to **13**.



12 **13**

The instability of **11** (or its equivalent) was verified in studies on model compounds. Methanesulfonylation of thallium(I) 2-pyridone (**14b**) in ether at room temperature gave *N*-mesyl-2-pyridone (**16b**, 48%) ($\nu_{C=O}$ 1670 cm^{-1}) and 2-pyridyl methanesulfonate (**15b**, 52%) (no C=O absorption). When **16b** was heated either alone at 175° or in methylene bromide at 135° it rearranged quantitatively to **15b**.[5] On the other hand, methanesulfonation of the thallium(I) salt **14a** in ether (the reaction in other solvents gave similar results) at room temperature (or below) gave **5** (25%) ($\nu_{C=O}$ 1670 cm^{-1}) and 3,4,5,6-tetraphenyl-2-pyridyl methanesulfonate (**15a**, 72%) (no C=O absorption). The *N*-sulfonyl derivative (**16a**) was never detected, even when the reaction was carried out at low temperature. It is undoubtedly formed (**15a** does not hydrolyze to **5** under the reaction conditions or during the isolation procedure; no reaction occurred between **15a** and mesyl chloride) but is unstable (probably owing to steric hindrance by the 6-phenyl group) and either rearranges to **15a** or eliminates methylene sulfene (or its equivalent)[6] to give **5**. With the bulkier ortho-disubstituted benzene elimination probably takes place before any N → O migration can occur (the *o*-sulfonyl azide function may also play a role in this elimination).



14a, R = Ph
b, R = H

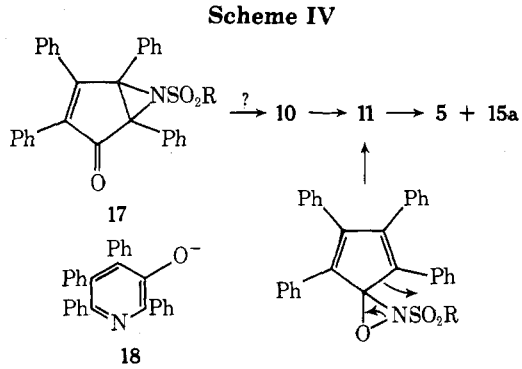
16 **15**

5

The reaction of sulfonyl azides with tetracyclone appears to have some generality. Thus, methanesulfonyl azide reacts with tetracyclone in methylene bromide at 135° to give **5** (12%), **15a** (12%), and methanesulfonamide (26%). No reaction took place at 80° so that this is not a 1,3-dipolar addition of azide to tetracyclone (such reactions with strained and unstrained double bonds occur at much lower temperature than 135° [7]) but suggests rather that a nitrene is the reactive intermediate.

Three possible modes of addition of a nitrene to tetracyclone can account for the formation of **5** and **15a**: (i) 1,2-addition to give **17** followed by rearrangement to the 1,4 adduct **10** and thence **11**, **5**, and **15a**; (ii) direct 1,4-addition to give **10**; (iii) 1,2-addition to C=O and then rearrangement to **11** (Scheme IV). Precedent for this last possibility

Scheme IV



17 **18**

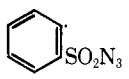
is the known reaction of methylene with acetone to give an oxirane.[8] This was tested by heating methanesulfonyl azide with fluorenone in methylene bromide; an addition to the carbonyl followed by rearrangement would lead to a phenanthridone, while both 1,2- and 1,4-addition to the cyclopentadienone portion are unlikely. In fact, no phenanthri-

done was formed; only a small amount of a monobromo-9-fluorenone was isolated and 9-fluorenone was recovered together with methanesulfonamide (67%) (abstraction from CH_2Br_2). Singlet ethoxycarbonyl nitrene is known[9] to undergo exclusive 1,2-addition to conjugated olefins, but the vinylaziridine so formed rearranges thermally to the apparent 1,4 adduct. On the other hand, its reactions with pyrrole and with 2,5-dimethylthiophene have been formulated as going via the 1,4 adduct.[10] If a 1,2 adduct (**17**) were indeed formed it might have been expected to rearrange to some extent to a betaine **18**. No such product was ever detected, however, which suggests that a direct 1,4-addition may indeed be occurring.

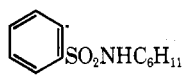
Thermolysis of the *o*-diazide **1** in cyclohexane at 135° gave *N*-cyclohexylbenzenesulfonamide and *N,N'*-dicyclohexyl-*o*-benzenedisulfonamide in 47 and 3% yields, respectively. The most striking feature of this reaction is that a

$$o\text{-}C_6H_4(SO_2N_3)_2 + C_6H_{12} \xrightarrow{\Delta} C_6H_5SO_2NHC_6H_{11} + o\text{-}C_6H_4(SO_2NHC_6H_{11})_2$$

sulfonyl azide moiety is completely lost. It is conceivable that an aryl radical (either **19** or **20**) is formed as an inter-



19



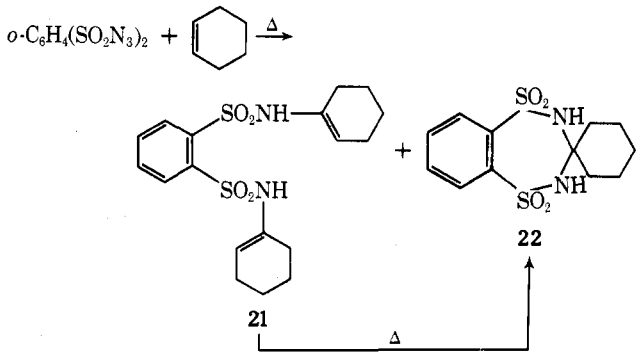
20

mediate which abstracts a hydrogen atom from solvent. Radical-catalyzed losses of SO_2 are well known in sulfonyl azide chemistry[2] and there is precedent for the formation of aryl radicals in the observation that thermolysis of diphenylsulfone-2-sulfonyl azide gave diphenylene sulfone, presumably via a Pschorr-type cyclization of any aryl radical intermediate.[11]

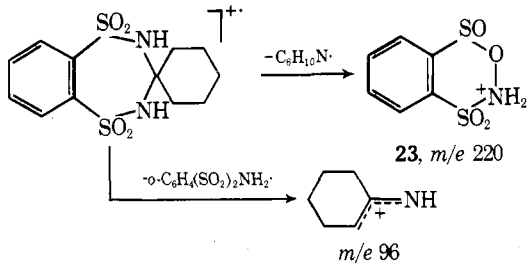
In an effort to find out if **20** was a plausible intermediate the synthesis of *N*-cyclohexylbenzenesulfonamide-2-sulfonyl azide (**21**) was attempted but was unsuccessful. Three different approaches were tried. Treatment of benzene-*o*-disulfonyl chloride with 1 equiv of sodium azide yielded only the disulfonyl azide (43%) and recovered disulfonyl chloride. When the disulfonyl chloride was treated with cyclohexylamine (1 equiv) and then with sodium azide in methanol a mixture of **1** (53%) and *N,N'*-dicyclohexyl-*o*-benzenedisulfonamide (29%) was obtained. Finally, diazotization of *o*-aminobenzenesulfonic acid followed by addition of SO_2 in the presence of $CuCl_2$ only gave the *o*-disulfonic acid and not the sulfonyl chloride *o*-sulfonic acid.

The thermal decomposition of the *o*-diazide (**1**) in cyclohexane containing tetracyclone gave 1,2,3,4-tetraphenylnaphthalene, *N*-cyclohexylbenzenesulfonamide, *N,N'*-dicyclohexyl-*o*-benzenedisulfonamide, and 3,4,5,6-tetraphenyl-2-pyridone in 6, 12, 8, and 18% yields, respectively. This experiment illustrated unequivocally that *o*-benzenedisulfonyl azide is indeed the precursor of benzyne and not the benzene solvent used in the previous thermolysis.

The decomposition of **1** in boiling cyclohexene gave the dienamine **21** as the primary product, and spiro[2*H*-1,5,2,4-benzodithiadiazepine-3(4*H*),1'-cyclohexane-1,1,5,5-tetroxide] (**22**) as a secondary product. Heating **21** in cyclohexene at 135° for 71 hr gave **22** (62%). The structure of **21** (rather than the imine tautomer[7b]) was confirmed by the presence of an NH band (3280 cm^{-1}) in the infrared, by its NMR spectrum [δ 7.23 (NH, 2 H, D_2O exchange) and 5.50 (m, 2 vinyl H)], and by its hydrolysis to cyclohexanone and *o*-benzenedisulfonamide. The spiro compound **22** also exhibited a strong NH absorption in the ir (3265 cm^{-1}) and its NMR and mass spectra were also compatible with the assigned structure. Thus, absorptions were observed at δ



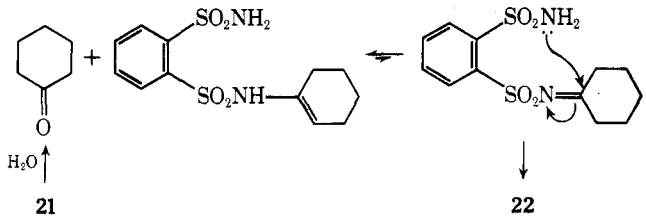
9.72 (NH, 2 H, D_2O exchange), 8.56 (d of d, $J_{3,4}$ = 6.25, $J_{3,5}$ = 3.0 Hz, H_3 and H_6 of aromatic ring), 8.30 (d of d, H_3 and H_5), 2.72–2.48 (m, 4 H, C_2 and C_6 protons of cyclohexane ring), and 2.14–1.92 (m, 6 H). In the mass spectrum, the base peak was at *m/e* 96 ($C_6H_{10}N^+$)[7b] [loss of *o*-$C_6H_4(SO_2)_2NH_2\cdot$], and an intense (83%) fragment at *m/e* 220 could be due to N–S bond cleavage (–$C_6H_{10}N$) to give



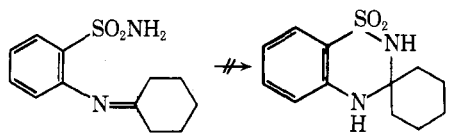
m/e 96

an ion (possibly **23**). Hydrolysis of **22** with aqueous acid gave *o*-benzenedisulfonamide.

There are several pathways by which the transformation of **21** → **22** can occur. If partial hydrolysis of **21** occurred to give *N*-(1-cyclohexenyl)-*o*-benzenedisulfonamide (**24**) and cyclohexanone, nucleophilic cyclization to **22** could follow.



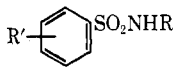
This mechanism is, however, rendered less plausible for a number of reasons. (i) The reaction was carried out in thoroughly dried cyclohexene. (ii) The amino group of a primary sulfonamide is a poor nucleophile. When *o*-benzenedisulfonamide was heated with cyclohexanone in acetonitrile or cyclohexane, no reaction occurred. Further, attempted cyclization of *N*-cyclohexylidene-*o*-aminobenzenesulfonamide (**25**) (from cyclohexanone and *o*-aminobenzenesulfonamide) to the spiro compound **26** failed. (iii)



When **21** was heated in cyclohexene at 135°, **22** was formed in 62% yield but only a trace of cyclohexanone was detected by gas–liquid chromatography.

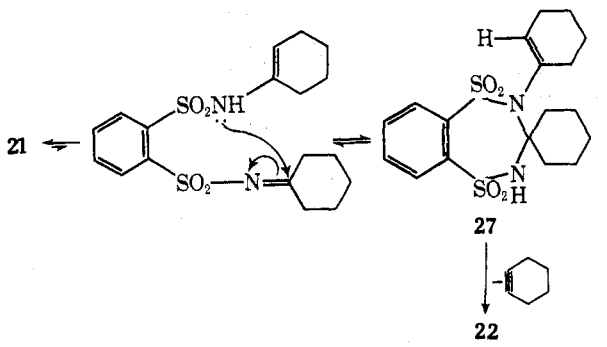
Another possible pathway for the cyclization is illustrated in Scheme V. This intramolecular route, which does not involve a preliminary hydrolysis step, does require, however, the elimination of cyclohexyne (which would be expected to polymerize) or its equivalent. Also, if anything, the sulfonylimino nitrogen might be expected to be even

Table I
Authentic Disubstituted Disulfonamides

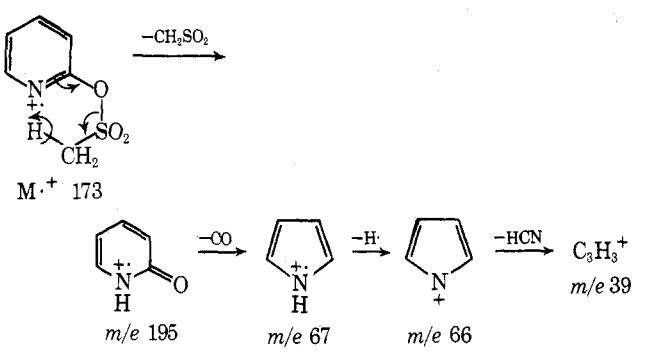


R	R'	Yield, %	Mp, °C	Molecular formula	Found, % C	Found, % H	Calcd, % C	Calcd, % H	Registry no.
C_6H_5	o-($C_6H_5NHSO_2$)	84	249–250	$C_{18}H_{16}N_2O_4S_2$	55.64	4.23	55.65	4.13	
C_6H_5	p-($C_6H_5NHSO_2$)	73	254–255	$C_{18}H_{16}N_2O_4S_2$	55.46	4.20	55.65	4.13	53965-93-8
C_6H_{11}	o-($C_6H_{11}NHSO_2$)	91	126–128	$C_{18}H_{28}N_2O_4S_2$	54.06	7.09	54.00	7.00	53965-94-9
C_6H_{11}	p-($C_6H_{11}NHSO_2$)	77	240–242	$C_{18}H_{28}N_2O_4S_2$	53.92	7.02	54.00	7.00	53965-95-0

Scheme V

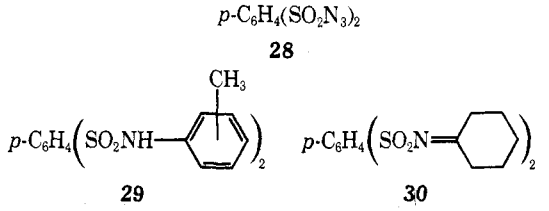


Scheme VI



less nucleophilic in this case. Further work is clearly needed to determine the mechanism of this reaction. Formation of **21** from the azide in unexceptional, however, and the mechanisms of such reactions have already been discussed.[7]

Thermolysis of p-benzenedisulfonyl azide (**28**) in benzene gave the p-dianilide (55%) as well as some black, intractable material. Thermolysis of the p-diazide in toluene at 135° gave a trace of bibenzyl and the isomeric p-benzenedisulfonyltoluidides (**29**, 84%). It has been reported[12] that



p-benzyne, generated from *cis*-1,5-hexadiyn-3-ene in toluene, gave diphenylmethane as a major product. No diphenylmethane could be detected by column or gas–liquid chromatography in the present reactions. Thermolysis of **28** in cyclohexane at 135° gave *N,N'*-dicyclohexyl-p-benzenedisulfonamide (55%) and *N*-cyclohexylbenzenedisulfonamide (5%) as the only isolable products. The decomposition of **28** in a large excess of an equimolar mixture of cyclohexene–benzene gave *N,N'*-dicyclohexylidene-p-benzenedisulfonamide (**30**, 97%) as already reported.[7b]

Nmr and Mass Spectra of *N*- and *O*-Mesyl-2-pyridones. 2-Pyridyl methanesulfonate (**15b**) exhibited a doublet of doublets ($J_{5,6}$ = 5.0, $J_{4,6}$ = 2.0 Hz) at δ 8.32 due to H_6, six lines centered at δ 7.79 ($J_{4,5}$ = $J_{3,4}$ = 8.0, $J_{4,6}$ = 2.0 Hz) due to H_4, a doublet of doublets at δ 7.23 ($J_{3,5}$ < 1.0 Hz) due to H_5, and a quartet at δ 7.08 due to H_3. *N*-Mesyl-2-pyridone (**16**) exhibited an nmr spectrum very similar to that of *N*-methyl-2-pyridone[13] except that the 4 and 6 protons were shifted somewhat downfield as expected and $J_{4,5}$ and $J_{5,6}$ were somewhat larger: δ 7.85 (q, $J_{5,6}$ = 8.0, $J_{4,6}$ = 2.0 Hz, H_6), 7.30 (d of d, $J_{3,4}$ = 9.2, $J_{4,5}$ = 6.8 Hz, H_4), 6.55 (q, $J_{3,5}$ = 1.2 Hz, H_3), and 6.26 (d of d of d, H_5).

The mass spectrum of **15b** showed an $M^{\cdot+}$ peak at *m/e* 173 (13%). The main fragment ions were at *m/e* 95 (100%), 79 (19%), 67 (55%), 66 (16%), and 39 (63%). These may be readily accounted for as in Scheme VI by a McLafferty-type rearrangement of the molecular ion accompanied by the loss of methylene sulfene to give the 2-pyridone radical cation as the base peak. Expulsion of CO would give the *m/e* 67 fragment, which has been formulated as a pyrrole ion.[14] The mass spectrum of **16b** exhibited the parent ion at *m/e* 173 (22%) and the base peak at *m/e* 95. The fragmentation pattern was identical with that of **15b**, as expected if the first step is a McLafferty-type rearrangement.

Experimental Section

Melting points are uncorrected. Nmr spectra were recorded on a Varian Associates Model HA-100 or a Perkin-Elmer Model R-20B spectrometer. Mass spectra were recorded on a C.E.C. Model 21-104 spectrometer at an ionizing voltage of 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrometer. Gas chromatographic analysis was carried out with a Varian Associates Model A-90-P chromatograph with helium as carrier gas. Fischer-Porter pressure tubes, equipped with a degassing valve, were used for the thermolysis at 135°. The initial reaction mixtures were degassed by evacuating the frozen solution and thawing. This procedure was repeated at least three times for each run.

Reagents. Reagent-grade solvents were purified by standard techniques and kept over a drying agent. They were fractionally distilled just prior to use.

Authentic *N,N'*-Dicyclohexylbenzenedisulfonamides and Benzenedisulfonylanilides. These were prepared from the appropriate amine and benzenedisulfonyl chloride with benzene or chloroform as solvent. The properties of the new compounds are given in Table I.

***o*-Benzenedisulfonyl Azide (1).** Powdered sodium azide (5.2 g, 0.080 mol) was added to a stirred solution of *o*-benzenedisulfonyl chloride[15] (8.0 g, 0.029 mol) in distilled methanol (100 ml) over a 0.5-hr period. The reaction mixture was stirred for a further 2 hr at room temperature and poured into ice–water (200 ml) with vigorous stirring, whereupon a white solid precipitated. Recrystallization from methanol gave *o*-benzenedisulfonyl azide (6.9 g, 83%): mp 115–116°; ir (KBr) 2150 (N_3), 1370 (SO_2), and 1175 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 8.30 (d of d, H_3 and H_6, $J_{3,4}$ = 6.0, $J_{3,5}$ = 3.8 Hz) and 7.85 (d of d, H_4 and H_5); MS (70 eV) *m/e* 246 ($M^{\cdot+}$ − 42), 106 (28), 98 (24), 96 (19), 90 (81), 78 (43), 76 (87), 63 (35), 50 (100).

Anal. Calcd for $C_6H_4N_6O_4S_2$: C, 25.00; H, 1.39. Found: C, 25.13; H, 1.48.

***p*-Benzenedisulfonyl Azide (28).** Prepared as described in the literature[16] from p-benzenedisulfonyl chloride[17] and sodium azide in methanol, it was obtained in 90% yield and had mp 136–137° (lit.[16] mp 133–134°).

Decompositions of o-Benzenedisulfonyl Azide. A. In Benzene. A thoroughly degassed solution of o-benzenedisulfonyl azide (0.707 g, 2.45 mmol) in dry benzene (20 ml, 0.226 mol) was heated in an oil bath at 135° for 7 days. The reaction mixture was cooled to room temperature, the gas under pressure was released, and a black, shiny material (ca. 0.26 g) was filtered and washed with hot acetonitrile (30 ml). The combined filtrates were chromatographed on silica gel (120 g). Elution with benzene–ether (9:1 v/v, 150 ml) gave a white, crystalline solid (0.199 g, 20.5%) whose ir and NMR spectra were identical with those of authentic o-benzenedisulfonylanilide. No other compounds were detected.

When the decomposition was repeated and the filtrate was analyzed by GLC using a 5 ft × 0.25 in. Apiezon M (15%) on Anakchrom (60–80 mesh) column at an oven temperature of 230°, no biphenyl, benzenesulfonamide, or benzenesulfonylanilide were detected.

B. In Benzene–Tetracyclone. A thoroughly degassed solution of o-benzenedisulfonyl azide (1.027 g 3.57 mmol) and tetracyclone (1.503 g, 3.91 mmol) in dry benzene (20 ml) was heated at 135° for 56 hr. The reaction mixture was worked up as before and the filtrate was chromatographed on silica gel (200 g). The light petroleum fraction (100 ml) gave biphenyl (12 mg, 2%), mp 67–68°, whose ir spectrum was identical with that of authentic material.

Light petroleum–benzene (4:1 v/v, 150 ml) eluted a light yellow oil which solidified on standing. Recrystallization from aqueous acetonitrile gave 1,2,3,4-tetraphenylnaphthalene (0.085 g, 5.5%): mp 204–205° (lit.[18] mp 204.5–205°); NMR ($CDCl_3$) δ 7.75–7.2 (m, 4 H), 7.20 (s, 10 H), and 6.80 (s, 10 H); MS (70 eV) *m/e* 432 ($M^{\cdot+}$, 100).

Light petroleum–benzene (2:1 v/v, 100 ml) and light petroleum–benzene (1:1 v/v, 250 ml) eluted unreacted tetracyclone (0.94 g, 64%). Benzene (150 ml) eluted o-benzenedisulfonylanilide (0.12 g, 8.7%). Benzene–ether (4:1 v/v, 150 ml) eluted an oily solid. Crystallization from chloroform–light petroleum (bp 60–110°) gave **benzenesulfonylanilide-o-sulfonamide (4)** (0.055 g, 5%): mp 208–209°; ir (KBr) 3360 and 3255 (NH_2), 3300 (N–H), 1340 (SO_2), and 1165 cm^{-1} (SO_2); NMR (DMSO-d_6) δ 9.66 (s, NH, 1 H, D_2O exchange), 8.20 (d of d, 1 H, $J_{3,4}$ = 6.5, $J_{3,5}$ = 2.5 Hz, H_3), 8.06–7.68 (m, 3 H), 7.42 (s, NH_2, 2 H, D_2O exchange), and 7.30–6.98 (m, 5 H); MS (70 eV) *m/e* 312 ($M^{\cdot+}$, 39), 295 (31), 278* (312 → 295, $-NH_3$), 93 ($C_6H_5O^+$, 100).

Anal. Calcd for $C_{12}H_{12}N_2O_4S_2$: C, 46.18; H, 3.85. Found: C, 46.18; H, 4.01.

Benzene–ether (3:2 v/v, 250 ml) and ether (200 ml) eluted a white solid. Recrystallization from aqueous acetonitrile gave granular crystals of 3,4,5,6-tetraphenyl-2-pyridone (0.18 g, 12.6%), mp 273–275° (lit.[19] mp 273–275°), whose ir spectrum was identical with that of an authentic sample.

Anal. Calcd for $C_{19}H_{21}NO$: C, 87.18; H, 5.30. Found: C, 87.32; H, 5.35.

C. In Cyclohexane. A degassed solution of o-benzenedisulfonyl azide (0.936 g, 3.25 mmol) in dry cyclohexane (20 ml) was heated in an oil bath at 135° for 72 hr. The reaction mixture was worked up as before and chromatographed on silica gel (150 g). Light petroleum–benzene (1:1 v/v, 100 ml) eluted ***N,N'*-dicyclohexyl-o-benzenedisulfonamide** (0.036 g, 2.6%) whose ir spectrum was identical with that of an authentic sample. Benzene–ether (4:1 v/v, 150 ml) eluted a colorless oil which slowly solidified on standing. Recrystallization from aqueous ethanol gave *N*-cyclohexylbenzenesulfonamide (0.368 g, 47.4%) whose ir spectrum was identical with that of an authentic sample prepared from benzenesulfonyl chloride and cyclohexylamine.

D. In Cyclohexane–Tetracyclone. A degassed solution of o-benzenedisulfonyl azide (1.003 g, 3.49 mmol) and tetracyclone (1.44 g, 3.75 mmol) in dry cyclohexane (20 ml) was heated in an oil bath at 135° for 116 hr. The reaction mixture was worked up as before and the product was chromatographed on silica gel (200 g). Light petroleum–benzene (4:1 v/v, 150 ml) eluted 1,2,3,4-tetraphenylnaphthalene (0.089 g, 6%). Light petroleum–benzene (2:1 v/v, 100 ml) eluted unreacted tetracyclone (0.71 g). Light petroleum–benzene (1:1 v/v, 200 ml) eluted *N,N'*-dicyclohexyl-o-benzenedisulfonamide (0.092 g, 8%). Benzene (250 ml) gave *N*-cyclohexylbenzenesulfonamide (0.101 g, 12%) and ether (350 ml) eluted 3,4,5,6-tetraphenyl-2-pyridone (0.245 g, 18%).

E. In Cyclohexene. A solution of 1 (0.716 g, 2.49 mmol) in freshly fractionated cyclohexene (bp 82.0–82.5°) (20 ml) was boiled under reflux ($CaCl_2$ drying tube) for 108 hr. The reaction mixture, which contained a white, crystalline material on the wall of the reaction vessel, was cooled to room temperature, filtered, and washed with benzene (15 ml). Recrystallization from acetonitrile–carbon tetrachloride gave **spiro[2*H*-1,5,2,4-benzodithiadiazepine-3(4*H*),1'-cyclohexane 1,1,5,5-tetroxide]** (**22**, 0.099 g, 13%): mp 240–242°; ir (KBr) 3265 (N–H), 1335 (SO_2), and 1170 cm^{-1} (SO_2).

Anal. Calcd for $C_{12}H_{16}N_2O_4S_2$: C, 45.58; H, 5.06. Found: C, 45.78; H, 5.17.

The filtrate was concentrated carefully under vacuum until an oily solid was left. Addition of anhydrous ether (ca. 15 ml) caused a white, crystalline solid to separate. This was quickly filtered in a drybox and identified as ***N,N'*-di-(1-cyclohexenyl)-o-benzenedisulfonamide** (0.64 g, 65%): mp 162–164°; ir (KBr) 3280 (N–H), 1575 (C=C), 1325 (SO_2), and 1175 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 8.10 (d of d, H_3 and H_6, $J_{3,4}$ = 6.0, $J_{3,5}$ = 3.0 Hz), 7.66 (d of d, H_4 and H_5), 7.23 (N–H, 2 H, D_2O exchange), 5.50 (m, 2 vinyl H), 2.04–1.82 (m, 8 allylic H), and 1.54–1.32 (m, 8 aliphatic H); MS (70 eV) *m/e* 396 ($M^{\cdot+}$, 3), 172 (16), 99 (24), 98 (100), 97 (64).

Anal. Calcd for $C_{18}H_{24}N_2O_4S_2$: C, 54.52; H, 6.06. Found: C, 54.37; H, 6.08.

The ether filtrate was concentrated under vacuum to give an oily solid. Its ir and NMR spectra were identical with those of the above dienamine. This oily solid was dissolved in ethanol–water (1:1 v/v, 10 ml) containing concentrated hydrochloric acid (1.0 ml). As this solution was heated to boiling a white solid precipitated from solution. Filtration gave o-benzenedisulfonamide (0.077 g, 13%): mp >310° (lit.[20] mp 335–338°); ir (KBr) 3360 and 3260 (NH_2), 1330 (SO_2), and 1165 cm^{-1} (SO_2).

Hydrolysis of 22. A solution of **22** (0.197 g) in ethanol–water (1:1 v/v, 20 ml) and concentrated HCl (2.5 ml) was boiled under reflux for 1 hr to give o-benzenedisulfonamide (0.134 g, 91%), mp >310°.

Thermolysis of *N,N'*-Di-(1-cyclohexenyl)-o-benzenedisulfonamide (21). A degassed solution of **21** (0.119 g, 0.300 mmol) in freshly fractionated cyclohexene (10 ml) was heated in an oil bath at 135° for 71 hr and cooled to room temperature and the insoluble spiro compound **22** was filtered (0.060 g, 62%), mp 241–243°. The filtrate was analyzed by GLC on a 10 ft × 0.25 in. column packed with Apiezon L (25%) on Anakchrom ABS (60–70 mesh) at an oven temperature of 200° and a helium flow rate of 60 ml/min. A trace of a compound with the same retention time as cyclohexanone was detected. When a sample of the title compound in anhydrous ether was analyzed under the same conditions, a small peak with the same retention time as cyclohexanone was also observed.

Concentration of the filtrate under vacuum gave an oily solid (ca. 40 mg) whose ir and NMR spectra were identical with those of starting material (no carbonyl absorption at 1680 cm^{-1}).

Attempted Preparation of *N*-Cyclohexylbenzenesulfonamide-2-sulfonyl Azide. Cyclohexylamine (1.8 ml) was added to a stirred solution of o-benzenedisulfonyl chloride (3.18 g) in dry benzene (50 ml). The mixture was boiled under reflux for 1 hr and cooled, and cyclohexylamine hydrochloride was filtered. Methanol (50 ml) was added to the filtrate followed by powdered sodium azide (1.7 g). The mixture was stirred overnight, poured into ice–water (300 ml), and extracted with ether (2 × 500 ml). The dried ($MgSO_4$) extracts were evaporated and the residue was chromatographed on a column of silica gel (250 g). Elution with benzene gave o-benzenedisulfonyl azide (1.64 g). Elution with benzene–ether (4:1 v/v) gave *N,N'*-dicyclohexyl-o-benzenedisulfonamide (1.21 g). No other product was detected.

A similar result was obtained when o-benzenedisulfonyl chloride (15.4 mmol) was treated with sodium azide (16.1 mmol) in acetone. Only unchanged disulfonyl chloride (55%) and also disulfonyl azide (1.80 g) were obtained. No monosulfonyl azide could be detected.

Attempted Preparation of *N*-Cyclohexylbenzenesulfonamide-2-sulfonyl Chloride. A suspension of 2-aminobenzenesulfonic acid (7.19 g) in glacial acetic acid (36 ml) and concentrated HCl (6 ml) was heated on a steam bath until the solution became homogeneous, and then cooled to 0–5°. Sodium nitrite (5.4 g) in water (25 ml) was added below 5° and the resulting solution was added to a stirred suspension of $CuCl_2$ (1.4 g) in benzene (130 ml) and glacial acetic acid saturated with SO_2. The mixture was stirred at 5–10° for 2 hr, then at 40° for 3 hr. No benzene-soluble product was formed. From the acidic layer was isolated a solid which, on treatment with thionyl chloride (30 ml) and DMF (1.7 ml) and boiling for 1 hr, gave o-benzenedisulfonyl chloride (8.3 g, 73%), mp 142–143°.

Decompositions of p-Benzenedisulfonyl Azide. A. In Benzene. A degassed solution of p-benzenedisulfonyl azide (1.005 g, 3.49 mmol) in dry benzene (20 ml) was heated in an oil bath at

135° for 72 hr. The reaction mixture was worked up as in the case of the ortho derivative and chromatographed on silica gel (100 g). Ether and ether–methanol (2:1 v/v, 100 ml) gave a white solid whose ir and NMR spectra were identical with those of authentic *p*-benzenedisulfonylanilide (0.854 g, 55%), mp 250–252°.

When the reaction was repeated and the filtrate analyzed by GLC using a 5 ft × 0.25 in. Apiezon M (15%) on Anakchrom (60–80 mesh) column at an oven temperature of 230° and a helium flow rate of 60 ml/min no biphenyl, benzenesulfonamide, or benzenesulfonylanilide were detected.

B. In Toluene. A degassed solution of the *p*-diazide (0.815 g, 2.83 mmol) in dry toluene (12.0 ml) was heated in an oil bath at 135° for 60 hr. The reaction mixture was dissolved in hot boiling acetonitrile (80 ml) and filtered and the filtrate was concentrated to ca. 2 ml. This was then analyzed by GLC on a 10 ft × 0.25 in. column packed with Apiezon L (25%) on Anakchrom ABS at an oven temperature of 220° and a helium flow rate of 60 ml/min. One product, with a retention time of 23.4 min, was collected and had a mass spectrum identical with that of authentic bibenzyl. Diphenylmethane was not detected. The concentrated filtrate was chromatographed on silica gel (150 g). Benzene–ether (1:1 v/v, 250 ml) and ether (350 ml) eluted a white, powdery solid (0.99 g, 84%), mp 240–245°. Two recrystallizations from acetonitrile gave granular crystals of a mixture of **p-benzenedisulfonyltoluidides:** mp 248–257°; ir (KBr) 3270–3220 (N–H), 1340 (SO_2), and 1165 cm^{-1} (SO_2); NMR (DMSO-d_6) δ 10.39, 9.93, and 9.86 (NH, 2 H, D_2O exchange), 7.89 (s, 4 H), 7.25–6.9 (m, 8 H), 2.24 (s), 2.03 (s), and 1.87 (s) (6 H); MS (70 eV) *m/e* 416 ($M\cdot^+$, 8), 107 (15), 106 (100), 79 (11), 78 (6), 77 (15).

Anal. Calcd for $C_{20}H_{20}N_2O_4S_2$: C, 57.67; H, 4.84. Found: C, 57.51; H, 4.68.

C. In Cyclohexane. A degassed solution of the *p*-diazide (1.006 g, 3.49 mmol) in dry cyclohexane (20 ml) was heated in an oil bath at 135° for 62 hr. The reaction mixture was worked up as before and chromatographed on silica gel (175 g). Benzene (50 ml) eluted an oil (0.038 g, 4.5%) which solidified on standing and whose ir, NMR, and mass spectra was identical with those of authentic *N*-cyclohexylbenzenesulfonamide.

Benzene–ether (1:1 v/v, 250 ml) and ether (150 ml) eluted *N,N'*-dicyclohexyl-*p*-benzenedisulfonamide (0.79 g, 55%) whose ir spectrum was identical with that of an authentic sample.

Methanesulfonation of Thallium(I) 3,4,5,6-Tetraphenyl-2-pyridone. Methanesulfonyl chloride (0.108 g, 0.94 mmol) in ether (5 ml) was added dropwise to a stirred heterogeneous solution of the title compound[21] (0.52 g, 0.86 mmol) in anhydrous ether (30 ml) ($CaCl_2$ drying tube). The reaction mixture was stirred at room temperature for 1.5 hr, methylene chloride (125 ml) was added, and the insoluble thallium(I) chloride was filtered. The filtrate was evaporated under vacuum to give a white solid which was chromatographed on silica gel (125 g). Benzene (275 ml) eluted **3,4,5,6-tetraphenyl-2-pyridyl methanesulfonate** (0.30 g, 72%): mp 208–209° (from $CHCl_3$–hexane); NMR ($CDCl_3$) δ 7.40–6.65 (m, 20 H), 3.45 (s, 3 H); MS (70 eV) *m/e* 477 ($M\cdot^+$, 92), 398 (100), 370 (8), 293 (23), 267 (27), 265 (31), 89 (10), 79 (12).

Anal. Calcd for $C_{30}H_{23}NO_3S$: C, 75.45; H, 4.85. Found: C, 75.51; H, 5.04.

Benzene–ether (1:1 v/v, 150 ml) and ether (250 ml) eluted 3,4,5,6-tetraphenyl-2-pyridone (0.086 g, 25%), identical with an authentic sample.

Similar results were obtained when the mesylation was carried out in homogeneous solution (dry benzene or $CHCl_3$).

Methanesulfonation of Thallium(I) 2-Pyridone. Methanesulfonyl chloride (0.54 g, 4.68 mmol) in ether (5 ml) was added dropwise to a stirred suspension of thallium(I) 2-pyridone[22] (1.77 g, 5.92 mmol) in anhydrous ether (50 ml). The reaction mixture was stirred at room temperature for 1 hr, and thallium(I) chloride and unreacted starting material were filtered and washed with anhydrous ether (25 ml). The combined filtrates were concentrated under vacuum to give a colorless oil which was chromatographed on silica gel (150 g). Benzene–ether (4:1 v/v, 100 ml) eluted a colorless oil (0.42 g, 52%) which solidified on standing. Recrystallization from ether at −78° gave **2-pyridyl methanesulfonate,** mp 52–53°.

Anal. Calcd for $C_6H_7NO_3S$: C, 41.61; H, 4.08. Found: C, 41.72; H, 4.22.

Benzene–ether (1:1 v/v, 150 ml) eluted a colorless oil (0.39 g, 48%) which crystallized from ether at −78° to give ***N*-methanesulfonyl-2-pyridone:** mp 68–69°; ir (KBr) 1670 (C=O), 1600 and 1580 (C=C), 1350 (SO_2), and 1170 cm^{-1} (SO_2).

Anal. Calcd for $C_6H_7NO_3S$: C, 41.61; H, 4.08. Found: C, 41.62; H, 4.19.

Isomerization of *N*-Mesyl-2-pyridone to 2-Pyridyl Methanesulfonate. A. In CH_2Br_2 at 135°. A solution of *N*-mesyl-2-pyridone (0.152 g) in freshly distilled CH_2Br_2 (10 ml) was heated at 135° for 30 hr. Evaporation gave an oil (0.153 g) which solidified (mp 52–53°) and whose infrared and NMR spectra were identical with those of 2-pyridyl methanesulfonate.

B. In the Absence of Solvent. A similar result was obtained by heating the *N*-mesyl derivative at 170–180° for 50 min, or by two distillations of the *N*-mesyl compound (bp 92° at 0.02 mm). In the first case, pure *O*-mesyl derivative was obtained; in the second, the ratio of *O*-:*N*-mesyl derivatives was 92:8 as indicated by the area ratios of the NMR peaks at δ 3.45 and 3.61.

***N*-Cyclohexylidene-*o*-aminobenzenesulfonamide (25).** A solution of *o*-aminobenzenesulfonamide[23] (0.505 g, 2.93 mmol) and cyclohexanone (0.52 g, 5.3 mmol) in benzene (25 ml) was boiled under reflux for 15 hr and cooled to room temperature, and the solvent was removed under vacuum to give a light tan solid. Recrystallization from chloroform gave white plates of ***N*-cyclohexylidene-*o*-aminobenzenesulfonamide (25,** 0.69 g, 93%): mp 204–206°; ir (KBr) 3365 and 3220 (NH_2), 1605 (C=N), 1340 (SO_2), and 1165 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.42 (d of d, H_3, $J_{3,4}$ = 8.0, $J_{3,5}$ = 1.0 Hz), 7.18 (d of d of d, H_4, $J_{4,5}$ = 7.0, $J_{4,6}$ < 0.5 Hz), 6.74 (d of d, H_6, $J_{5,6}$ = 8.5 Hz), 6.66 (d of d of d, H_5), 6.17 (NH_2, 2 H, D_2O exchange), 2.44–2.1 (m, 2 H), and 1.9–1.2 (m, 8 H); MS (70 eV) *m/e* 252 ($M\cdot^+$, 76), 223 (16), 210 (26), 209 (100), 196 (21), 172 (31), 170 (16), 156 (34), 145 (34), 108 (28), 96 (24), 93 (27), 92 (94).

Anal. Calcd for $C_{12}H_{16}N_2O_4S$: C, 57.14; H, 6.35. Found: C, 57.23; H, 6.47.

A solution of **25** (0.633 g, 2.51 mmol) in dry benzene (20 ml) was heated in a pressure tube in an oil bath at 135° for 35 hr. Concentration of the reaction mixture under vacuum gave unchanged starting material (0.63 g).

Attempted Reaction of *o*-Benzenedisulfonamide with Cyclohexanone. A degassed solution of *o*-benzenedisulfonamide (0.288 g, 0.966 mmol) and cyclohexanone (0.155 g, 1.58 mmol) in freshly fractionated cyclohexene (15 ml) was heated in an oil bath at 135° for 45 hr. Only starting materials were isolated. A similar result was obtained when acetonitrile was used as solvent.

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Registry No.—**1,** 21691-17-8; **2,** 53965-87-0; **3,** 751-38-2; **4,** 53965-88-1; **5,** 51954-59-7; **14a,** 53371-23-6; **14b,** 20877-39-8; **15a,** 53371-21-4; **15b,** 25795-97-5; **16b,** 53371-22-5; **21,** 53965-89-2; **22,** 53965-90-5; **25,** 53965-91-6; **28,** 53965-92-7; **29,** 53965-96-1; benzenamine, 62-53-3; cyclohexanamine, 108-91-8; *p*-benzenedisulfonyl chloride, 6461-77-4; *o*-benzenedisulfonyl chloride, 6461-76-3; tetracyclone, 479-33-4; *o*-aminobenzenesulfonamide, 3306-62-5; cyclohexanone, 108-94-1; methanesulfonyl chloride, 124-63-0.

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Base-Promoted Rearrangement of Arenesulfonamides of N-Substituted Anilines to N-Substituted 2-Aminodiaryl Sulfones[1]

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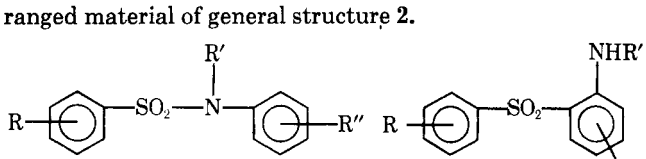
Arenesulfonamides of N-substituted aromatic amines react readily with lithium bases (e.g., methyllithium) in ether solvents to give N-substituted 2-aminodiaryl sulfones in quite respectable yield. The reaction is probably intramolecular, and involves formation of a dianion from the sulfonamide before rearrangement occurs. The immediate product of the rearrangement is a dianion with a carbanionic carbon ortho to the sulfonyl group in the nonamino ring. The reaction would appear to be the method of choice for synthesizing such amino sulfones, particularly when electron-donating groups are present. The NMR spectra of these amino sulfones indicate that the N–H proton is hydrogen bonded to a sulfone oxygen.

While previous work indicated that treatment of arenesulfonamides of unsubstituted anilines or of dialkylamines with strong bases (phenyl- or butyllithium) in THF resulted only in metalation ortho to the sulfonyl group[2] (or, in the case of *o*-toluenesulfonamides, at the *o*-methyl group),[3] we have observed that treatment of sulfonamides of general structure **1** with excess alkyl- or aryllithium in THF, followed by quenching with water, yields a rearranged material of general structure **2**.



1

2

a, R = R″ = H; R′ = CH_3
b, R = *p*-CH_3; R′ = CH_3; R″ = *p*-CH_3O
c, R = R″ = H; R′ = CH_3CH_2
d, R = *p*-CH_3; R′ = CH_3CH_2; R″ = H
e, R = *p*-CH_3O; R′ = CH_3CH_2; R″ = H
f, R = R″ = H; R′ = C_6H_5
g, R = *p*-$(CH_3)_2N$; R′ = CH_3; R″ = H
h, R = *p*-CH_3O; R′ = CH_3; R″ = H
i, R = *p*-CH_3O; R′ = CH_3; R″ = *p*-CH_3O
j, R = *o*-CH_3; R′ = CH_3; R″ = H
k, R = *p*-CH_3; R′ = CH_3; R″ = H

Initially, reactions were carried out by injecting a 2.5- to threefold excess of *n*-butyllithium (in hexane) into a solution of the sulfonamide in THF at 0°, allowing the mixture to stir for 5–15 min, and then quenching with water. Under these conditions **1a** gave about a 50% yield of **2a** as well as ca. 40% of *N*-methylaniline, presumably resulting from direct attack of the lithium alkyl on the sulfonamide sulfonyl group. Further investigation showed that methyl-, phenyl-, and *tert*-butyllithium, as well as the hindered bases derived from butyllithium and dicyclohexyl- and diisopropylamine, all brought about the rearrangement. Bases examined which did not cause rearrangement were sodium and lithium hydride, sodium amide, lithium metal, and methylmagnesium iodide. Phenylsodium caused very small amounts of rearrangement but its use was not examined in detail. Methyllithium proved to be the most economical and efficient reagent, a 97% yield (by gc) of **2a** being obtainable.

Table I
Yields and Properties of 2-Aminodiaryl Sulfones[a]

Sulfone	Base	Yield, %	Mp, °C	Registry no.
2a	CH_3Li	89	136–137	53973-76-5
2b	CH_3Li	61	150–151	53973-77-6
2c	CH_3Li	40	106–107	53973-78-7
2d	CH_3Li	81	87–88	53973-79-8
2e	CH_3Li	57	110–111	53973-80-1
2f	n-C_4H_9Li	86	79–80	52914-17-7
2g	n-C_4H_9Li	54	152–153	53973-81-2
2h	n-C_4H_9Li	45	144–145	53973-82-3
2i	n-C_4H_9Li	53	164–165	53973-83-4
2j[b]	CH_3Li	50	103–104	53973-84-5
2k	n-C_4H_9Li	52	134–135	53973-85-6

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all compounds in the table. [b] Prepared by methylating dianion of **2a** with methyl iodide.

In Table I are given isolated yields and physical properties of the aminosulfones. The reactions with methyllithium were most conveniently carried out at 25°, allowing about 2 hr for reaction before quencing. The sulfones were easily isolated by recrystallization and the progress of the reaction could readily be followed by TLC, all of the aminosulfones exhibiting a characteristic blue fluorescence on excitation by uv. Several of the entries in Table I involve use of butyllithium. The yields in these cases could probably be improved through use of methyllithium.

The major structural requirement of the sulfonamide for rearrangement was that the nitrogen be completely substituted. Sulfonamides of primary anilines merely formed the normal salt and were recovered unchanged. Halogen substituents did not survive, as would be expected, and alkyl groups ortho to the sulfonyl seriously interfered (vide infra).[3]

Proof of the structures of the aminosulfones was established by several means. The least substituted sulfone, **2a**,