Reactions of Sulfonyl Azides and Sulfonamides with Vinyl Ethers

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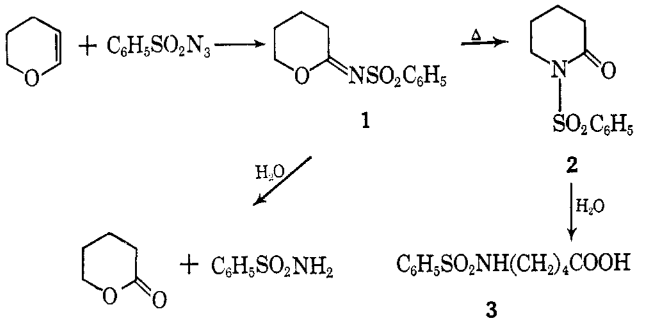
The reactions of vinyl ethers with benzenesulfonyl azide are described. 3,4-Dihydro-2H-pyran produces N-phenylsulfonyltetrahydropyranon-2-imine which can be thermally rearranged to N-phenylsulfonyl-2-piperidone in good yield. 2-Methoxy-3,4-dihydro-2H-pyran reacts with benzenesulfonyl azide to yield a piperidone directly. In a related reaction the latter pyran interacts with benzenesulfonamide to produce N-phenylsulfonyl-2-methoxy-1,2,3,4-tetrahydropyridine in excellent yield. Alkyl vinyl ethers and benzenesulfonyl azide evolve 1 mole of nitrogen and form 1:1 polymers. Alkyl imido esters are produced in a simultaneous reaction. High yields of 1,4-bis(phenylsulfonyl)-2-alkoxy-1,2,3,4-tetrahydropyrazines are obtained by the acid-catalyzed alcoholysis of the polymers. Reaction mechanisms are presented.

The reaction of vinyl ethers with sulfonyl azides was first reported by us[1] in 1963. In view of recent communications[2,3] dealing with this subject we now wish to disclose the details of our work in this area.

A mixture of excess 3,4-dihydro-2H-pyran and benzenesulfonyl azide liberated nitrogen at a moderate rate at room temperature to produce N-phenylsulfonyltetrahydropyranon-2-imine (**1**) as a viscous oil. Hydrolysis of the imine **1** to benzenesulfonamide and δ-valerolactone[2] occurred readily at room temperature. Distillation of **1** at 180° (0.1 mm) produced N-phenylsulfonyl-2-piperidone (**2**) in good yield. The structure of **2** was established by elemental analysis, the infrared absorption at 5.9 μ, and a ready hydrolysis to 5-phenylsulfonamidovaleric acid[4] (**3**) as indicated in Scheme I.

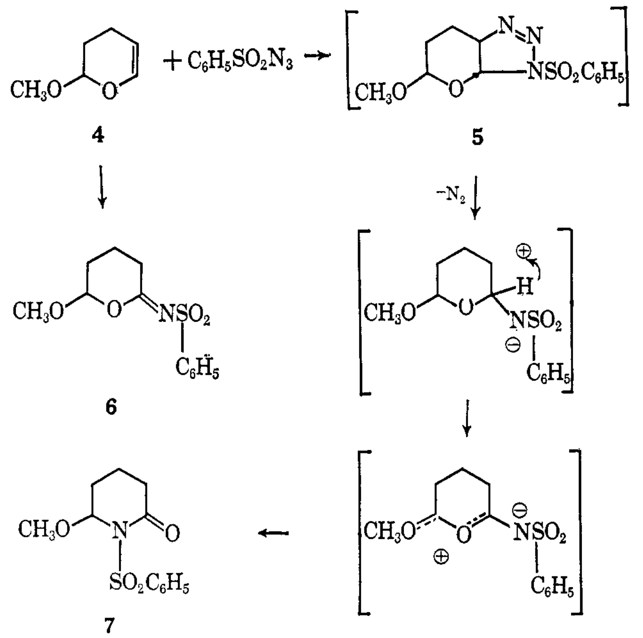
Scheme I



Although the conversion of **1** to **2** is formally a rearrangement of the Chapman type, the mechanism is unknown. A polymerization–depolymerization sequence may be operative.

The pmr spectra of **1** and **2** are quite similar. In the spectrum of **1** absorptions are centered at 7.5 (multiplet, five aromatic hydrogens), 4.14 (triplet, methylene group adjacent to oxygen), 2.47 (triplet, methylene group adjacent to imino carbon), and 1.66 ppm (multiplet, four aliphatic protons). A similar pattern is observed for **2** with corresponding peaks at 8.2, 4.14, 2.36, and 1.88 ppm.

Scheme II



In contrast to 3,4-dihydro-2H-pyran, the reaction of benzenesulfonyl azide with 2-methoxy-3,4-dihydro-2H-pyran (**4**) is relatively sluggish and more complex. Acidic impurities in the azide were found to initiate formation of aldehydes, ethers and dark-colored polymers of the dihydropyran. Similar products were obtained when an acetonitrile solution of **4** was refluxed in the presence of a catalytic amount of benzene sulfonyl chloride. The side reactions were minimized by stirring an acetonitrile solution of the reactants with solid sodium bicarbonate prior to heating. At room temperature the rate of reaction of **4** with the azide is very slow. In refluxing acetonitrile, however, nitrogen is evolved at an appreciable rate and medium intensity bands at 5.85 and 6.3 μ, indicating aldehyde and imine, respectively, soon appear in the infrared spectrum. After a short time, these bands become static and a lactam absorption at 5.9 μ progressively increases. Scheme II shows the reaction sequence. The aldehyde and imine (presumably **6**) were readily removed from the crude product by extraction with aqueous sodium carbonate. N-Phenylsulfonyl-6-methoxy-2-piperidone (**7**) was obtained in 71% yield. Structure **7** is supported by elemental analysis and infrared and pmr spectra. There was no evidence that **6** rearranged to **7** under the reaction conditions employed but by analogy with **1** this reorganization would be expected at higher temperatures.

Apparently, 2-alkoxydihydropyrans undergo ring cleavage more readily than 3,4-dihydro-2H-pyran. Thus, the latter and tetracyanoethylene are reported[5] to form a simple 1:1 adduct **8** whereas 2-ethoxy-3,4-di-

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[1] J. E. Franz and C. Osuch, *Tetrahedron Letters*, **No. 13**, 840 (1963).

[2] R. Huisgen, L. Mobius, and G. Szeimies, *Ber.*, **98**, 1138 (1965).

[3] R. Harmon and D. Rector, *Chem. Ind.* (London), 1264 (1965).

[4] W. Treibs and H. Reinheckel, *Ber.*, **89**, 117 (1956).

[5] J. Williams, D. Wiley, and B. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

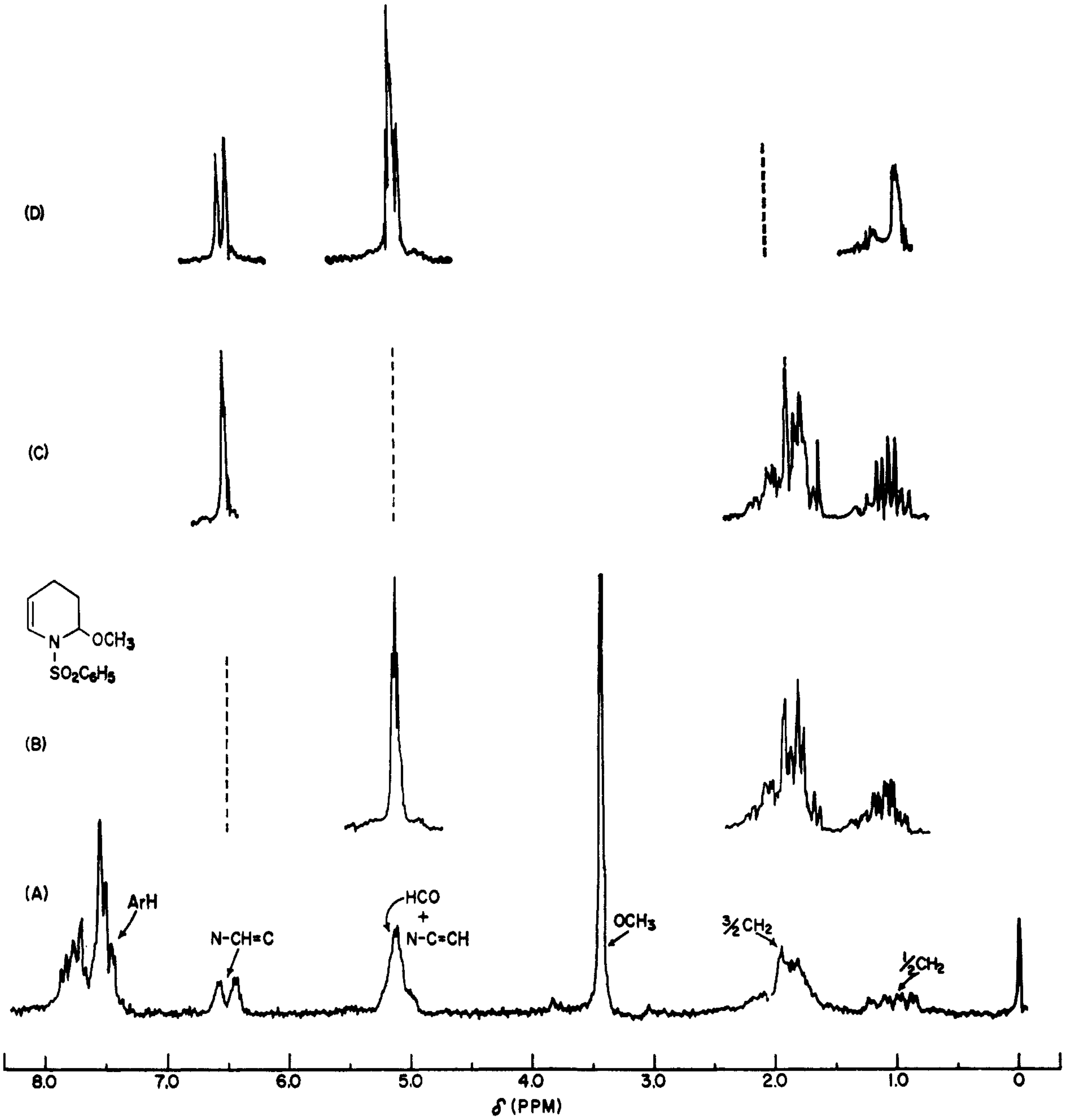

Figure 1.—Pmr spectra of structure **13**. (a) Single irradiation. (b) Double irradiation at 6.5 ppm. (c) Double irradiation at 5.1 ppm. (d) Double irradiation at 1.8 ppm. Spectra run at 100 Mc/sec.

hydro-2H-pyran yields a rearrangement product **9** as indicated in Scheme III. In a reaction sequence similar to Scheme III benzenesulfonyl azide and **4** would be expected to produce **10**. Since the latter pyrrolidine is not detected, the formation of an analogous intermediate in which the benzenesulfonylamido group is attached at the β position of the vinyl ether probably does not occur. The triazoline adduct **5** or a labile aziridine (discussed later) represent logical intermediates of the proper orientation to decompose or rearrange according to Scheme II.

The reactions of benzenesulfonamide with the dihydropyrans further illustrates the greater ease of ring opening of **4**. Speziale, Ratts, and Marco report[6] that the acid-catalyzed reaction between 3,4-dihydro-2H-pyran and benzenesulfonamide yields a simple 1:1 adduct **11**. Under similar reaction conditions, however, we have found that 2 moles of **4** are consumed/mole of sulfonamide. An acid catalyst is not required and the major products are glutaric aldehyde hemiacetal (**12**) and N-phenylsulfonyl-2-methoxy-1,2,3,4-tetrahydropyridine (**13**). A mechanism for the formation of the latter product is illustrated in Scheme IV. The structure of **14**, isolated in minor amount, is supported by elemental analysis and infrared and pmr spectra.

The infrared spectrum of **13** has a sharp 6.1-μ band and is consistent with the structure indicated. Additional strong support for this structure is obtained from the pmr spectrum shown in Figure 1a (spectrum obtained at 60 Mc/sec). Peak area measurements are correct for the spectral analysis given. Confirmation of this analysis was obtained from frequency sweep double-resonance measurements at 100 Mc/sec.[7] Figures 1b–d were obtained by irradiation of the peaks at 6.5, 5.1, and 1.8 ppm, respectively (only sig-

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[6] A. J. Speziale, K. Ratts, and G. Marco, *J. Org. Chem.*, **26**, 4311 (1961).

[7] We are indebted to L. F. Johnson and N. S. Bhacca of Varian Associates for providing the double-resonance spectra included in this paper.

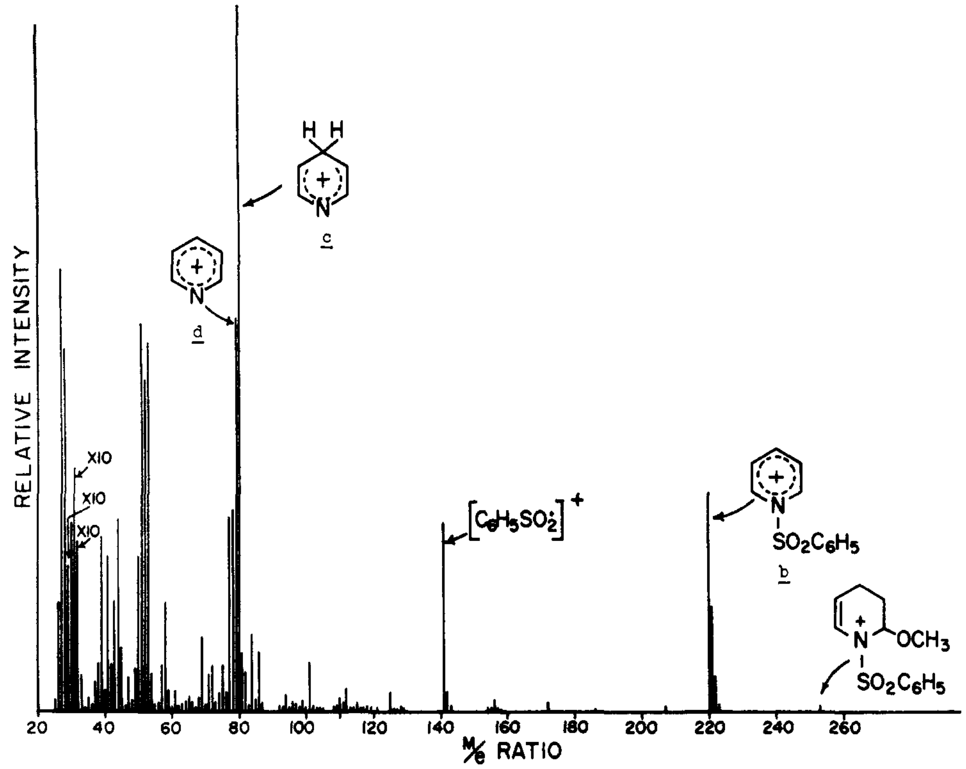
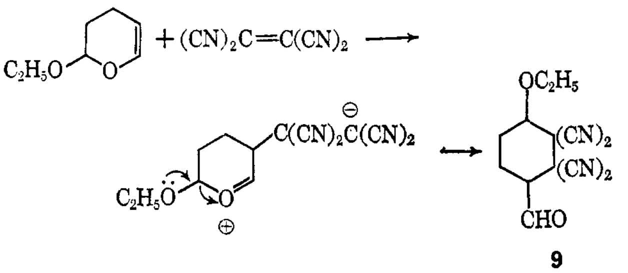
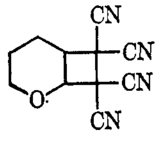


Figure 2.—Mass spectrum of structure **13**.

Scheme III





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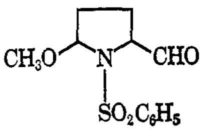

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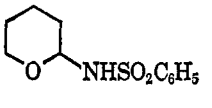

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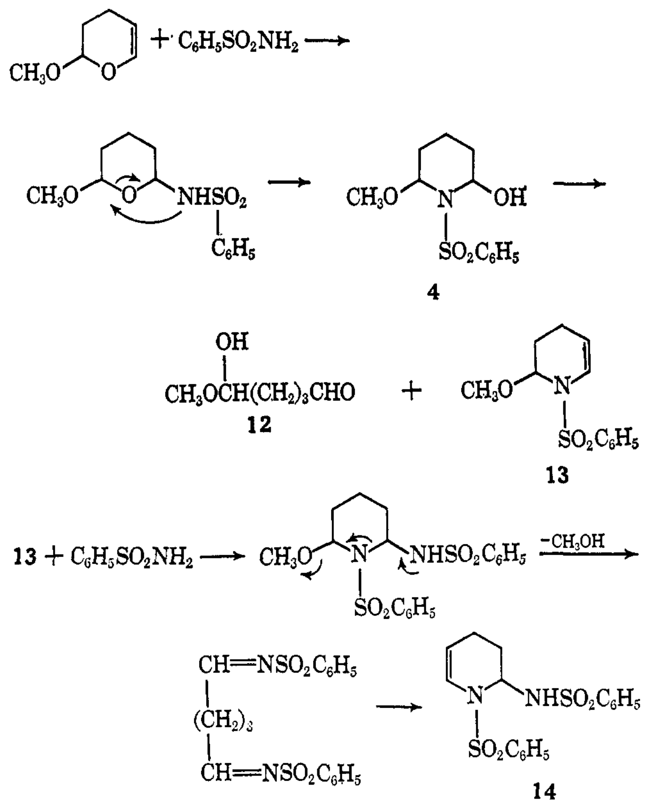
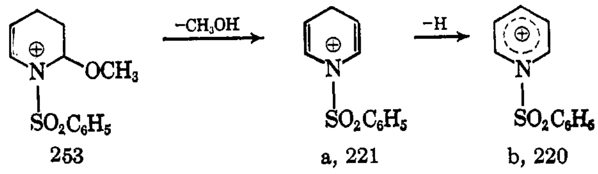
Scheme IV



nificant portions of the spectra are shown). The positions of irradiation are indicated by the dotted lines. Spectra are obtained in which all couplings caused by the protons of the irradiated peak are absent. The following couplings were observed: peak at 6.5 coupled with peaks at 5.1 and 1.8 ppm; peak at 5.1 coupled with peaks at 6.5, 1.8, and 0.9 ppm; peak at 1.8 coupled with peaks at 6.5, 5.1, and 0.9 ppm. The single methylene hydrogen can not be assigned unequivocally on the basis of these spectra. The apparent absence of a coupling between this peak and the peak at 6.5 ppm, however, suggests that it arises from one of the hydrogens at position 3 of **13**.

The mass spectrum of **13** at 105° is shown in Figure 2. The low abundance of the parent ion (*m/e* 253) is probably due in part to thermal decomposition of the sample in the mass spectrometer, since a small increase in temperature causes the parent peak to disappear. The abundant *m/e* 32 and 31 ions indicate that elimination of methanol probably occurs both on pyrolysis and as a result of electron impact. This is consistent with the high abundance of the *m/e* 221 and 220 ions, *i.e.*



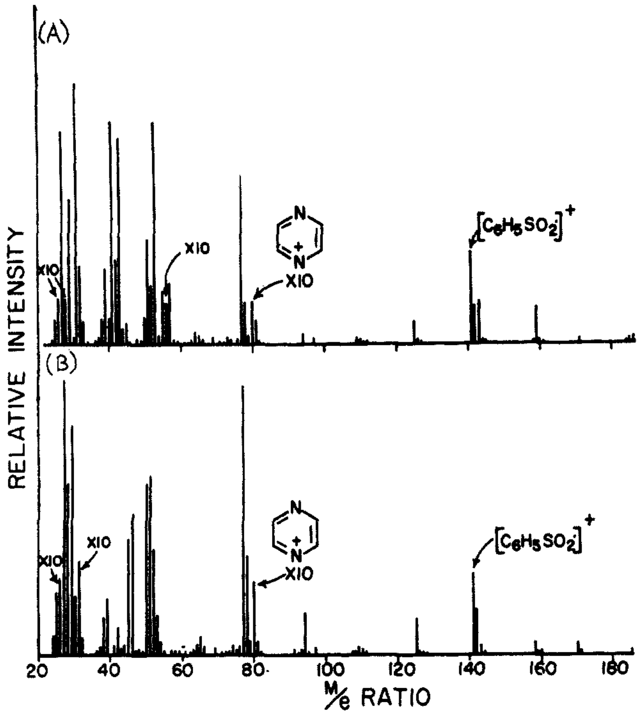
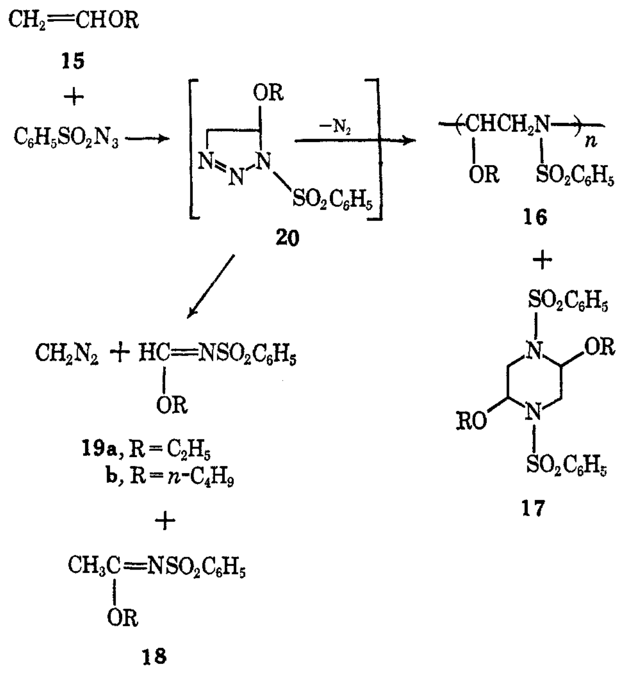


Figure 3.—Pyrolysis mass spectra. (a) Structure **17b**. (b) Structure **23b**.

Loss of the phenylsulfonyl radical from a and b apparently gives rise to ions c and d. Other major peaks at *m/e* 78, 77, 52, 51, 50, and 39 etc. can be attributed to the breakdown of a pyridine ring. The abundant ion observed at *m/e* 53 is probably due to loss of HCN from c.

SCHEME V



Benzenesulfonyl azide reacted more rapidly with ethyl vinyl ether (**15a**) and butyl vinyl ether (**15b**) than with the dihydropyrans. At moderate temperatures the major products were 1:1 polymers **16**. Minor products were dimers **17** and imido esters **18** as shown in Scheme V.

The dimers are crystalline solids, the polymers amorphous powders or viscous oils. Structures **16** and **17** are supported by elemental analysis, infrared and pmr spectra, and molecular weight determinations. The pyrolysis mass spectrum of **17b** at 175° (Figure 3a) is consistent with the assignment of a piperazine structure. The major peaks in the spectrum, *m/e* 80, 53, 52, 51; *m/e* 56, 43, 42, 41, 31, 29, 27; and *m/e* 141, 125, 109, 77 can be attributed to pyrazine, butanol, and phenylsulfonyl fragments, respectively.

Polymer molecular weights increased at lower reaction temperatures. At 25° a polymer of **16a** containing an average of 17 units was obtained, whereas at 0–15° the molecular weight was 6170 (27 units).

The reaction of butyl vinyl ether and benzenesulfonylazide was studied in more detail. At higher reaction temperatures polymer formation decreases and imidoesters become major products. One uncontrolled exothermic reaction between the azide and **15b** yielded a viscous oil containing 48 mole % of the imidoformate **19b**, 12 mole % **18b** and polymers **16** and **17**. Apparently, under these conditions cleavage of diazomethane from the triazoline intermediate **20** is more facile than loss of nitrogen. An analogous reaction has been reported[8] in which certain enamines yield formamidines.

Products **18** and **19** exhibited sharp singlets in the pmr spectrum at 2.45 and 8.4 ppm, respectively. The infrared and pmr spectrum of the sodium formate, sodium acetate, and benzenesulfonamide obtained by hydrolysis were identical to authentic samples.

Polymer **16a** was inert to refluxing aqueous sodium hydroxide or hydrochloric acid. In the presence of hot concentrated hydrochloric acid and ethanol, however, **16a** softened, formed an oil, and finally dissolved. By concentration of the solution there was obtained an excellent yield of a white crystalline compound $C_{18}H_{19}N_2S_2O_5$. The infrared spectrum of this product has a characteristic enamine absorption at 6.1 μ. The 100-Mc/sec pmr spectrum is illustrated in Figure 4a. Peaks for aromatic protons (7.6 ppm, 10 H, multiplet) and methyl protons (0.8 ppm, 6 H, triplet) are not shown. The spectral analysis indicated was confirmed by frequency sweep double-resonance measurements, Figures 4b–d.[7] The following couplings are observed: peak at 5.1 coupled with peaks at 6.0, 3.9, and 2.1 ppm; peak at 3.9 coupled with peaks at 6.4, 5.1, and 2.1 ppm; peak at 2.1 coupled with peaks at 5.1 and 3.9 ppm. The values for J obtained are J_{ab} = 6.5 cps, J_{ad} = 1.0 cps, J_{bc} = 1.5 cps, J_{cd} = *ca.* 2 cps, $J_{cd'}$ = 2.0 cps, $J_{dd'}$ = 13.3 cps. All other couplings are less than *ca.* 0.7 cps. There was no significant change in the pmr spectrum from −34 to 150°.

The pyrolysis mass spectrum, Figure 3b, indicates that pyrazine and ethanol are major decomposition products together with smaller quantities of ethyl benzenesulfonate.

The data indicate that the product is 1,4-bis(phenylsulfonyl)-2-ethoxy-1,2,3,4-tetrahydropyrazine (**23b**) presumably formed as illustrated in Scheme VI. Acid hydrolysis of the aminal **16** would initially produce phenylsulfonamidoacetaldehyde (**21**). Dimerization and dehydration of **21** would yield the dihydropyrazine **22**. The course of the reaction in various alcoholic solvents suggests that **22** is a primary intermediate.

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[8] R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Ber.*, **96**, 802 (1963).

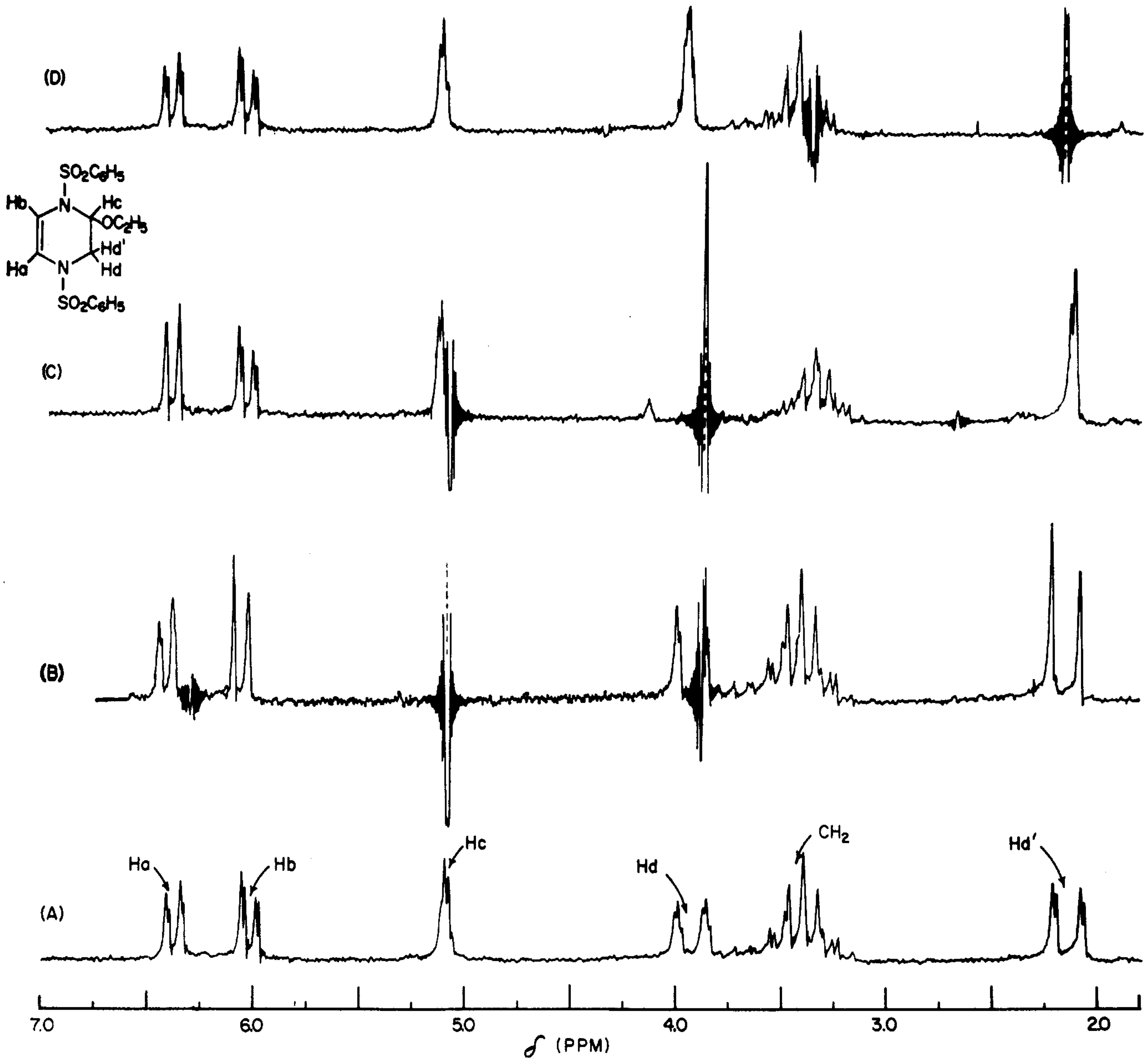
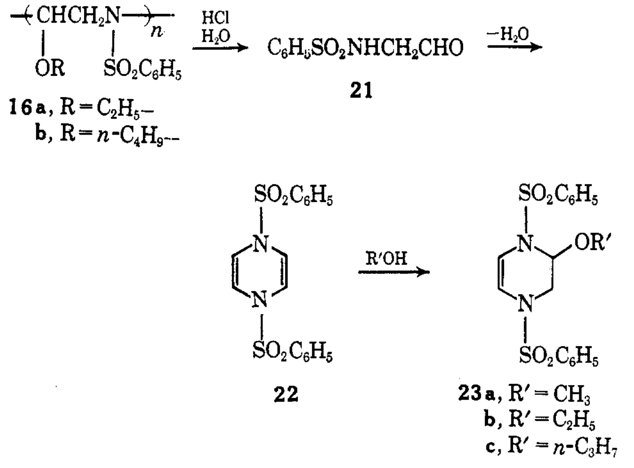


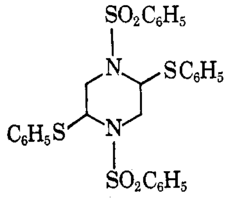
Figure 4.—Pmr spectra of structure **23b**. (a) Single irradiation. (b) Double irradiation at 5.1 ppm. (c) Double irradiation at 3.9 ppm. (d) Double irradiation at 2.1 ppm. Spectra run at 100 Mc/sec. Aromatic and methyl group protons are not shown.

SCHEME VI



Thus, in acidic methanol **23a** is produced from **16a**. Alternatively, the boron trifluoride catalyzed reaction of **23b** with *n*-propyl alcohol yields **23c**. Finally, refluxing **16b** in acidic ethanol yields **23b**. At the melting point **23** evolves alcohol forming a dark brown oil. Presumably, conversion to **22** occurs followed by polymerization.

Attempts to add alcohols to the enamine double bond of **23** under acidic conditions failed. In the presence of boron trifluoride, however, **23b** and thiophenol formed a crystalline bisadduct **24**. An attempt to reductively cleave **24** to **25** with Raney nickel in refluxing benzene failed possibly owing to the high insolubility of the product in the reaction medium.



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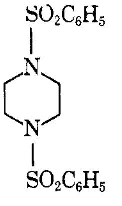

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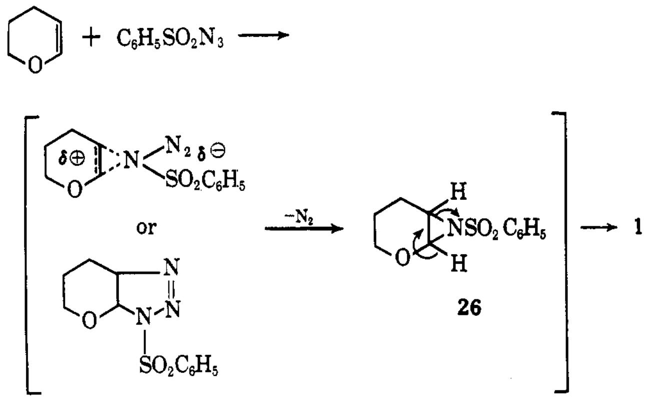
The mechanism(s) of the reactions of vinyl ethers with sulfonyl azides is unsettled. Unlike the reactions of azides with unsubstituted olefins, neither triazolines[9] nor aziridines[10] have been detected. By analogy with the phenyl azide–dihydropyran reaction,[2] an attractive intermediate is an unstable sulfonyltriazoline which decomposes with migration of an α-hydrogen atom (Schemes I and II). This sequence also resembles the mechanism postulated[2,8] for the enamine–sulfonyl azide reaction. An alternate mechanism involving rearrangement of an unstable aziridine intermediate **26** to the most resonance stabilized product, however, equally well explains the results as indicated in Scheme VII. Apparently, only a few α-alkoxyaziridines have been described.[11] N-Sulfonyl derivatives such as **26**, however, have not been prepared.

SCHEME VII



Although enamine derivatives of acetaldehyde react with sulfonyl azides to produce rearranged products (amidines),[7] unrearranged polymers are the predominant products obtained from the corresponding enol ethers. It is also interesting that yet another type of product (triazoles) is formed on decomposition of phenyl azide-alkyl vinyl ether triazoline adducts.[2] Again, an unstable sulfonyl aziridine intermediate could adequately account for the predominant formation of aziridine-like dimers and polymers from alkyl vinyl ethers although a triazoline (Scheme V) appears to be involved in the formation of imidoformates.

In conclusion we do not feel that sufficient data is yet available to invoke a single mechanism for the reactions of vinyl ethers and enamines with sulfonyl azides.

Experimental Section[12]

N-Phenylsulfonyltetrahydropyranon-2-imine (**1**).—A mixture of 9 g (0.05 mole) of benzenesulfonyl azide and 12.6 g (0.15 mole) of redistilled 3,4-dihydro-2H-pyran evolved nitrogen at a moderate rate at room temperature. After 4 days the azide band was absent in the infrared spectrum and the mixture was concentrated at 100° (20 mm). The crude product (14 g) yielded 12 g (100%) of hexane insoluble viscous oil. The infrared and integrated pmr spectra are consistent with the title structure. The imine readily hydrolyzed in water at room temperature to yield benzenesulfonamide and δ-valerolactone. The latter products were separated by chromatography on neutral alumina and identified by their infrared spectra.

N-Phenylsulfonyl-2-piperidone (**2**).—Imine **1** was distilled through a Holzman column at reduced pressure. After a small forerun containing benzenesulfonamide and δ-valerolactone had been collected, the major product was distilled at 180° (0.1 mm). The latter product was a viscous oil which soon crystallized. The crude piperidone (mp 58–67°) was recrystallized from 95% ethanol, mp 71–71.5°.

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.20; H, 5.49; N, 5.85; Found: C, 55.13; H, 5.71; N, 5.95.

The piperidone readily dissolved in warm aqueous sodium hydroxide. On acidification, 5-phenylsulfonamidovaleric acid (**3**) precipitated in quantitative yield. The product was recrystallized from hot water, mp 96–97° (lit.[4] mp 95.5°).

N-Phenylsulfonyl-6-methoxy-2-piperidone (**7**).—A mixture of 3.5 g (0.03 mole) of 2-methoxy-3,4-dihydro-2H-pyran, 3.7 g (0.02 mole) of benzenesulfonyl azide and 10 ml of acetonitrile was stirred with 0.5 g. of sodium bicarbonate. The latter was removed by centrifugation and the supernatant solution heated at the reflux temperature for 10 hr. Solvent and volatile byproducts were removed first at 25° (20 mm) and finally at 100° (0.5 mm). The crude product was a viscous yellow oil (5.25 g, 97%) which partially crystallized. The latter product (4.2 g) was dissolved in ether and washed with aqueous 5% sodium carbonate. After washing with water and drying over magnesium sulfate, the organic layer was concentrated at reduced pressure. The piperidone (**7**) was obtained as a white crystalline solid weighing 3.0 g (71%). After recrystallization from hexane, the product was obtained as white needles, mp 90–91°.

Anal. Calcd for $C_{12}H_{15}NO_4S$: C, 53.51; H, 5.63; N, 5.20. Found: C, 53.35; H, 5.66; N, 4.99.

N-Phenylsulfonyl-2-phenylsulfonamido-1,2,3,4-tetrahydropyridine (**14**) **and N-Phenylsulfonyl-2-methoxy-1,2,3,4-tetrahydropyridine** (**13**).—A solution of 6.8 g (0.06 mole) of 2-methoxy-3,4-dihydro-2H-pyran and 4.7 g (0.03 mole) of benzenesulfonamide in 10 ml of acetonitrile was refluxed for 14 hr. After removal of solvent at reduced pressure, a viscous oil (11.3 g) was obtained. The latter product was extracted with hot hexane to yield 8.8 g of hexane soluble oil and 1.8 g which was insoluble. Ether was added to the insoluble product and the crystalline material was collected by filtration. After recrystallization from benzene, **14** melted at 162–163°.

Anal. Calcd for $C_{17}H_{18}N_2O_4S_2$: C, 53.94; H, 4.80; N, 7.40. Found: C, 53.77; H, 4.82; N, 7.24.

The hexane soluble oil (8.8 g) was dissolved in ether and washed with aqueous sodium bicarbonate. After drying over magnesium sulfate and removal of solvent, there was obtained 6.4 g (84%) of crude **13**. The latter material (1 g) was chromatographed on neutral alumina. The ether elute yielded 0.8 g of pure enamine **13**. After recrystallization from petroleum ether (bp 30–60°) at 0°, the product melted at 59–60°.

Anal. Calcd for $C_{12}H_{15}NO_3S$: C, 56.89; H, 5.98; N, 5.53. Found: C, 56.67; H, 6.09; N, 5.60.

Reaction of Ethyl Vinyl Ether and Benzenesulfonyl Azide.—A mixture of 10.8 g (0.15 mole) of ethyl vinyl ether and 9 g (0.05 mole) of benzenesulfonyl azide immediately underwent a vigorous reaction with nitrogen evolution. A water bath was used to moderate the reaction. After 24 hr, excess vinyl ether was removed at reduced pressure and the residue was extracted repeatedly with ether. The ether insoluble amorphous polymer **16a** weighed 9.3 g (87%). The product was reprecipitated from chloroform solution with ether.

Anal. Calcd for $(C_{10}H_{13}NO_3S)_{17}$: C, 52.83; H, 5.78; N, 6.16; mol wt, 3859. Found: C, 52.50; H, 5.87; N, 6.24; mol wt, 3870.

The infrared spectrum of the ether soluble viscous oil (1.8 g) had a strong 6.3 μ band characteristic of an imido ester. A crystalline solid was separated from a mixture of the oil and a little ether after several hr. The product was recrystallized from benzene, mp 154° dec. The infrared and pmr spectra indicate that this compound is N,N′-bis(phenylsulfonyl)-2,5-diethoxypiperazine (**17a**).

Anal. Calcd for $C_{20}H_{26}N_2O_6S_2$: C, 52.83; H, 5.78; N, 6.16. Found: C, 52.92; H, 5.86, N, 5.96.

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[9] K. Alder and G. Stein, *Ann.*, **501**, 1 (1933).

[10] J. E. Franz, C. Osuch, and M. W. Dietrich, *J. Org. Chem.*, **29**, 2922 (1964).

[11] (a) M. Hatch and D. Cram, *J. Am. Chem. Soc.*, **75**, 38 (1953); (b) R. Parcell, *Chem. Ind.* (London), 1396 (1963); (c) J. A. Deyrup and R. B. Greenwald, *J. Am. Chem. Soc.*, **87**, 4538 (1965).

[12] All melting and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. Nuclear magnetic resonance spectra were obtained on a Varian Associate A-60 pmr spectrometer with tetramethylsilane as reference. Double-resonance spectra were obtained by Varian Associates, Palo Alto, Calif., on a Varian HA-100 nmr spectrometer. Mass spectral data were obtained using a Consolidated Electrodynamics 21-130 mass spectrometer.

When the reaction was carried out at 0–15°, polymer **16a** was obtained with a molecular weight of 6160 (27 units)

Reaction of Butyl Vinyl Ether and Benzenesulfonyl Azide. A. Exothermic Reaction.—A mixture of 7.5 g (0.075 mole) of butyl vinyl ether and 9.0 g (0.049 mole) of benzenesulfonyl azide became warm and began to liberate nitrogen immediately. After a short time the reaction became quite exothermic and was complete in about 20 min. After removal of excess vinyl ether at 100° (20 mm), there was obtained 13.4 g (107%) of viscous orange oil. The infrared spectrum had residual absorption at 4.75 μ and a strong imido ester band at 6.3 μ. The pmr spectrum of the crude product indicated 48 mole % imidoformate (singlet, 8.4 ppm) and 12 mole % imidoacetate (singlet, 2.45 ppm). A portion (10.3 g) of the viscous oil was extracted several times with petroleum ether. The insoluble amorphous polymer (1.3 g, 13%) was reprecipitated from ether with petroleum ether. The infrared and integrated pmr spectra are consistent with a 1:1 polymer structure **16b**.

Anal. Calcd for $C_{12}H_{17}NO_3S$: C, 56.44; H, 6.72; N, 5.49. Found: C, 56.28; H, 6.72; N, 5.85.

The petroleum ether soluble yellow oil weighed 9.0 g (87%). The oil was diluted with a small quantity of ether and cooled in a Dry Ice–acetone mixture. The supernatant solution was decanted from the crystalline precipitate and the latter washed several times with ether. The product **17b** was recrystallized from benzene–petroleum ether, mp 148–149°.

Anal. Calcd for $C_{24}H_{34}N_2O_6S_2$: C, 56.44; H, 6.72; N, 5.49; mol wt, 510. Found: C, 56.18; H, 6.57; N, 5.73; mol wt, 496.

The major portion (7.25 g) of the ether soluble yellow oil was refluxed for several hours with excess 5% aqueous sodium hydroxide. The mixture was cooled, extracted with ether, and the aqueous layer saturated with carbon dioxide. The yield of precipitated benzenesulfonamide was 2.75 g. The dry salt mixture obtained by concentration of the filtrate was extracted with methanol and the methanol soluble fraction (1.2 g) was dissolved in deuterium oxide. The pmr spectrum of the latter solution had a strong sharp singlet at 8.4 (formate) and at 2.0 ppm (acetate) in the ratio of 4:1. A minor amount of aromatic absorption was observed centered at 7.6 ppm. The infrared spectrum of the salt mixture indicated the presence of an anion with absorption at 4.8 μ. The latter was identified as azide by the red coloration produced with acidic ferric chloride. A sample (0.14 g) of the salt mixture was extracted with acetone. The infrared spectrum of the residue (0.11 g) indicated a mixture of sodium formate, sodium acetate, and sodium azide. The soluble portion (0.03 g) was found to contain minor amounts of benzenesulfonamide and sodium benzenesulfonate. The major acetone soluble product was an unidentified benzenesulfonamidocarboxylic acid salt. Acidification of the latter yielded the free acid which had infrared bands at 3.1, 2.9–4.0, 5.9, 7.0, 7.55, 8.25, 8.65, 9.25, 10.1, 10.65, 11.75, 13.35, 14.0, and 14.70 μ.

The ether extract of the hydrolyzed product was dried over magnesium sulfate and concentrated at 100° (20 mm) to remove butanol. The integrated pmr spectrum of the residual orange oil (3.4 g) indicated a low polymer containing benzenesulfonamido and butyl vinyl ether units in a ratio of 3:4. A sample of the latter product was dissolved in petroleum ether and cooled to −78°. The oil soluble in petroleum ether at this temperature had infrared, pmr, and mass spectra consistent with a butyl vinyl ether polymer.

B. Temperature-Moderated Reaction.—A mixture of 0.9 g (0.009 mole) of butyl vinyl ether and 0.9 g (0.005 mole) of benzenesulfonyl azide became spontaneously warm to 34°. Although nitrogen evolution was evident at this temperature, the azide band at 4.7 (infrared) did not decrease at an appreciable rate until 60° was attained. After the reaction was complete, the solution was concentrated at 100° (20 mm) to yield 1.3 g (100%) of viscous yellow oil. After extraction with petroleum ether there was obtained 0.9 g (69%) of amorphous polymer and 0.4 g (31%) of colorless oil. The pmr spectrum of the latter oil indicated the presence of 41 mole % of imidoformate. Crystals of dimer **17b** separated from the oil after a few days at room temperature.

N,N′-Bis(Phenylsulfonyl)-2-alkoxy-1,2,3,4-tetrahydropyrazines (23). A. Ethoxy Derivative 23b.—A mixture of 3.5 g (0.015 mole) of polymer **16a**, 20 ml of ethanol, and 1 ml of concentrated hydrochloric acid was heated at the reflux temperature for 3 hr. During this time the insoluble polymer gradually formed a red insoluble oil which finally dissolved. An additional 1 ml of concentrated hydrochloric acid was then added and the solvent was distilled from the solution. Eventually, crystals began to deposit. The product was recovered by filtration, more ethanol was added to the filtrate, and the distillation process was repeated. The combined yield of crude product was 2.5 g (80%). The latter was decolorized with carbon and recrystallized from ethanol, mp 167.5–168.5°. The same product was obtained from polymer **16b** using the procedure outlined above.

Anal. Calcd for $C_{18}H_{20}N_2O_5S_2$: C, 52.94; H, 4.90; N, 6.86; S, 15.70; mol wt, 408. Found: C, 52.87; H, 5.10; N, 6.88; S, 15.67; mol wt, 415.

B. Methoxy Derivative 23a.—Using the procedure described for the ethoxy analog, 2.3 g (0.1 mole) of polymer **16a**, methanol, and concentrated hydrochloric acid yielded 1.75 g (88%) of the methoxy derivative. Recrystallization from benzene-petroleum ether gave mp 159.5–160.5°.

Anal. Calcd for $C_{17}H_{18}N_2O_5S_2$: C, 51.75; H, 4.68; N, 7.13. Found: C, 51.97; H, 4.67; N, 6.92.

C. Propoxy Derivative 23c.—This product was prepared by refluxing a solution of ethoxy derivative **23b**, *n*-propyl alcohol, and a catalytic amount of boron trifluoride etherate. Recrystallization from ethanol gave mp 154°.

N,N′-Bis(phenylsulfonyl)-2,6-bis(phenylthio)piperazine (24).—A mixture of 0.5 g (0.0012 mole) of the tetrahydropyrazine **23b**, 0.5 g (0.0045 mole) of thiophenol, and 2 drops of boron trifluoride etherate was heated at 100° for 1 hr. Ether was added to the pasty product and the insoluble white powder (0.3 g, 43%) was collected by filtration. The crude product, mp 181–185°, was recrystallized from benzene–ether, mp 195–196°.

Anal. Calcd for $C_{28}H_{26}N_2O_4S_4$: C, 57.70; H, 4.51; S, 22.00. Found: C, 57.81; H, 4.58; S, 21.91.

The ether extracts were concentrated and extracted with hexane to remove excess thiophenol. The residual tan powder weighed 0.35 g (50%). The infrared spectrum of the latter product was different but similar in many respects to the product of mp 195–196°. This material was not investigated.