Intramolecular Insertion of Arylsulfonylnitrenes into Aliphatic Side Chains[1]

Rudolph A. Abramovitch,* Therinadar Chellathurai, William D. Holcomb, Ian T. McMaster, and Danny P. Vanderpool

Department of Chemistry, University of Alabama, University, Alabama 35486

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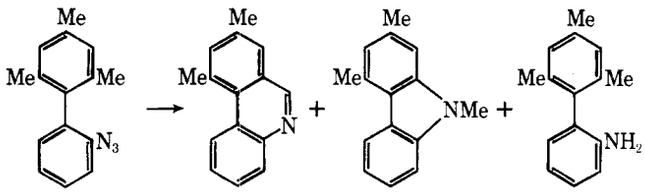
The thermolysis of *o*-methylbenzenesulfonyl azides in solution leads to the low-yield intramolecular insertion of the sulfonylnitrene into the ortho C–H group. Intermolecular insertion into, and hydrogen abstraction from, the solvent compete efficiently with cyclization. Curtius-type rearrangements of the sulfonyl azides have been observed and, in one case, the intermediate sulfonylimine (**15**) has been trapped as the sulfanilide (**14**). Sulfonyl azides are, therefore, no longer to be considered "rigid" azides. Intramolecular C–H insertion occurs also with an ortho cyclohexyl group to give a mixture of axial and equatorial isomers, but not into an ortho methoxyl, thiomethoxyl, or dimethylamino group. In the latter case, the sulfonylnitrene is trapped by the nucleophilic amine to give a zwitterion (**46**) which rearranges thermally to the *N,N'*-dimethyl compound **47**. Hydrogen abstraction and intermolecular insertion products, as well as products resulting from a free-radical decomposition of the sulfonyl azide, are also observed.

In the preceding paper[2] intramolecular aromatic substitution of arylsulfonylnitrenes was reported in the cases of the thermolysis and photolysis of 2-biarylsulfonyl azide. The present paper deals with some intramolecular insertions of arylsulfonylnitrenes into aliphatic side chains and the observation of Curtius-type rearrangements of sulfonyl azides in nonprotic solvents.

Results and Discussion

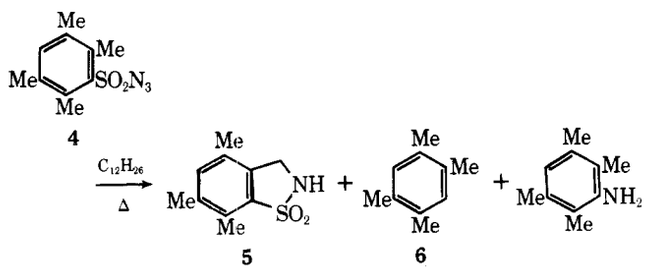
We first examined intramolecular insertions into a methyl group ortho to the sulfonyl azide. Intramolecular arylnitrene insertion into a suitably located methyl group has been reported previously. Thus, 2-azido-2',4',6'-trimethylbiphenyl gives the phenanthridine **1** (48%), as well as the carbazole **2**



1 **2** **3**

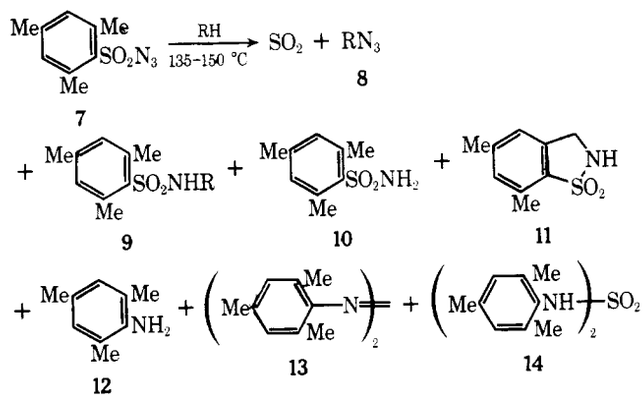
(5%) and the hydrogen-abstraction product **3** (29%) on thermolysis.[3] Similar cyclizations to give phenanthridines and indolines have also been reported.[4] On the other hand, thermolysis of 2-azido-*m*-xylene led only to polymer formation, which can readily be understood in terms of the geometrical constraints imposed by a C–H insertion process, so that hydrogen abstraction leading to an *o*-quinone imine methide can occur and thence lead to polymer. Such geometrical constraints should not apply to toluene-*o*-sulfonylnitrenes so that C–H insertion was expected to occur, at least to a moderate extent, and thus open up a new route to 2,3-dihydro-1,2-benzoisothiazole 1,1-dioxides.

Durene-3-sulfonyl azide (**4**) was readily prepared from the sulfonyl chloride (76% overall from durene). Thermolysis of **4** in *n*-dodecane gave the desired C–H insertion product **5**



4 **5** **6**

Scheme I



7 **8** **9** **10** **11** **12** **13** **14**

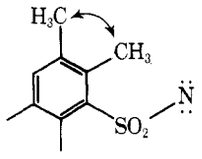
(10–15%), together with some durene (**6**) (12–36%) and some 3-aminodurene (11%). The hydrocarbon probably arises by a competing radical process: $ArSO_2N_3 \rightarrow N_3\cdot + ArSO_2\cdot \rightarrow SO_2 + Ar\cdot \rightarrow ArH$.[1,2] The amine undoubtedly results from a Curtius-type rearrangement (see below).

The thermolysis of mesitylene-2-sulfonyl azide (**7**) was studied in much greater detail (Scheme I). When **7** was heated in *n*-dodecane at 150 °C at atmospheric pressure seven products were isolated: SO_2 (18–22%), a mixture of dodecyl azides (**8**, R = $C_{12}H_{25}$) (2–4%), *N*-dodecylmesitylene-2-sulfonamides (**9**, R = $C_{12}H_{25}$) (19–23%), mesitylene-3-sulfonamide (**10**) (1–3%), 2,3-dihydro-5,7-dimethyl-1,2-benzoisothiazole 1,1-dioxide (**11**) (2–3%), mesitylamine (**12**) (18–21%), and 2,2',4,4',6,6'-hexamethylazobenzene (**13**) (trace). When the reaction was repeated in degassed *n*-dodecane in a sealed tube at 150 °C, one additional product was obtained, namely, 2,2',4,4',6,6'-hexamethylsulfanilide (**14**) (33%). These results, as well as the thermolyses of **7** in cyclohexane and benzene at 135 °C, are summarized in Table I.

These results make clear a number of points, the main one being that the geometry for intramolecular insertion into an ortho methyl group is still not that favorable as to compete very effectively with intermolecular processes. In all cases, though the desired cyclization product was obtained, the main products were those of intermolecular insertion or hydrogen abstraction, or of rearrangement. In this connection, it is interesting to note that the yield of intramolecular insertion product form durene-3-sulfonyl azide, though low, is appreciably (and reproducibly) higher than that from mesitylene-2-sulfonyl azide under otherwise identical conditions. This would suggest that some buttressing effect (A) by the 3-methyl group brings the ortho methyl closer to the nitrene nitrogen,

Table I. Thermolysis of Mesitylene-2-sulfonyl Azide in Various Solvents

Solvent RH	Temp, °C	Yield, % 8	9	10	11	12	13	14
n-Dodecane (1 atm)	150	2–4	19–23	1–3	2–3	18–21	Tr	0
n-Dodecane (pressure)	150	Tr	21	Tr	4	2.2	Tr	33
n-Dodecane (pressure)	135	Tr	22	1	3	Tr	2.2	32
Cyclohexane (pressure)	150	0	27	0	7.7	3.1	Tr	43
Cyclohexane (pressure)	135	0	27	1	5	3	0	43
Benzene (pressure)	135	0	2	10	1	12	0	10



A

facilitating insertion somewhat relative to the mesitylene derivative. Formation of **8** supports the mechanism for loss of SO_2 proposed by Breslow and his co-workers.[5]

$$R'\cdot + RSO_2N_3 \rightarrow R'N_3 + RSO_2\cdot$$

$$RSO_2\cdot \rightarrow R\cdot + SO_2$$

$$R'H + R\cdot \rightarrow R'\cdot + RH$$

The source of the original alkyl radical could be hydrogen abstraction by the triplet sulfonyl nitrene formed from the originally generated singlet by intersystem crossing, or triplet arylnitrene formed as discussed below. Such a mechanism accounts also for the formation of *some* of the SO_2 (vide infra), of the sulfonamide **10**, and of durene (**6**).

Formation of aniline (**12**), azobenzene (**13**), and sulfanilide (**14**) are all best accounted for by a Curtius-type rearrangement of the sulfonylnitrene to the unstable sulfonylaniline (**15**). This can either lose SO_2 (the balance of the SO_2 isolated) to give the arylnitrene which can hydrogen abstract or dimerize[6] to give **12** and **13**, respectively. When the reaction is carried out in a sealed tube to prevent loss of SO_2, decomposition of **15** is apparently either sufficiently retarded or is reversible so that **15** can trap the aniline formed giving the sulfanilide (**14**). An attempt was made to synthesize authentic **14** but treatment of **12** with sulfuryl chloride in pyridine at −5 to 0 °C[7] gave none of the desired sulfanilide, the only product isolated being the azobenzene (**13**). Others[8] also reported low

$$ArSO_2\ddot{N}: \rightarrow ArN{=}SO_2 \longrightarrow \longrightarrow \mathbf{12} + \mathbf{13}$$

15

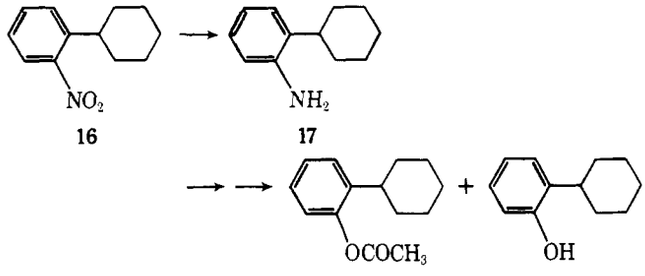
$\downarrow$ 12

14

yields of azobenzene in this type of reaction (in ether solvent) but did get good yields of the corresponding sulfanilide. The structure of our sulfanilide is supported by microanalysis, its infrared spectrum [ν_{NH} 3255 cm^{-1}, ν_{SO_2} (1295, 1140 cm^{-1})], its mass spectrum [$M^{+}\cdot$ 332, *m/e* 134 (100) ($Me_3C_6H_2NH^+$)], and its NMR spectrum [4 H singlet at δ 6.92 (ArH), 2 H singlet (exchangeable) at δ 5.91 (NH), 12 H singlet at δ 2.33 (ortho CH_3), 6 H singlet at δ 2.27 (para CH_3)].

Until part of the present work was originally published[1] sulfonyl azides were generally thought to be "rigid" (Curtius' "starre" azides[9]), i.e., they did not undergo Curtius-type rearrangements. Photolysis of benzenesulfonyl azide in methanol did give *N*-methoxysulfamate,[10] and decomposition of the triethylammonium salt of *N*-*p*-nitrobenzenesulfonoxybenzenesulfonamide in methanol, ethanol, and aniline gave products derived from a Lossen-type rearrangement to sulfurylaniline.[10] It was felt[10] that these rearrangements involved a protonated species and not a free sulfonylnitrene. The vapor-phase pyrolysis of benzenesulfonyl azide at 625 °C gave a 17.5% yield of azobenzene,[11] and trace amounts of the latter could be obtained by boiling the azide in cyclohexanone.[12] The work reported here shows that sulfonyl nitrenes will indeed also undergo the Curtius rearrangement readily in nonprotic solvents provided that competing reactions are rendered less likely.

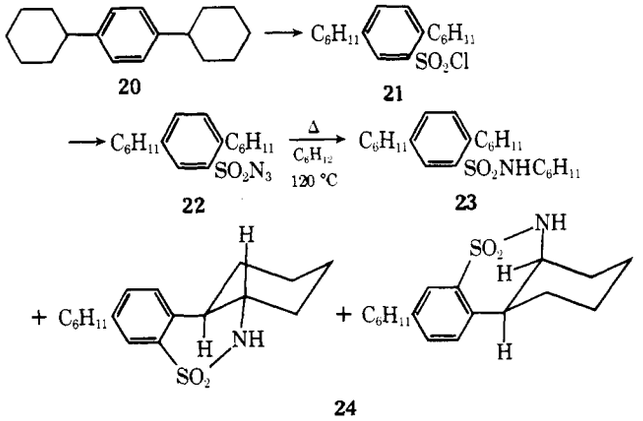
It was next attempted to determine whether, if a choice were available, C–H insertion by a sulfonylnitrene would occur at the more reactive α proton of an ortho isopropyl side chain or at the more accessible β proton. To this end we attempted to prepare 2-cyclohexylbenzenesulfonyl azide. Nitration of cyclohexylbenzene gave a mixture of *o*- and *p*-nitrocyclohexylbenzenes which were resolved by preparative gas–liquid chromatography. The *o*-nitro derivative (**16**) was reduced to the primary amine (**17**) which, on diazotization and treatment with SO_2 in acetic acid and benzene containing $CuCl_2$,[13] did not give the desired sulfonyl chloride. Instead, a mixture of *o*-acetoxyphenylcyclohexane (**18**) and the corresponding phenol (**19**) was obtained. When the solid diazonium tetrafluoroborate of **17** was decomposed similarly (but in the absence of water) **18** (47%) was the only product isolated. Attempted chlorosulfonation of *p*-nitrocyclohexylbenzene with $ClSO_3H$ in $CHCl_3$ at 60 °C or in cyclohexane at 80 °C gave only starting material; at 110 °C tarry products were obtained.



16 **17**

18 **19**

Chlorosulfonation of *p*-dicyclohexylbenzene (**20**) with $ClSO_3H$ in $CHCl_3$ at 0–55 °C failed. At 80 °C in $(CH_2Cl)_2$ the product formed analyzes correctly for a 4-cyclohexylbiphenyldisulfonyl chloride. Successful chlorosulfonation could be



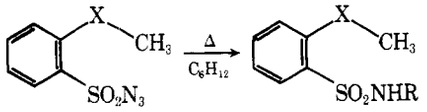
20 **21**

22 **23**

24

effected, however, in cyclohexane at 80 °C, whereby an 80% yield of **21** was obtained. This was converted readily to the azide **22,** thermolysis of which in cyclohexane gave the *intermolecular* insertion product **23** (48%), and a mixture (cis and trans) of the intramolecular insertion products (**24**) (9%) which could not be resolved. Insertion does appear to have occurred at the β-C–H position since **24** exhibits a signal for two benzylic protons in the NMR.

2-Methoxy- (**25**) and 2-methylthiobenzenesulfonyl azide (**26**) were synthesized and thermolyzed. The methoxy derivative **25** (from *o*-anisidine) was decomposed in cyclohexane at 130 °C to give *N*-cyclohexyl-2-methoxybenzenesulfonamide (**27**) (42%) together with much tar. Its decomposition in Freon E 3 at 130 °C gave only tarry products. Similar thermolysis of the methylthio derivative **26** (prepared from *o*-chloronitrobenzene with sodium thiomethoxide followed by reduction to the amine, diazotization, modified Meerwein reaction, and treatment of the sulfonyl chloride with sodium azide) in cyclohexane at 130 °C gave *N*-cyclohexyl-2-methylthiobenzenesulfonamide (**28**) (20%) and 2-methylthiobenzenesulfonamide (**29**) (21%). Interestingly, no attack by the nitrene or the azide occurred at the ortho sulfur atom (cf. ref 1). Neither was any intramolecular C–H insertion product observed in either of these cases.



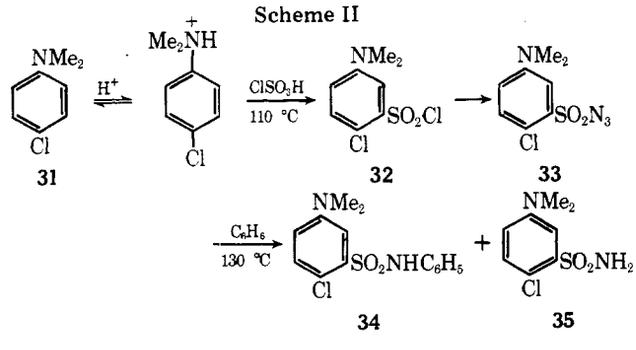
25, X = O
26, X = S
30, X = NMe

27, X = O; R = C_6H_{11}
28, X = S; R = C_6H_{11}
29, X = S; R = H

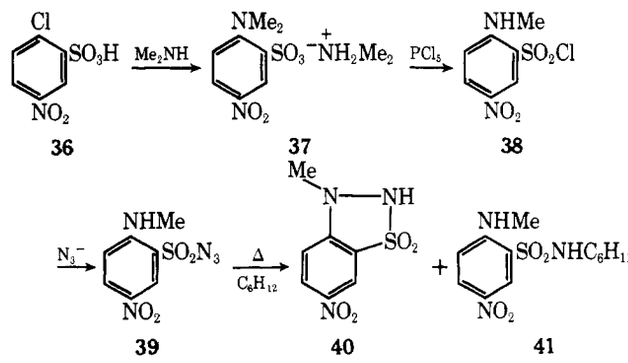
We next turned our attention to the synthesis and decomposition of *N,N*-dimethylaniline-2-sulfonyl azides (**30**). A number of attempts to chlorosulfonate *N,N*-dimethyl-*p*-nitroaniline and *p*-chloro-*N,N*-dimethylaniline (**31**) failed. Chlorosulfonation of **31** with chlorosulfonic acid for 18 h at 110 °C gave 4-chloro-*N,N*-dimethylaniline-3-sulfonyl chloride (**32**) (20%). Presumably, the amino group is protonated under these conditions and electrophilic substitution occurs meta to the ammonium ion. The sulfonyl chloride was converted to the azide (**33**) which was thermolyzed in benzene at 130 °C to give products of insertion into the solvent (**34**) (14%) and hydrogen abstraction (**35**) (15%) (Scheme II). The fact that none of the characteristic products obtained from the thermolysis of *o*-dimethylaminobenzenesulfonyl azides (see below) are formed in this reaction confirms the orientation assigned to **32.**

Treatment of 2-chloro-5-nitrobenzenesulfonic acid (**36**) with dimethylamine gave the dimethylammonium salt of 2-dimethylamino-5-nitrobenzenesulfonic acid (**37**), which, with PCl_5, gave 2-methylamino-5-nitrobenzenesulfonyl chloride (**38**), mono-N-demethylation accompanying chlorination. The secondary amine so formed could not be N-acetylated or N-mesylated with Ac_2O and $MeSO_2Cl$, respectively. It was converted to the sulfonyl azide (**39**), which, on thermolysis in

Scheme II

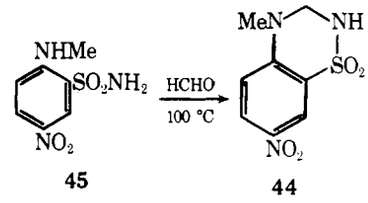


Scheme III



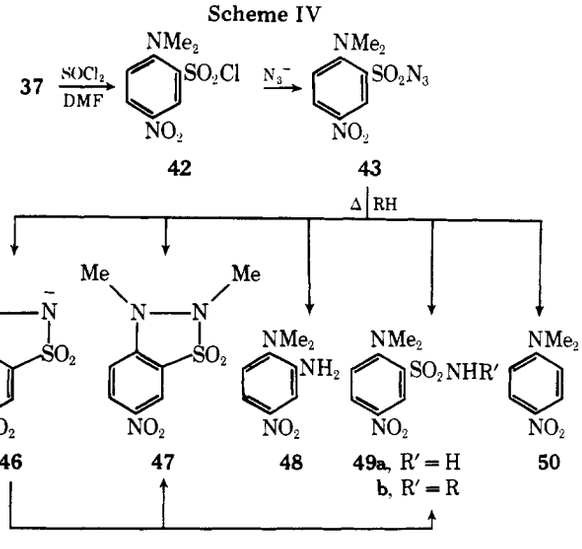
cyclohexane at 135 °C, gave **40** (30%) and **41** (10%) (Scheme III).

Heating **37** with thionyl chloride and dimethylformamide gave the desired sulfonyl chloride (**42**) which was converted to the azide (**43**). Thermolysis of **43** in cyclohexane or benzene at 120 °C gave an array of products shown in Scheme IV. Again, as with **25** and **26,** no product of intramolecular C–H insertion (**44**) was observed. An authentic sample of **44** was



prepared from 2-methylamino-5-nitrobenzenesulfonamide (**45**) and formaldehyde. After this work was completed, Martin, Meth-Cohn, and Suschitzky[14] reported the thermolysis of a number of 2-dialkylamino-5-nitrosulfonyl azides with results somewhat similar to the above. They prepared their sulfonyl azides from 2-chloro-5-nitrobenzenesulfonyl azide and the secondary amine. Of great interest was the fact that their 2-*N*-pyrrolidyl derivative did undergo intramolecular C–H insertion (13%) but that, as also reported here, the *N,N*-dimethyl derivative **43** did not. These authors did not obtain a product corresponding to **47** above. Indeed, the only product they reported isolating from the thermolysis of **43** itself was **46.** Both **47** and **49a** arise from **46** as shown by the thermolysis of the latter in cyclohexane at 130 °C. The electrophilic nitrene is trapped by the nucleophilic amino group to give the ylide **46,** a process for which there is precedent.[15] The amine **48** probably arises as discussed above via a Curtius-type rearrangement, while formation of **50** most likely involves a free-radical process. The 1,2-alkyl shift **46** → **47** is

Scheme IV



not unexpected. One unusual feature is the absence of solvent insertion product **49b** (R′ = C_6H_5) when benzene is used as the solvent but its formation (**49b**, R′ = C_6H_{11}) in cyclohexane since it has been estimated[16] that a singlet sulfonylnitrene adds to a benzene double bond about eight times as fast as it inserts into a cyclohexane C–H bond.

Experimental Section

Melting points are uncorrected.

Durene-3-sulfonyl Azide (4). Sodium azide (1.30 g) in water (10 mL) was poured into a stirred solution of durene-3-sulfonyl chloride[17] (4.65 g) in acetone (50 mL) at room temperature and the mixture was stirred for a further 10 h. It was then concentrated in vacuo down to one-third of its volume and poured into water (20 mL) and the precipitated solid was filtered, washed with water, and dried to give the azide (4.83 g, 100%): mp 68.5 °C (EtOH); IR (KBr) 2330, 2120, 1350, 1155 cm^{-1}.

Anal. Calcd for $C_{10}H_{13}N_3O_2S$: C, 50.21; H, 5.44. Found: C, 50.58; H, 5.76.

Thermolysis of Durene-3-sulfonyl Azide in *n*-Dodecane. A suspension of **4** (1.195 g) in *n*-dodecane (25 mL) was heated with stirring at 150 °C for 21 h. The mixture was cooled to room temperature and chromatographed on a column of neutral alumina (140 g). Elution with light petroleum gave *n*-dodecane. Further elution with light petroleum gave durene **6** (0.083 g, 12%), mp 78–79 °C (sublimation, then recrystallization from aqueous EtOH), identical with an authentic sample. Elution with ether gave a light brown solid (0.072 g) which crystallized from EtOH as a buff solid (0.053 g), mp 157–198 °C. Vacuum sublimation gave a colorless solid (0.042 g): mp 190–202 °C; mass spectrum M^+· *m/e* 360; IR (KBr) 3310, 3260, 1290, 1170, 1160 cm^{-1}. This was not characterized further. Elution with ether gave 3-aminodurene (11%), identical with an authentic sample. Elution with ether–methanol (95:5 v/v) gave **2,3-dihydro-4,6,7-trimethyl-1,2-benzoisothiazole 1,1-dioxide** (**5**, 0.153 g, 15%): mp 229.5–230 °C (vacuum sublimation and recrystallization from EtOH); mass spectrum M^+· *m/e* 211; IR (KBr) 3270, 1305, 1285, 1160 cm^{-1}; NMR (acetone-d_6) δ 8.04 (s, 1, NH), 7.52 (s, 1, ArH), 4.54 (s, 2, CH_2), 2.68 (s, 3, CH_3), 2.55 (s, 3, CH_3), 2.49 (s, 3, CH_3).

Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.87; H, 6.16. Found: C, 56.91; H, 6.38.

Mesitylene-2-sulfonyl Azide (7). This was prepared from mesitylene-2-sulfonyl chloride as for **4** above. The azide (79%) had bp 79–80 °C (22 μ); IR (film) 2120 (N_3), 1360, 1165 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.06 (s, 2, ArH), 2.68 (s, 6, 2 CH_3), 2.35 (s, 3, CH_3); mass spectrum *m/e* (rel intensity) 225 (M^+·, 3.5), 197 (3), 183 (20), 119 (100), 91 (28).

Anal. Calcd for $C_9H_{11}N_3O_2S$: C, 47.99; H, 4.95. Found: C, 47.98; H, 4.77.

Thermolysis of Mesitylene-2-sulfonyl Azide. A. In *n*-Dodecane at 1 Atm. The azide **7** (4.402 g) in *n*-dodecane (37.8 g) was placed in a thermolysis vessel connected to sulfur dioxide traps filled with 5% aqueous NaOH solution (25 mL each), the system was purged with dry, O_2-free nitrogen, and the thermolysis vessel was immersed in an oil bath at 150 °C and kept at that temperature for 20 h, at which time no more nitrogen was evolved. The volume of N_2 collected over water at 25 °C corrected to STP was 408 mL (93%). The system was cooled and purged with dry, O_2-free N_2 for 30 min to remove any further SO_2. The SO_2 traps were each transferred to 250-mL flasks, rinsed with water (2 × 25 ml), and hydrogen peroxide (30%, 1 mL) was added to each flask (and to a blank). After stirring the solutions for 5 min at room temperature they were acidified with 3 N HCl and heated almost to boiling and $BaCl_2$ solution (2.61 g/100 mL) was added with stirring until no more precipitate formed. Gravimetric workup of the $BaSO_4$ as usual gave a yield of 22.5% of SO_2.

The reaction mixture was chromatographed on a column of neutral alumina (2.5 × 45 cm). Elution with light petroleum (bp 30–60 °C) gave first *n*-dodecane, followed by a mixture of dodecyl azides (**8**, 0.098 g, 1.5%): bp 50 °C (20 μ); IR (film) 2960, 2940, 2860, 2100, 1260, 665 cm^{-1}; mass spectrum *m/e* (rel intensity) 183 (M^+· − 28, 0.9), 182 (1.3), 168 (4), 154 (14), 140 (14), 126 (16), 112 (21), 98 (28), 85 (14), 84 (35), 71 (42), 70 (40), 69 (13), 58 (10), 57 (100), 56 (37), 55 (29).

Elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave 2,2′,4,4′,6,6′-hexamethylazobenzene (**13**, 0.006 g), identical (IR and mass spectrum) with an authentic sample.[18] Elution with benzene–trichloroethylene (95:5 v/v) gave 2,4,6-trimethylaniline (**12**, 0.469 g), identical [IR, NMR, mass spectrum, and GLC retention time on an OV-17 (10%) on Gas Chrom Q column] with an authentic sample (Aldrich). Elution with benzene–ether (85:15 v/v) gave a viscous oil of ***N*-dodecylmesitylene-2-sulfonamides** (1.414 g, 19.5%): bp 150–152 °C (9 μ); IR (film) 3300, 2970, 2930, 2865, 1325, 1165 cm^{-1}; NMR ($CDCl_3$) δ 6.98 (s, 2, ArH), 4.58–4.44 (d, 1, $J_{H,NH}$ = 8 Hz, exchanges with D_2O, NH), 3.35–2.95 (br s, 1, RR′C**H**NH), 2.67 (s, 6, 2 CH_3), 2.30 (s, 3, CH_3), 1.6–0.9 (br m, 24); mass spectrum *m/e* (rel intensity) 367 (M^+·, 0.3), 352 (0.9), 338 (0.8), 324 (9), 310 (9), 296 (9), 282 (9), 268 (12), 254 (15), 183 (27), 135 (64), 134 (41), 120 (64), 105 (13), 91 (22), 77 (14).

Anal. Calcd for $C_{21}H_{37}NO_2S$: C, 68.62; H, 10.15. Found: C, 68.68; H, 10.12.

Elution with ether gave mesitylene-2-sulfonamide (0.113 g, 30%), identical with an authentic sample.[19] Elution with ether–methanol (98:2 v/v) gave a tan solid which was sublimed (110 °C at 10 μm) and recrystallized from light petroleum (bp 60–110 °C)–ethyl acetate to give colorless needles of **2,3-dihydro-5,7-dimethyl-1,2-benzoisothiazole 1,1-dioxide** (0.118 g, 3.1%): mp 114.5–115.5 °C; IR (KBr) 3220, 1280, 1170 cm^{-1}; NMR ($CDCl_3$) δ 7.1 (s, 1, ArH), 7.01 (s, 1, ArH), 5.3–4.9 (br s, 1, exchanges with D_2O, NH), 4.46 (d, 2, $J_{C_3H,NH}$ = 5.6 Hz, becomes singlet on D_2O exchange, C_3H, NH), 2.60 (s, 3, CH_3), 2.41 (s, 3, CH); mass spectrum *m/e* (rel intensity) 197 (M^+·, 4.5), 196 (2), 58 (23), 43 (100).

Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.96; H, 5.88.

B. In *n*-Dodecane under Pressure. Mesitylene-2-sulfonyl azide (1.997 g) was dissolved in *n*-dodecane (40 mL), and the solution was degassed and flushed with dry, O_2-free nitrogen and thermolyzed in a glass-lined steel bomb at 135 °C with stirring under a N_2 atmosphere for 16 h. The thermolysis solution was pale yellow and contained much black solid and a few white crystals in suspension. The odor of SO_2 was detected when the bomb was opened. The whole suspension was chromatographed on a column of neutral alumina (2.3 × 25 cm). Elution as above gave dodecyl azides (0.045 g, 2%), 2,2′,4,4′,6,6′-hexamethylazobenzene (trace), 2,4,6-trimethylaniline (0.026 g, 2.2%), *N*-dodecylmesitylene-2-sulfonamides (0.722 g, 22%), and a series of fractions which were not resolved but recombined and rechromatographed on a column of neutral alumina (2.3 × 25 cm). Elution with benzene–ethyl acetate (85:15 v/v) gave a tan solid which was recrystallized from light petroleum (bp 60–110 °C) to give **2,2′,4,4′,6,6′-hexamethylsulfanilide** (**14**, 0.484 g, 32%): mp 164–166 °C; IR (KBr) 3255, 1295, 1140 cm^{-1}; NMR discussed in text; mass spectrum *m/e* (rel intensity) 332 (M^+·, 6), 136 (12), 135 (55), 134 (100), 120 (27).

Anal. Calcd for $C_{18}H_{24}N_2O_2S$: C, 65.03; H, 7.28. Found: C, 65.49; H, 7.43.

Elution with ethyl acetate gave mesitylene-2-sulfonamide (0.017 g, 1%), identical with an authentic sample. Elution with ethyl acetate–ethanol (98:2 v/v) gave 2,3-dihydro-5,7-dimethyl-1,2-benzoisothiazole 1,1-dioxide (0.046 g, 2.6%).

C. In Cyclohexane under Pressure. The reaction was carried out as under B above except that cyclohexane (40 mL) was used as the solvent. The results are summarized in Table I. ***N*-Cyclohexylmesitylene-2-sulfonamide** (**9**, R = C_6H_{11}) (27%) eluted with benzene–ethyl acetate (85:15 v/v) and had mp 95–96 °C [from light petroleum (bp 60–110 °C)]; IR (KBr) 3260, 1310, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.00 (s, 2, ArH), 4.8–4.0 (br s, 1, exchanges with D_2O, NH), 3.3–2.9 (br s, 1, CHN<), 2.69 (s, 6, 2 CH_3), 2.32 (s, 3, CH_3), 2.0–0.9 (br m, 10); mass spectrum *m/e* (rel intensity) 281 (M^+·, 12), 238 (13), 183 (21), 120 (26), 119 (100), 118 (34), 105 (24), 98 (31), 91 (30), 77 (23), 57 (39), 56 (26), 55 (41).

Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.23. Found: C, 63.92; H, 8.19.

An authentic sample was prepared in 77% yield from mesitylene-2-sulfonyl chloride and cyclohexylamine.

Attempted Preparation of 2,2′,4,4′,6,6′-Hexamethylsulfanilide. Sulfuryl chloride (2.33 g) was slowly added dropwise to a stirred solution of 2,4,6-trimethylaniline (4.82 g) in dry pyridine (20 mL) cooled in an ice–salt bath. After stirring for 30 min the temperature of the solution was allowed to reach that of the room, and the solution was poured into 3 N HCl (100 mL) and extracted with $CHCl_3$ (3 × 50 mL). The extracts were dried ($CaCl_2$), evaporated, and chromatographed on neutral alumina (2.3 × 25 cm). Elution with light petroleum–benzene (85:15 v/v) gave the azobenzene **13** (0.338 g, 8%), mp 73–74 °C, identical with an authentic sample.[18] No **14** could be detected.

Attempted Preparation of 2-Cyclohexylbenzenesulfonyl Chloride. 2-Cyclohexylnitrobenzene (**16**) was prepared from cyclohexylbenzene and fuming nitric acid by the method of Neunhoeffer.[21] It was purified from traces of para isomer remaining after distillation on a spinning band column by preparative gas–liquid chromatography. It was reduced[13b] to 2-cyclohexylaniline (85%), bp 89–90 °C (0.15 mm). The amine (1.3 g) in 20% aqueous HCl (10 mL) at 0 °C was diazotized with sodium nitrite (1 g) in water (5 mL). The solution was added to a cold solution of acetic acid (20 mL) and cupric chloride

(0.25 g). The solution was stirred for 1 h at 0–5 °C and for 3 h at 40 °C, and then poured into water (100 mL). It was extracted with ether, and the ether was dried (Na_2SO_4) and distilled. The residue was chromatographed on a column of silica gel (30 g). Elution with light petroleum–benzene (1:1 v/v) gave *o*-acetoxyphenylcyclohexane (**18**, 0.54 g, 33%), identical with an authentic sample prepared[22] by acetylation of the phenol. Elution with benzene gave *o*-cyclohexylphenol (**19**, 0.2 g, 15%), mp 56–57 °C (from light petroleum), identical with an authentic sample.[23]

The dry diazonium tetrafluoroborate (1.9 g) was prepared (95%) from the amine **17**. It was added at 0 °C to the above solution of SO_2, stirred for 1 h at 0 °C, and then heated at 50 °C for 1 h. Workup as above gave **18** (0.76 g, 47%) as the only identifiable product.

Chlorosulfonation of *p*-Dicyclohexylbenzene. A. In Ethylene Chloride. *p*-Dicyclohexylbenzene (1 g) in ethylene chloride (25 mL) was cooled in an ice bath and treated dropwise with chlorosulfonic acid (6 mL). The mixture was heated at 80 °C for 1 h, poured over ice, and extracted with ether. The dried (Na_2SO_4) ether extract was evaporated and chromatographed on a silica gel column (30 g). Elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave 4-cyclohexylbiphenyldisulfonyl chloride (0.35 g): mp 145–146 °C [light petroleum (bp 60–110 °C)]; NMR ($CDCl_3$) δ 8.2 (s, 1), 7.9 (d, 1), 7.8–7.5 (m, 5 H), 2.1–1.0 (m, 11 H); M^+· *m/e* 432 (2 ^{35}Cl).

Anal. Calcd for $C_{18}H_{18}Cl_2O_4S_2$: C, 49.93; H, 4.17. Found: C, 50.22; H, 4.36.

B. In Cyclohexane. *p*-Dicyclohexylbenzene (1 g) in cyclohexane (20 mL) at 0 °C was treated dropwise with chlorosulfonic acid (6 mL) and the mixture was then heated at 80 °C for 3 h. Workup as above followed by chromatography on silica gel (30 g) and elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave **1,4-dicyclohexylbenzene-2-sulfonyl chloride** (**21**, 1.13 g, 80%), mp 99–100 °C, M^+· (^{35}Cl) *m/e* 340.

Anal. Calcd for $C_{18}H_{25}ClO_2S$: C, 63.41; H, 7.39. Found: C, 63.25; H, 7.56.

1,4-Dicyclohexylbenzene-2-sulfonyl Azide (22). The sulfonyl chloride (1 g) in acetone (25 mL) at 0 °C was treated with sodium azide (1 g) in water (5 mL) and the mixture stirred for 1 h at 0 °C. It was then diluted with ice water (75 mL) and extracted with ether. The dried (Na_2SO_4) ether extract was evaporated to give the azide (0.87 g, 85%), mp 62–63 °C (MeOH), M^+· *m/e* 347.

Anal. Calcd for $C_{18}H_{25}N_3O_2S$: C, 62.20; H, 7.25. Found: C, 62.22; H, 7.28.

Thermolysis of 1,4-Dicyclohexylbenzene-2-sulfonyl Azide. The azide (1 g) in freshly distilled cyclohexane (20 mL) was heated in a glass-lined steel bomb under dry, O_2-free nitrogen for 72 h at 120 °C. The solvent was evaporated and the residue chromatographed on a column of silica gel (40 g). Elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave unchanged azide (0.1 g, 10%). Elution with benzene gave ***N*,1,4-tricyclohexylbenzene-2-sulfonamide** (**23**, 0.5 g, 48%): mp 145–146 °C (aqueous MeOH); M^+· *m/e* 403; identical with an authentic sample prepared (50% yield) from the sulfonyl chloride (**21**) and cyclohexylamine in boiling benzene for 12 h.

Anal. Calcd for $C_{24}H_{37}NO_2S$: C, 71.42; H, 9.24. Found: C, 71.58; H, 9.39.

Elution with benzene–ether (1:1 v/v) gave a mixture of sultams (**24**) (0.077 g, 9%), mp 65–85 °C (dilute EtOH or MeOH), which could not be resolved: IR (KBr) 3300 (s) (NH), 1325, 1160, 1150 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.6–7.2 (m, 3, ArH), 5.2 (d, 0.75, exchanges with D_2O, NH), 5.06 (s, 0.25, exchanges with D_2O, NH), 3.4 (br m, 0.25, equatorial (?) CHN<), 2.6 (br m, 0.75, axial (?) CHN<, overlapping with 2 H due to benzylic protons), 2.2–1.0 (br m, 18); mass spectrum *m/e* (rel intensity) 321 (M^+· + 2, 6), 320 (M^+· + 1, 8), 319 (M^+·, 32), 278 (20), 277 (100), 256 (35), 255 (M^+· − SO_2, 20), 197 (31), 142 (22), 130 (25), 78 (35), 57 (25), 56 (39), 55 (50), 43 (48), 41 (64).

Anal. Calcd for $C_{18}H_{25}NO_2S$: C, 67.67; H, 7.90. Found: C, 67.48; H, 8.07.

2-Methoxybenzenesulfonyl Azide (25). 2-Methoxybenzenesulfonyl chloride[24] (2.5 g) in acetone (60 mL) at 0 °C was treated with a solution of sodium azide (2.5 g) in water (15 mL) and stirred for 1 h at 0 °C. It was then poured into water (100 mL) and extracted with ether. The dried (Na_2SO_4) extract was evaporated to give the azide (2.2 g, 85%): mp 75–76 °C (MeOH); IR (KBr) 2140 (N_3), 1360, 1160 cm^{-1} (SO_2); M^+· *m/e* 213 (8).

Anal. Calcd for $C_7H_7N_3O_3S$: C, 39.43; H, 3.31. Found: C, 39.53; H, 3.42.

Thermolysis of 2-Methoxybenzenesulfonyl Azide. The azide (1 g) in cyclohexane (20 mL) under dry, O_2-free N_2 was heated in a glass-lined steel bomb at 120 °C for 72 h. The solvent was evaporated and the black residual mass was chromatographed on a column of silica gel (40 g). Elution with benzene–ether (1:1 v/v) gave ***N*-cyclohexyl-2-methoxybenzenesulfonamide** (**27**, 0.53 g, 42%): mp 103–104 °C (dilute MeOH); IR (KBr) 3280 (NH), 1320, 1160 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.9 (dd, 1), 7.5 (m, 1), 7.04 (m, 2), 5.1 (d, 1, exchanges with D_2O, NH), 3.96 (s, 3, OCH_3), 3.1 (br m, 1, CH<), 1.73–1.2 (m, 10); mass spectrum *m/e* (rel intensity) 271 (1), 270 (3), 269 (M^+·, 17), 226 (76), 177 (100), 92 (22), 79 (24), 77 (97).

Anal. Calcd for $C_{13}H_{19}NO_3S$: C, 57.96; H, 7.11. Found: C, 58.39; H, 7.24.

An authentic sample of **27** was prepared (84% yield) from the sulfonyl chloride and cyclohexylamine in boiling benzene and was identical with the above product.

2-Thiomethoxybenzenesulfonyl Chloride. 2-Nitrothioanisole[25] (5.5 g) in ethanol (10 mL) was treated with iron powder (14 g) and then 10% HCl (8 drops) and the mixture was boiled under reflux for 20 h. It was cooled, ether (75 mL) was added, and the mixture was filtered through a plug of cotton. The filtrate was extracted with ether, and the combined ether extracts were dried (Na_2SO_4) and evaporated to give 2-aminothioanisole (3.3 g, 73%). This was used without further purification. It was dissolved in glacial acetic acid (15 mL) and concentrated HCl (6 mL), and the solution was cooled to 0 °C and diazotized with sodium nitrite (2.7 g) in water (15 mL). The solution was added at 0 °C to acetic acid (60 mL) and cupric chloride (0.66 g). After 0.5 h at 0 °C the mixture was stirred at 45 °C for 2 h and then poured into ice–water (200 mL). It was extracted with ether and the dried (Na_2SO_4) extracts were evaporated. The semisolid residue was chromatographed on a silica gel column (30 g). Elution with light petroleum (bp 30–60 °C)–benzene (1:1 v/v) gave the sulfonyl chloride (2.2 g, 42%): mp 67–68 °C (light petroleum); IR (KBr) 1370, 1175 cm^{-1}; M^+· (^{37}Cl) *m/e* 224, (^{35}Cl) 222.

Anal. Calcd for $C_7H_7ClO_2S_2$: C, 37.75; H, 3.17. Found: C, 37.70; H, 3.11.

2-Thiomethoxybenzenesulfonyl Azide (26). This was prepared in the usual way from the sulfonyl chloride to give the azide (81%): mp 47–48 °C (dilute MeOH); IR (KBr) 2140, 1355, 1165 cm^{-1}; M^+· *m/e* 229.

Anal. Calcd for $C_7H_7N_3O_2S_2$: C, 36.67; H, 3.08. Found: C, 36.80; H, 3.14.

Thermolysis of 2-Thiomethoxybenzenesulfonyl Azide. The azide (0.6 g) in cyclohexane (20 mL) was thermolyzed as usual at 130 °C for 72 h. Chromatography of the reaction products on silica gel and elution with benzene gave ***N*-cyclohexyl-2-thiomethoxybenzenesulfonamide** (**28**, 0.14 g, 19.7%), mp 83–84 °C (MeOH), identical with an authentic sample prepared (74% yield) from the sulfonyl chloride and cyclohexylamine in boiling benzene.

Anal. Calcd for $C_{13}H_{19}NO_2S_2$: C, 54.74; H, 6.67. Found: C, 54.40; H, 6.91.

Elution with ether gave **2-thiomethoxybenzenesulfonamide** (**29**, 0.11 g, 20.7%), mp 182–183 °C (MeOH), identical with an authentic sample prepared from the sulfonyl chloride and ammonium hydroxide (79% yield).

Anal. Calcd for $C_7H_9NO_2S_2$: C, 41.38; H, 4.43. Found: C, 40.97; H, 4.20.

2-Chloro-5-dimethylaminobenzenesulfonyl Chloride (32). *p*-Chloro-*N*,*N*-dimethylaniline (1 g) was heated with chlorosulfonic acid (6 mL) dropwise at 0 °C over a period of 20 min. The mixture was then heated at 110 °C for 18 h, cooled to room temperature, poured over crushed ice, and extracted with ether. The dried (Na_2SO_4) extract was evaporated to give a green oil which was chromatographed on a column of silica gel (30 g). Elution with benzene gave the sulfonyl chloride (0.33 g, 20.2%) as yellow needles, mp 105–106 °C (light petroleum).

Anal. Calcd for $C_8H_9Cl_2NO_2S$: C, 37.81; H, 3.57. Found: C, 38.00; H, 3.67.

2-Chloro-5-dimethylaminobenzenesulfonyl Azide (33). This was prepared as usual from **32** in 60% yield and had mp 54–55 °C [from light petroleum–$CHCl_3$ (9:1 v/v)].

Anal. Calcd for $C_8H_9ClN_4O_2S$: C, 36.85; H, 3.48. Found: C, 37.07; H, 3.64.

Thermolysis of 2-Chloro-5-dimethylaminobenzenesulfonyl Azide in Benzene. The azide (1 g) in benzene (20 mL) was decomposed as usual at 130 °C for 48 h. The products were chromatographed on silica gel (40 g). Elution with benzene–light petroleum (1:1 v/v) gave recovered azide (0.1 g, 10%). Elution with benzene gave **2-chloro-5-dimethylaminobenzenesulfonanilide** (**34**, 0.15 g, 14%), mp 215–216 °C (dilute MeOH), identical with an authentic sample prepared in 96% yield from **32** and aniline.

Anal. Calcd for $C_{14}H_{15}ClN_2O_2S$: C, 54.10; H, 4.87. Found: C, 53.74; H, 5.24.

Elution with benzene–ether (1:1 v/v) gave **2-chloro-5-dimethylaminobenzenesulfonamide** (0.12 g, 15%), mp 160–161 °C (ben-

zene–light petroleum), identical with an authentic sample prepared in 67% yield from the sulfonyl chloride and ammonium hydroxide.

Anal. Calcd for $C_8H_{11}ClN_2O_2S$: C, 40.94; H, 4.72. Found: C, 41.29; H, 4.64.

2-Methylamino-5-nitrobenzenesulfonyl Chloride (38). Dimethylammonium 2-dimethylamino-5-nitrobenzenesulfonate[26] (7.0 g) was heated with phosphorus pentachloride (7.0 g) at 150 °C for 3 h. Water (30 mL) was added, the mixture was extracted with chloroform (3 × 50 mL), and the chloroform was washed with water (2 × 20 mL), 1% aqueous NaOH (10 mL), and then again with water (20 mL). It was dried ($MgSO_4$) and concentrated to afford a dark residue which was chromatographed on a column of silica gel (50 g). Elution with chloroform (200 ml) gave **2-methylamino-5-nitrobenzenesulfonyl chloride** as yellow prisms (3.1 g, 50%): mp 146–147 °C (from chloroform); IR (KBr) 3400 (s) (NH), 1360 (s), 1330 (s), 1310 (s) (SO_2), 1160 cm^{-1} (SO_2); NMR (acetone-d_6) δ 8.57 (d, 1, J = 3 Hz, H_6), 8.35 (dd, 1, J = 3 and 9 Hz, H_4), 7.25 (d, 2, J = 9 Hz, one proton exchanges with D_2O, H_3 and NH), 3.21 (d, 3, J = 6 Hz, CH_3); mass spectrum (70 eV) m/e (rel intensity) 252 (42), 250 (100), 234 (1), 222 (1), 220 (2), 215 (25), 197 (50), 167 (33), 151 (75), 155.3*.

Anal. Calcd for $C_7H_7ClN_2O_4S$: C, 33.54; H, 2.82. Found: C, 33.60; H, 2.84.

2-Methylamino-5-nitrobenzenesulfonyl Azide (39). The sulfonyl chloride (1.3 g) in acetone (30 mL) at 0 °C was treated with sodium azide (1.2 g) in water (6 mL). After stirring the mixture for 1 h it was poured into water (100 mL) and extracted with chloroform to give the azide (**39**, 1 g, 75%), mp 138–139 °C (MeOH).

Anal. Calcd for $C_7H_7N_5O_4S$: C, 32.68; H, 2.74. Found: C, 32.81; H, 2.81.

Thermolysis of 2-Methylamino-5-nitrobenzenesulfonyl Azide in Cyclohexane. The azide (1 g) in cyclohexane (20 mL) was decomposed as usual at 135 °C for 30 h. Chromatography of the products on a column of silica gel (40 g) and elution with light petroleum–benzene (1:1 v/v) gave recovered azide (0.2 g) and ***N*-cyclohexyl-2-methylamino-5-nitrobenzenesulfonamide** (**41**), mp 161–162 °C (dilute MeOH), identical with an authentic sample prepared from the sulfonyl chloride **38** and cyclohexylamine in boiling benzene.

Anal. Calcd for $C_{13}H_{19}N_3O_4S$: C, 49.82; H, 6.11. Found: C, 49.87; H, 6.21.

Elution with benzene–ether (1:1 v/v) gave **3-methyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide** (**40**, 0.22 g, 30.8%): mp 233–234 °C (dilute MeOH); NMR ($CDCl_3$) δ 7.95 (s, 1), 7.62 (d, 1), 7.10 (d, 1), 7.0 (br s, 1, exchangeable, NH), 3.32 (s, 3, NCH_3): $M^+\cdot$ m/e 229.

Anal. Calcd for $C_7H_7N_3O_4S$: C, 36.68; H, 3.08. Found: C, 36.91; H, 3.20.

2-Dimethylamino-5-nitrobenzenesulfonyl Chloride (42). Dimethylammonium 2-dimethylamino-5-nitrobenzenesulfonate (10 g) was heated with thionyl chloride (10 mL) and dimethylformamide (0.5 mL) until the mixture became homogeneous, then for 1 h more. Excess thionyl chloride was removed in vacuo and water was added to the residue. An oil separated which crystallized. Recrystallization from benzene–hexane gave yellow crystals of **2-dimethylamino-5-nitrobenzenesulfonyl chloride** (7 g, 74%): mp 111–113 °C dec (benzene–light petroleum); IR (KBr) 1360 (s), 1325 (vs), 1265, 1155 cm^{-1} (s); NMR ($CDCl_3$) δ 8.98 (d, 1, J = 2.5 Hz, H_6), 8.33 (dd, 1, J = 2.5 and 10 Hz, H_4), 7.12 (d, 1, J = 10 Hz, H_3), 3.30 (s, 6, dimethylamino); mass spectrum m/e (rel intensity) 266 (7), 264 (19), 166 (90), 165 (30), 136 (45), 135 (27), 120 (31), 119 (100).

Anal. Calcd for $C_8H_9ClN_2O_4S$: C, 36.72; H, 3.43. Found: C, 36.83; H, 3.58.

2-Dimethylamino-5-nitrobenzenesulfonyl Azide (43). To an acetone (25 mL) solution of 2-dimethylamino-5-nitrobenzenesulfonyl chloride (0.5 g) at 0 °C was was added an aqueous solution (50 mL) of sodium azide (1.1 g). The mixture was stirred for 12 h at ambient temperature, then poured over ice water (100 mL). The organic portion was extracted with chloroform (30 mL), dried ($MgSO_4$), and concentrated to afford 2-dimethylamino-5-nitrobenzenesulfonyl azide as a yellow solid (0.4 g, 78%): mp 87–88.5 °C dec (lit.[14] 87 °C); IR (KBr) 2120 (s), 1355 (s), 1320 (s), 1160 cm^{-1} (s); NMR ($CDCl_3$) δ 8.88 (d, 1, J = 2.5 Hz, H_6), 8.40 (dd, 1, J = 2.5 and 7 Hz, H_4), 7.35 (d, 1, J = 7 Hz, H_3), 3.11 (s, 6, dimethylamino); mass spectrum m/e (rel intensity) 271 ($M^+\cdot$ 22), 229 (22), 228 (27), 214 (14), 167 (13), 151 (15), 150 (13), 149 (11), 136 (18), 135 (11), 133 (14), 132 (65), 119 (100), 118 (39), 105 (51), 104 (30).

Anal. Calcd for $C_8H_9N_5O_4S$: C, 35.42; H, 3.34. Found: C, 35.53; H, 3.29.

2-Dimethylamino-5-nitrobenzenesulfonamide (49a). Ammonia was bubbled through a benzene solution (30 mL) of 2-dimethylamino-5-nitrobenzenesulfonyl chloride (0.5 g) at room temperature. After 1 h ammonium chloride was filtered. The filtrate was concentrated to give a yellow solid. Recrystallization from benzene afforded **2-dimethylamino-5-nitrobenzenesulfonamide** (0.27 g, 55%): mp 164–166 °C; IR (KBr) 3340 (s), 3250 (s), 1340 (vs), 1155 cm^{-1} (s); NMR (CD_3CN) δ 8.90 (d, 1, J = Hz, H_6), 8.55 (dd, 1, J = 3 and 9 Hz, H_4), 7.75 (d, 1, J = 9 Hz, H_3), 6.2 (br s, 1, exchanges with D_2O, NH), 3.05 (s, 6, dimethylamino); $M^+\cdot$, m/e 245.

Anal. Calcd for $C_8H_{11}N_3O_4S$: C, 39.18; H, 4.52. Found: C, 39.29; H, 4.54.

***N*-Cyclohexyl-2-dimethylamino-5-nitrobenzenesulfonamide (49b).** 2-Dimethylamino-5-nitrobenzenesulfonyl chloride (0.5 g) and cyclohexylamine (0.5 g) in benzene (25 mL) were stirred at room temperature for 1 h. The cyclohexylamine hydrochloride (0.24 g, 90%) was filtered. The filtrate was concentrated to give a yellow solid, recrystallization of which from benzene–hexane gave ***N*-cyclohexyl-2-dimethylamino-5-nitrobenzenesulfonamide** (0.44 g, 70%): mp 141–142 °C; IR (KBr) 3240 (s), 1130 (vs), 1150 cm^{-1} (s); $M^+\cdot$, m/e 327.

Anal. Calcd for $C_{14}H_{21}N_3O_4S$: C, 51.36; H, 6.47. Found: C, 51.19; H, 6.55.

2-Dimethylamino-5-nitrobenzenesulfonanilide (49b). 2-Dimethylamino-5-nitrobenzenesulfonyl chloride (0.1 g) and aniline (0.5 mL) in benzene (10 mL) were kept at room temperature for 4 h. Aniline hydrochloride was filtered and the filtrate concentrated to give **2-dimethylamino-5-nitrobenzenesulfonanilide** (0.1 g, 82%): mp 129–130 °C (EtOH); IR (KBr) 3260 (s), 1340 (s), 1157 cm^{-1} (s); NMR ($CDCl_3$) δ 8.87 (d, 1, J = 3 Hz, H_6), 8.37 (dd, 1, J = 3 and 9 Hz, H_4), 7.92 (br s, 1, exchanges with D_2O, NH), 7.40 (d, 1, J = 9 Hz, H_3), 7.15 (s, 5, phenyl), 3.05 (s, 3, methyl); $M^+\cdot$, m/e 321.

Anal. Calcd for $C_{14}H_{15}N_3O_4S$: C, 52.33; H, 4.70. Found: C, 52.29; H, 4.79.

2-Methylamino-5-nitrobenzenesulfonamide (45). Ammonia was bubbled through a 1,2-dimethoxyethane (20 mL) solution of 2-methylamino-5-nitrobenzenesulfonyl chloride (**38**) for 30 min at room temperature. Filtration of the ammonium chloride and concentration of the filtrate gave **2-methylamino-5-nitrobenzenesulfonamide** (0.39 g, 64%): mp 260–262 °C (Me_2SO); IR (KBr) 3360 (s), 3240 (s), 1325 (vs), 1155 cm^{-1} (s); NMR ($CDCl_3$) δ 8.72 (d, 1, J = 3 Hz, H_6), 8.30 (dd, 1, J = 3 and 9 Hz, H_4), 7.42 (d, 1, J = 9 Hz, H_3), 5.64 (br s, 1, NH), 2.92 (s, 3, methyl); $M^+\cdot$ m/e 231.

Anal. Calcd for $C_7H_9N_3O_4S$: C, 36.35; H, 3.92. Found: C, 36.41; H, 3.94.

3,4-Dihydro-4-methyl-7-nitro-(2*H*)-benzo[*e*]-1,2,4-thiadiazine 1,1-Dioxide (44). 2-Methylamino-5-nitrobenzenesulfonamide (1.2 g) in aqueous 37% formaldehyde solution (9 mL) was heated in a sealed tube at 100 °C for 2 days. On cooling, a yellow oil separated. Crystallization from acetonitrile afforded **3,4-dihydro-4-methyl-7-nitro-(2*H*)-benzo[*e*]-1,2,4-thiadiazine 1,1-dioxide** (0.8 g, 67%): mp 226–228 °C; IR (KBr) 3300 (m), 1300 (vs), 1165 cm^{-1} (s); NMR (CD_3CN) δ 3.1 (s, 3, CH_3), 4.8 (d, 2, J = 8 Hz, CH_2), 6.2 (br s, 1, NH), 6.8 (d, 1, J = 12 Hz, H_5), 8.2 (dd, 1, J = 12 Hz and 3 H_6), 8.4 (d, 1, J = 3 Hz, H_8); $M^+\cdot$ m/e 243.

Anal. Calcd for $C_8H_9N_3O_4S$: C, 39.50; H, 3.73. Found: C, 39.52; H, 3.77.

Decomposition of 2-Dimethylamino-5-nitrobenzenesulfonyl Azide. a. In Cyclohexane. 2-Dimethylamino-5-nitrobenzenesulfonyl azide (1.0 g) in cyclohexane (60 mL) was heated at 120 °C for 2 days. The cyclohexane was decanted from orange 3,3-dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (**46**, 0.65 g, 72%): mp 183–186 °C dec (acetonitrile) (lit.[14] 188 °C); IR (KBr) 1350 (s), 1280 (s), 1160 (s), 1120 cm^{-1} (s); NMR (CD_3CN/D_2O) δ 8.8 (m, 3, aromatic), 4.09 (s, 6, methyl); mass spectrum m/e (rel intensity) 243 ($M^+\cdot$, 85), 241 (19), 227 (10), 215 (34), 214 (56), 213 (19), 211 (41), 207 (29), 178 (14), 167 (33), 151 (45), 150 (34), 121 (20), 120 (49), 105 (100).

Anal. Calcd for $C_8H_9N_3O_4S$: C, 39.50; H, 3.73. Found: C, 39.58; H, 3.83.

Evaporation of the cyclohexane solution afforded an orange oil (0.17 g) which was resolved by TLC (silica gel, 1.5 mm thick, benzene development) into the following.

(a) 2-Dimethylamino-5-nitroaniline (**48**, 5.2 mg, 1%): R_f 0.7; mp 59–60 °C (from water) (lit.[27] 63 °C); identical with an authentic sample.

(b) **2,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide** (**47**, 33 mg, 4%): R_f 0.5; mp 135 °C (from ethanol); IR (KBr) 1500 (s), 1320 (s), 1160 cm^{-1} (s); NMR ($CDCl_3$) δ 8.45 (d, 1, J = 2 Hz, H_6), 8.39 (dd, 1, J = 2 and 9 Hz, H_4), 7.05 (d, 1, J = 9 Hz, H_3), 3.33 (s, 3, methyl), 2.96 (s, 3, methyl); mass spectrum m/e (rel intensity) 243 ($M^+\cdot$, 25), 179 (54), 178 (32), 151 (14), 150 (26), 149 (11), 133 (38), 132 (81), 120 (21), 106 (13), 105 (78), 92 (100).

Anal. Calcd for $C_8H_9N_3O_4S$: C, 39.51; H, 3.73. Found: C, 39.35; H, 3.82.

(c) *N*-Cyclohexyl-2-dimethylamino-5-nitrobenzenesulfonamide (**49b**, 16 mg, 2%): R_f 0.4; mp 140–142 °C (from ethanol); mmp 140–142 °C; identical with an authentic sample.

(d) An orange oil (38 mg, 4% by weight of azide): R_f 0.3; IR (KBr) 3120 (s, br), 1500 (s), 1340 (vs), 1310 (s), 1170 cm^{-1} (s); NMR (acetone-d_6) δ 8.78 (br s, 1, exchanges with D_2O, NH), 8.48 (d, 1, J = 2 Hz, H_6), 8.38 (dd, 1, J = 2 and 9 Hz, H_4), 7.36 (d, 1, J = 9 Hz, H_3), 3.42 (s, 3, methyl); this was different from **40** and has not been identified yet.

(e) 2-Dimethylamino-5-nitrobenzenesulfonamide (**49a**) (43 mg, 4%): R_f 0.2; mp 164–164.5 °C (from ethanol); identical with the sample prepared above.

B. In Benzene. 2-Dimethylamino-5-nitrobenzenesulfonyl azide (2 g) in benzene (130 mL) was heated at 120 °C for 2 days. 3,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (1.47 g, 81%), mp 183–186 °C, identical with that obtained above, separated. The filtrate was concentrated to afford an oil (0.344 g) which was resolved into its components by TLC (silica gel, 1.5 mm thick, benzene development) to give the following fractions. (a) 2-dimethylamino-5-nitrobenzenesulfonyl azide (44 mg, 2%), mp 88–89 °C, IR (KBr) 2110 cm^{-1}. (b) 2-Dimethylamino-5-nitroaniline (**48**, 42 mg, 3%), mp 60 °C. (c) 2,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (**47**, 16 mg, 1%), mp 129–132 °C. (d) The same unidentified orange oil (62 mg, 3%) as that obtained above. (e) 2-Dimethylamino-5-nitrobenzenesulfonamide (**49a**, 65 mg, 3%), mp 173–175 °C.

C. In Chlorobenzene. 2-Dimethylamino-5-nitrobenzenesulfonyl azide (1.5 g) was heated in chlorobenzene at 150 °C for 50 h. The solution had turned from yellow to red-brown. Concentration afforded a dark oil which was resolved into its components by TLC (silica gel, benzene–2-propanol, 9:1 v/v, developer). There were thus isolated the following. (a) 2,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (118 mg, 9%), mp 135 °C. (b) 4-Nitrodimethylaniline (137 mg, 15%), mp 162–163 °C (lit.[28] 163 °C), identical with an authentic sample.

Thermolysis of 3,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiazoline 1,1-Dioxide (46). 3,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (197 mg) was heated in cyclohexane (30 mL) for 2 days at 130 °C. Undecomposed thiadiazoline (0.13 g) was filtered off, and the cyclohexane solution was concentrated to an orange residue which was resolved into its components by TLC (silica gel, 1.5 mm thick, benzene then ethanol developer). The following components were separated. (a) 2,3-Dimethyl-6-nitrobenzo[*d*]-1,2,3-thiadiazoline 1,1-dioxide (11 mg, 19%), mp 135 °C. (b) An unidentified oil (17 mg): IR (KBr) 3120 (s, br), 1500 (s), 1360 (s), 1170 cm^{-1} (s). (c) 2-Dimethylamino-5-nitrobenzenesulfonamide (**49a**, 3 mg, 4%), identical with an authentic sample.

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References and Notes

(1) For preliminary communications on part of this work, see R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Am. Chem. Soc.*, **91**, 1219 (1969); R. A. Abramovitch and W. D. Holcomb, *Chem. Commun.*, 1298 (1969).
(2) R. A. Abramovitch, T. Chellathurai, I. T. McMaster, T. Takaya, C. I. Azogu, and D. P. Vanderpool, preceding paper in this issue.
(3) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960).
(4) G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 2487 (1961); *J. Org. Chem.*, **26**, 4108 (1961).
(5) D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, *J. Am. Chem. Soc.*, **91**, 2273 (1969).
(6) P. A. S. Smith, in "Nitrenes", W. Lwowski, Ed., Interscience, New York, N.Y., 1970, Chapter 4, p 99; R. A. Abramovitch in "Organic Reactive Intermediates", S. P. McManus, Ed., Academic Press, New York, N.Y., 1973, Chapter 3, p 127.
(7) E. W. Parnell, *J. Chem. Soc.*, 4366 (1960).
(8) A. Wohl and F. Koch, *Ber.*, **43**, 3295 (1910).
(9) T. Curtius, *Angew. Chem.*, **27**, 213 (1914); A. Bertho, *J. Prakt. Chem.*, **120**, 89 (1929); T. Curtius, *ibid.*, **125**, 303 (1930).
(10) W. Lwowski and E. Scheiffele, *J. Am. Chem. Soc.*, **87**, 4359 (1965).
(11) W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964).
(12) G. P. Balabanov, Yr. I. Dergunov, and V. A. Gal'perin, *J. Org. Chem. USSR (Engl. Transl.)*, **2**, 1797 (1966).
(13) (a) H. Meerwein, G. Dittmar, R. Göllner, K. Haffner, F. Mensch, and O. Steinfort, *Chem. Ber.*, **90**, 841 (1957). (b) A. J. Neale, T. J. Rawlings, and E. B. McCall, *Tetrahedron*, **21**, 1299 (1965).
(14) J. Martin, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 2451 (1974); *Chem. Commun.*, 1319 (1971).
(15) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **37**, 2022 (1972).
(16) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Lett.*, 2945 (1964).
(17) H. R. Snyder and R. E. Heckert, *J. Am. Chem. Soc.*, **74**, 2006 (1952).
(18) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).
(19) E. H. Huntress and J. S. Autenrieth, *J. Am. Chem. Soc.*, **63**, 3446 (1941).
(20) R. A. Abramovitch and J. S. Williams, *Chem. Ind. (London)*, 1786 (1965).
(21) O. Neunhoeffer, *J. Prakt. Chem.*, **133**, 95 (1932).
(22) G. T. Bottger, A. P. Yerington, and S. I. Gertler, *U.S. Bur. Entomol. Plant Quarantine*, E-859 (1953); *Chem. Abstr.*, **47**, 7724*c* (1953).
(23) S. Skraup and W. Beifuss, *Ber.*, **60**, 1070 (1927); J. F. Bartlett and C. E. Garland, *J. Am. Chem. Soc.*, **55**, 2064 (1933).
(24) H. J. Weigmann and G. Malewski, *Spectrochim. Acta*, **22**, 1045 (1966).
(25) M. Claasz, *Ber.*, **45**, 1022 (1912).
(26) L. W. Jones and E. B. Hartshorn, *J. Am. Chem. Soc.*, **46**, 1852 (1924).
(27) A. I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd. ed, Longmans, Green and Co., New York, N.Y., 1958, p 573.
(28) E. Heim, *Ber.*, **21**, 2308 (1888).