following the decrease in the absorbance of the solution with time at 440 nm.

Reaction of 2b with Thiol. The reaction of **2b** with the thiol was studied by using the same general procedure as just described for the reaction of *n*-BuSH with **2a**. The progress of the reaction was followed by monitoring the decrease in the absorbance of the solution with time at 425 nm.

Reaction of 1b with Thiol. To 3.5 mL of 60% dioxane in a 1-cm spectrophotometer cell thermostated at 25 °C was added 35 μL of a freshly prepared stock solution of **2b** (5×10^{-3} M) in dioxane, followed by 3.5 μL of a 1 M solution of perchloric acid. The solution was allowed to stand for 5 min to ensure that hydrolysis of **2b** to **1b** was complete. Then the proper amounts of buffer (or perchloric acid) and lithium perchlorate solutions to afford the desired reaction conditions were added by microsyringe. This was followed by the initiation of the reaction by the addition of the proper amount of a stock solution of the thiol in dioxane via another microsyringe. The reaction of **1b** with the thiol was followed by observing the decrease in the absorbance of the solution with time at 410 nm.

Reaction of 1a with Thiol. For the runs in dilute perchloric acid, or in trifluoroacetate buffers, the procedure was as follows. To a 60% dioxane solution (3.5 mL) containing the desired concentrations of perchloric acid (or buffer) and lithium perchlorate was added 35 μL of a stock solution of **2a** (5×10^{-3} M) in dioxane. The absorbance of the solution at 440 nm was then monitored in order to determine when the hydrolysis of **2a** to **1a** was complete (for some reaction conditions several hours were required). At that point the desired amount of a stock solution of *n*-BuSH in dioxane was added by microsyringe, and the decrease in the absorbance of the solution at 440 nm, due to the reaction of **1a** with the thiol, was followed.

For the runs in H_3PO_4–$H_2PO_4^-$ buffers the procedure was slightly different. A stock solution of **1a** (0.01 M) in 90% dioxane was prepared by dissolving **2a** (5×10^{-3} M) in 90% dioxane containing 0.01 N $HClO_4$ and allowing the hydrolysis of the selenenic anhydride to proceed to completion. (The progress of the hydrolysis was monitored by removing aliquots, and, after appropriate dilution, measuring the absorbance at 440 nm.) A portion (35 μL) of this stock solution of **1a** was added to 3.5 mL of a 60% dioxane solution containing the proper concentrations of buffer and lithium perchlorate, and the reaction of **1a** with the thiol was then initiated by the addition via microsyringe of the correct amount of a stock solution of *n*-BuSH in dioxane.

Products of the Reaction of 2a and 1a with 2-Methyl-2-propanethiol. Selenenic anhydride **2a** (0.29 g, 0.70 mmol) was dissolved in 15 mL of dioxane. To this was then added 0.5 mL of a 3 M solution of 2-methyl-2-propanethiol (1.40 mmol) in dioxane and 0.515 mL of 0.97 M aqueous perchloric acid, followed by enough water to bring the final volume of the solution to 25 mL. The solution was allowed to stand at room temperature. Periodically 2.5-μL aliquots were removed and diluted to 3.0 mL with 60% dioxane, and their ultraviolet spectrum was scanned between 320 and 460 nm. When the scan indicated that the reaction was complete, the solution was poured into 100 mL of water and extracted three times with 10-mL portions of chloroform. The chloroform was dried (Na_2SO_4), the solvent was removed under reduced pressure at room temperature, and the residue was subjected to an oil pump vacuum for several hours to remove the last traces of solvent and dioxane. The residue, a yellow oil, was shown by TLC to consist of a single compound that was identified as *tert*-butyl *o*-nitrobenzeneselenenyl sulfide, *t*-BuSSeC$_6$H$_4$NO$_2$-*o*, 0.39 g (94%): NMR ($CDCl_3$) δ 7.2–8.5 (m, 4 H), 1.38 (s, 9 H); mass spectrum, *m/e* 291 (M^+, ^{80}Se), 289 (M^+, ^{78}Se), 235 ($M^+ - C_4H_8$), 202 ($M^+ - C_4H_9S$), 186, 154, 106, 88, 57, 41.

Registry No. **1a**, 56790-60-4; **1b**, 84250-81-7; **2b**, 84250-80-6; **7** (R = Bu), 90941-71-2; **8**, 90941-72-3; *t*-BuSSeC$_6$H$_4$NO$_2$-*o*, 90941-75-6; (*o*-NO$_2$C$_6$H$_4$Se)$_2$O, 84250-76-0; BuS^-, 20733-16-8; BuSH, 109-79-5; $CH_3C(CH_3)_2SH$, 75-66-1.

Supplementary Material Available: Tabulation of results of individual kinetic runs for **2a** (Table V), **2b** (Table VI), **1b** (Table VII), and **1a** (Table VIII) (13 pages). Ordering information is given on any current masthead page.

Solution and Flash Vacuum Pyrolyses of 3-Arylpropanesulfonyl and 2-(Aryloxy)ethanesulfonyl Azides. Synthesis of 7-Membered Sultams

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Received January 13, 1984

The solution and flash vacuum pyrolyses of 3-arylpropanesulfonyl azides have been studied and the results compared with those of the corresponding 2-arylethanesulfonyl azides. The best yields of 7-membered ring sultams are formed on solution decomposition in Freon 113. Hydrogen abstraction and solvent insertion products are obtained mainly in hydrocarbon solvents. The structures of the 7-membered sultams have been established unambiguously and an authentic sample of the parent 2,3,4,5-tetrahydro[*c*]-1,2-thiazepine 1,1-dioxide prepared. Decomposition of 3-(2,6-dichlorophenyl)propanesulfonyl azide (**22**) leads to a 6,9-dichloro sultam (**33c**) via a 1,2-chlorine shift. FVP of 3-(2-mesityl)propanesulfonyl azide (**20**) gave a good yield of the 7-membered ring sultam (**34**) (1,2-methyl shift). FVP of 3-phenyl-1-propanesulfonyl azide (**16**) at 995 °C (0.05 mm) gave, among other products, a 6.2% yield of 5,6,7,8-tetrahydroquinoline (**39**). The formation of these products is discussed. Thermolysis of 2-(aryloxy)ethanesulfonyl azides gave the corresponding 7-membered ring sultams **27** as well.

The thermal decomposition of sulfonyl azides in solution in saturated or aromatic hydrocarbons is a unimolecular process[1] leading to sulfonylnitrenes[2] which can then undergo inter- or intramolecular reactions. Thus, the solution decomposition of 2-phenylethanesulfonyl azides in hydrocarbon solvents was found to yield small amounts of intramolecular cyclization products together with products of intermolecular reactions, namely C–H insertion and

† Some of this work was performed at the University of Alabama, Tuscaloosa, AL 35486.

(1) McManus, S. P; Smith, M. R.; Abramovitch, R. A.; Offor, M. N. *J. Org. Chem.* **1984**, *49*, 683.

(2) Abramovitch, R. A.; Sutherland, R. G. *Fortsch. Chem. Forsch.* **1970**, *16*, 1. Abramovitch, R. A. *Mech. React. Sulfur Compd.* **1968**, *3*, 1. Abramovitch, R. A.; Kyba, E. P. In "The Chemistry of the Azido Group"; Patai, S., Ed; Interscience: New York, 1971. Breslow, D. S. In "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; p 245.

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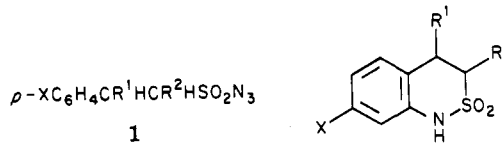
hydrogen abstraction.[3] The use of an excess of a relatively inert solvent Freon 113 led to better yields of the desired 3,4-dihydro-2,1-benzothiazine 2,2-dioxides.

To avoid troublesome intermolecular reactions the flash vacuum pyrolysis (FVP) of 2-phenylethanesulfonyl azides (1) was studied.[3] At 250–300 °C, FVP of 1 gave the sultam



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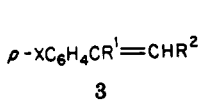

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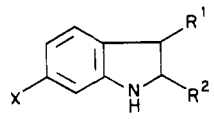

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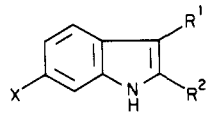

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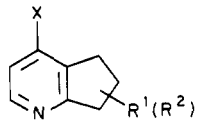

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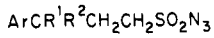


7

(2), but the use of higher temperatures led to the formation of styrenes (3), indolines (4), indoles (5), sulfur dioxide, and a remarkable transformation product, the 4-substituted 6,7-dihydro-5*H*-1-pyrindine (6). When R^1 = Me, R^2 = H or R^1 = H, R^2 = Me the same ratio of a mixture of 6- and 7-methyl-6,7-dihydro-5*H*-1-pyrindine (6) was obtained.[3] A mechanism was proposed to account for these results.

As an extension of this work, we decided to lengthen the side chain by one atom to see whether or not (a) 7-membered sultams can be synthesized in this way, (b) side chain C–H insertion to yield an isothiazolidine can compete with intramolecular addition[4] of the sulfonylnitrene to the aromatic nucleus, (c) a similar ring transformation would occur as with the 2-phenethanesulfonyl azides, leading in this case to 5,6,7,8-tetrahydroquinolines, and also (d) the ratio of intramolecular 7-membered ring formation to intermolecular reactions with solvent compares with that from the corresponding 2-phenethanesulfonyl azide.

Results and Discussion

Most of the 3-arylpropanesulfonyl azides were prepared by the following sequence (see Experimental Section):

$$ArCH_2Br \rightarrow ArCH_2CH(CO_2Et)_2 \rightarrow ArCH_2CH_2CO_2H \rightarrow ArCH_2CH_2CH_2OH \rightarrow Ar(CH_2)_3Br \rightarrow [Ar(CH_2)_3S]_2 \rightarrow Ar(CH_2)_3SO_2Cl \rightarrow Ar(CH_2)_3SO_2N_3$$

Attempts to prepare the propanols by using the benzylmagnesium bromides and ethylene oxide gave, in addition to the desired alcohols, bibenzyls as well as other products. This was particularly so with 3,5-dimethylbenzyl bromide that gave 3,3′,5,5′-tetramethylbibenzyl (46%) as the only isolated product. An authentic sample of the latter was made from the benzyl bromide and *n*-butyllithium using the procedure of Parham and his co-workers.[5] The sulfonyl chlorides were made from the sulfonate salt (from bromide and sodium sulfite) using thionyl chloride. In some cases (3-phenylpropanesulfonyl azides) yields were very low owing to decomposition of the chloride on heating with concurrent loss of SO_2.[6] In these instances, much higher yields were obtained by converting the propyl bromide to the disulfide and then oxidizing the latter with Cl_2 in aqueous acetic acid. The sulfonyl chlorides were converted to the azides either with sodium azide in aqueous acetone or with 1,1,3,3-tetramethylguanidinium azide in chloroform. The yields were usually better using the latter reagent which also had the advantage of avoiding aqueous conditions.

The 2-(aryloxy)ethanesulfonyl azides were synthesized by using a procedure similar to that used for compounds 7. The appropriate phenol was condensed with 2-chloroethanol to give the 2-hydroxyethyl aryl ether (8) which,

$$ArOCH_2CH_2X$$

8, X = OH **11**, X = SO_2Cl

9, X = Cl **12**, X = SO_2N_3

10, X = SO_3Na

with thionyl chloride, was converted to the 2-chloroethyl aryl ether (9). This with sodium sulfite gave the sodium sulfonate (10) which was converted to the sulfonyl chloride (11) and then to the azide (12). Unlike the sulfur analogue, $PhSCH_2CH_2SO_3^-Na^+$, which reacted with thionyl chloride with neighboring sulfur participation giving $PhSCH_2CH_2Cl$,[7] the oxygen derivative 10 appeared to react without oxygen participation.

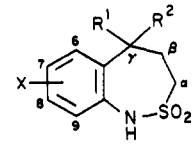
Solution Decompositions. The sulfonyl azides were decomposed in three solvents: cyclohexane, benzene, and Freon 113. Authentic samples of sulfonamides (13), *N*-

$$ArCRR'CH_2CH_2SO_2NHR''$$

13, R″ = H; **14**, R″ = *c*-C_6H_{11}; **15**, R″ = Ph

cyclohexylsulfonamides (14), and *N*-phenylsulfonamides (15) were obtained from the corresponding sulfonyl chloride and ammonia, cyclohexylamine, or aniline, respectively. The results of the thermolyses are summarized in Table I.

The decompositions in cyclohexane give poor yields of hydrogen abstraction products (13), usually average to good yields of solvent insertion products (14), and poor yields of intramolecular cyclization products. In addition, sulfur dioxide was detected (a radical process[2]). The thermolysis in benzene proceeded similarly, the main product again being the solvent insertion product 15. The best yields of intramolecular cyclization products were obtained in Freon 113 which, except for the cyclization of 20 (see below), provide the best preparative conditions for the synthesis of the corresponding sultams 26 and 27.



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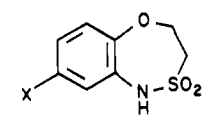

27

Azides 16–19, 21, and 22 yield 7-membered sultams 26, while azides 23–25 gave the oxa derivatives 27. The structures of sultams 26 were established on the basis of

(3) Abramovitch, R. A.; Holcomb, W. D.; Wake, S. *J. Am. Chem. Soc.* **1981**, *103*, 1525.
(4) Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340.
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(6) Bain, P. J.; Blackman, E. J.; Cummings, W.; Hughes, S. A.; Lynch, E. R.; McCall, E. B.; Roberts, R. J. *Proc. Chem. Soc.* **1962**, 186.
(7) McManus, S. P.; Smith, M. R.; Herrmann, F. T.; Abramovitch, R. A. *J. Org. Chem.* **1978**, *43*, 647.

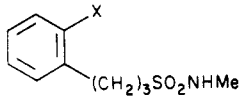
Table I. Solution Thermolysis of Sulfonyl Azides[d]

azide	solvent	temp, °C	time, h	recovered azide, %	yield of products,[a] % 13	14	15	sultam
$Ph(CH_2)_3SO_2N_3$ (16)	cyclohexane	137	36	0.9	2.9	11.3		1.9
	benzene	138	50	10.9	2.6		71.2	9.9
	Freon 113	135	36	37.3				44.4
$PhCH(CH_3)CH_2CH_2SO_2N_3$ (17)	cyclohexane	140	58	44.7	1.0	77.2		8.2
	benzene	138	50	12.4	7.6		25.7	6.6
	Freon 113	124	48	3.4	1.2			27.6
$PhC(CH_3)_2CH_2CH_2SO_2N_3$ (18)	cyclohexane	149	36	37.5	1.6	53.2		15.9
	benzene	149	36	44.9	4.0		77.0	7.4
	Freon 113	149	36	30.2	1.9			74.9
$3,5\text{-}Me_2C_6H_3(CH_2)_3SO_2N_3$ (19)	cyclohexane	140	38	35.9	2.9	12.0		5.0
	benzene	154	36	40.0	2.3		68.6	8.2
	Freon 113	140	38	4.3				71.7
$2,4,6\text{-}Me_3C_6H_2(CH_2)_3SO_2N_3$ (20)	cyclohexane	140	58	10.9	10.8	75.5		*b*
	benzene	138	50	11.1	1.3		28.7	*b*
	Freon 113	124	40	18.5				2.3
		140	25[e]		2.6			9.2
		160	36					*c*
$2\text{-}ClC_6H_4(CH_2)_3SO_2N_3$ (21)	cyclohexane	140	58	15.7	1.3	43.9		2.7
	benzene	138	50	5.5			29.3	12.3
	Freon 113	124	48	10.2	2.9			29.7
$2,6\text{-}Cl_2C_6H_3(CH_2)_3SO_2N_3$ (22)	cyclohexane	154	36	15.3	28.3	46.5		
	benzene	154	36	15.9			79.3	6.8
	Freon 113	154	36	20.8	19.5			34.9
$PhOCH_2CH_2SO_2N_3$ (23)	Freon 113	135	36					49.4
$4\text{-}MeOC_6H_4OCH_2CH_2SO_2N_3$ (24)	Freon 113	135	36					29.3
$4\text{-}ClC_6H_4OCH_2CH_2SO_2N_3$ (25)	Freon 113	135	36					36.5

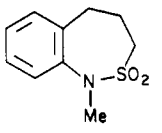
[a] Based on the amount of azide consumed. [b] Trace. [c] Only tars isolated. [d] Spectral and analytical data for some starting materials and products are given in supplementary material. [e] This time is given in days not hours.

their infrared, NMR, and mass spectral properties (and microanalytical data). As expected,[8] the mass spectra of the sultams show clear molecular ions as well as strong M − 1 and M − 1 − SO_2 fragment ions.

The structure of the cyclization product from **16** was established conclusively by the synthesis of an authentic sample. Treatment of 3-(2-chlorophenyl)-1-propanesulfonamide with potassium amide in liquid ammonia gave only recovered starting amide. Similarly, treatment of 3-(2-chlorophenyl)- (**28**) or 3-(2-bromophenyl)-*N*-methyl-



28, X = Cl
29, X = Br



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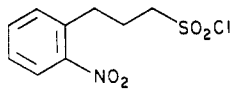

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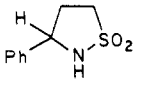

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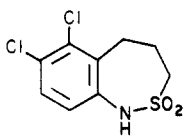
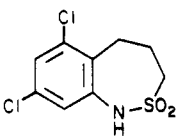
1-propanesulfonamide (**29**) with sodium hydride in THF, with KNH_2/NH_3(l), or with lithium diisopropylamide in THF at 150 °C did not lead to cyclization. On the other hand, the desired aryne could be generated from **29** and lithium 2,2,6,6-tetramethylpiperidide in boiling THF to give a good yield of the desired 1-methyl-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**30**), identical with the product obtained on *N*-methylation of **26** (X = R^1 = R^2 = H). Finally, an authentic sample of **26** (X = R^1 = R^2 = H) itself was achieved by using the procedure devised by Loev and Kormandy[9] for the preparation of the corresponding 6-membered sultam: 3-(2-nitrophenyl)-1-propanesulfonyl chloride (**31**) was hydrolyzed to the sodium sulfonate and reduced with hydrogen over Pd-C, and the amine was cyclized (via the sulfonyl chloride) by treatment with PCl_5 in acetyl chloride. A 30% yield of **26** was thus obtained. The product was identical with that formed in the decomposition of **16**. The NMR spectrum and the synthesis of an authentic sample eliminate the alternative isomeric structure, the isothiazolidine 1,1-dioxide **32** which could have been formed by insertion of the nitrene into the γ CH_2 of the side chain. Indeed, in no case studied here was an isothiazolidine 1,1-dioxide detected.

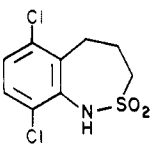
The solution decomposition of **22** leads to the formation of a sultam still containing two chlorine atoms and for which three structures are possible, namely **33a–c**. The



33a



33b



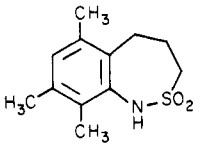
33c

NMR spectrum (60 MHz) exhibits a 2 H *singlet* for the aromatic protons, a triplet for the NH (exchangeable), and multiplets at δ 3.25 and 2.2, integrating approximately for 4 H and 2 H, respectively. These data might suggest either structure **33b** or **33c**. On the other hand, a 1,2-chlorine shift (similar to a related NIH shift of a 1-chloroarene oxide) has been shown to occur in the corresponding 2-phenethyl derivative,[10] which would support structure **33c** for the rearranged sultam. This will be discussed further in a future paper on the decomposition of 2,6-disubstituted 2-phenylethanesulfonyl azides.

The sultam, $C_{12}H_{17}NO_2S$, obtained from the thermolysis of 3-mesityl-1-propanesulfonyl azide (**20**) contained an NH and an SO_2 group (3240, 1300, and 1140 cm^{-1}). The aromatic proton gave rise to a 1 H singlet at δ 6.86; a 2 H triplet at δ 3.33 was assigned to the CH_2 α to SO_2, and a

(8) Shulten, H.-R.; Beckey, H.; Eckhardt, G.; Doss, S. H. *Tetrahedron* **1973**, *29*, 3861.
(9) Loev, B.; Kormendy, M. F. *J. Org. Chem.* **1965**, *30*, 3163.
(10) Abramovitch, R. A.; Thompson, W. M., unpublished results.

2 H triplet at δ 2.95 to the benzylic CH_2 group. An 11 H band at δ 2.4–1.7 (two sharp Me singlets (9 H) superimposed upon a very broad 2 H band) was assigned to three CH_3 groups and the remaining CH_2. The NH absorbed at δ 6.2. On that basis, we assign structure **34**, in which a 1,2-methyl shift has occurred, to this compound rather than the isomeric 3-mesitylisothiazolidine 1,1-dioxide one **35** or 8-membered sultam (insertion into CH_3). Indolization of ethyl pyruvate 2,6-dimethylphenylhydrazone takes place with a similar 1,2-methyl shift.[11a]



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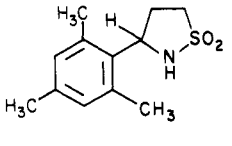
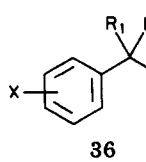


35

The 2-(aryloxy)ethanesulfonyl azides gave only the corresponding sultams (**27**) on thermolysis in Freon 113, no hydrogen abstration products being observed. The structures assigned were consistent with the NMR spectra.

Flash Vacuum Pyrolyses. 3-Phenyl-1-propanesulfonyl azide (**16**) was pyrolyzed under a variety of experimental conditions. When a static system[3] was used at 360 °C and 0.25 mm, the products formed were the sultam (**26**, X = R^1 = R^2 = H) (27%), sulfonamide (**13**) (1.1%), allylbenzene (**36a**) (3.7%), and 1,2,3,4-tetrahydroquinoline (**37a**) (5.3%). The allylbenzene undoubtedly arises in the same way as does the stryene in the corresponding FVP of 2-phenylethanesulfonyl azide,[3] i.e., a stepwise or cyclic radical process:



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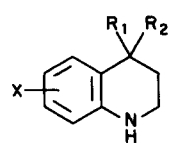
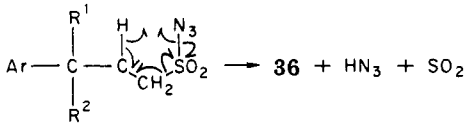


37

a, X = R^1 = R^2 = H
b, X = R^1 = H, R^2 = Me
c, X = H, R^1 = R^2 = Me
d, X = 3,5-Me_2, R^1 = R^2 = H
e, X = 2,4,6-Me_3, R^1 = R^2 = H
f, X = 2-Cl, R^1 = R^2 = H
g, X = 2,6-Cl_2, R^1 = R^2 = H



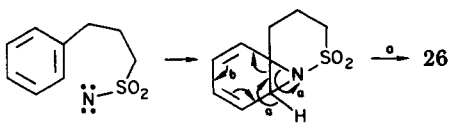
Loss of sulfur dioxide from **26** to give the tetrahydroquinoline (**37**) on FVP has many precedents in sulfone and sultam chemistry.[3,11,12] That this was indeed the source of **37** was confirmed by the FVP of **26** (X = R^1 = R^2 = H) at 360 °C (0.005 mm) (flow system[3]) when a 2.9% yield of **37a** was obtained. At 650 °C (0.005 mm) (N_2 flow rate 0.9 mL/min) the yield was 86.9%. Similarly, FVP of **26** (X = 7,9-Me_2, R^1 = R^2 = H) at 665 °C (0.15 mm) (static system) gave **37d** (94.6%).

At 450 °C (0.5 mm) (static system) the yield of sultam dropped slightly to 22.9%, that of **13** stayed constant, but those of **36a** and **37a** increased to 11.8% and 46.3%, respectively. At 650 °C (0.5 mm) the yield of sultam dropped drastically to 7.5% and only a trace of allylbenzene was obtained. On the other hand, tetrahydroquinoline (formed at the expense of sultam) was isolated in 60.3% yield. The most interesting results were obtained at 995 °C (0.05 mm) (flow system). The yield of sultam dropped almost to nil (0.4%), but that of allylbenzene was 11.9% and that of **37e** was 66.2%. Three new products were obtained. Hydrocinnamonitrile (**38**) (3.2%) was probably formed by the extrusion of SO_2 from **16** followed by loss of nitrogen to give 3-phenyl-1-propylnitrene, 1,2-hydrogen shift, and dehydrogenation of the imine:

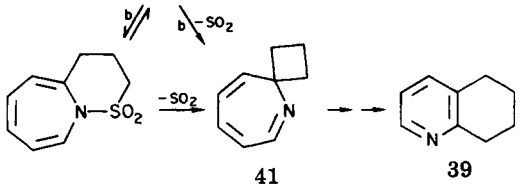
$$16 \rightarrow SO_2 + Ph(CH_2)_3N_3 \rightarrow N_2 + Ph(CH_2)_2\ddot{C}H_2: \rightarrow Ph(CH_2)_2CH{=}NH \rightarrow Ph(CH_2)_2C{\equiv}N$$

38

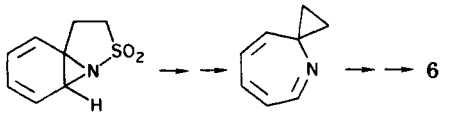
Quinoline was undoubtedly formed by dehydrogenation of the tetrahydro derivative. 5,6,7,8-Tetrahydroquinoline (**39**) (6.2%) was isolated by column chromatography of the crude reaction mixture. This is the homologue of the dihydropyrindine isolated from 2-phenethanesulfonyl azide under much milder conditions. Indeed, no **39** was detected at the lower FVP temperatures used (<650 °C). It undoubtedly arises from ring expansion of the initial product (**40**) of intramolecular addition of the sulfonylnitrene to the adjacent benzene ring either followed or preceded by loss of SO_2 to give **41** (by analogy with the mechanism proposed for dihydropyrindine formation[3]). The detailed steps remain to be established. What is clear from the much more drastic reaction conditions required to obtain any **39** and from the important yield of 1,2,3,4-tetrahydroquinoline **37a**—and hence of its precursor **26**—even under these vigorous conditions is that the transformation of **40** to **41** is either much more energy demanding than the conversion of **42** to **43** or that the process **40** → **26** is more facile than **42** → **2**.



40



41 **39**



42 **43**

FVP of the 2-(aryloxy)ethanesulfonyl azides **23** and **24** gave low yields of the corresponding sultams **27**. The gas chromatographic analysis of the crude reaction mixture showed the presence of twelve other components, one of which was identified in the case of the FVP of **23** as the 1,4-benzoxazine **44**, isolated in trace amounts and compared with an authentic sample.[13] The latter was stable under the FVP conditions. On the other hand, **27** was not, only 52.4% being recovered on FVP at 450° C (1 mm) together with a trace of **44**. At 650 °C (1 mm) **27** was

(11) (a) Carlin, R. B.; Henley, W. O.; Carlson, D. P. *J. Am. Chem. Soc.* **1957**, *79*, 5712. (b) Leonard, Jr., E. C. *J. Org. Chem.* **1962**, *27*, 1921. Oliver, J. A.; Ongley, P. A. *Chem. Ind. (London)* **1965**, 1024. DeJongh, D. C.; Evenson, G. N. *J. Org. Chem.* **1972**, *37*, 2152.

(12) Abramovitch, R. A.; Wake, S. *J. Chem. Soc., Chem. Commun.* **1977**, 673.

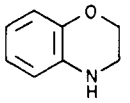
(13) Knorr, L. *Chem. Ber.* **1889**, *22*, 2086.

Table II. Flash Vacuum Pyrolysis of Sulfonyl Azides

azide	conditions[b]	tube temp, C°	pressure, mmHg	recovered azide, %	products,[a] % sultam	37	13	36	other
16	A	360	0.25		27.0	5.3	1.1	3.7	
	A	460	0.5	0.6	22.9	46.3	1.1	1.8	
	A	600	0.5		7.5	60.3		tr	
	B (1.5)	995	0.05	0.8	0.4	66.2		11.9	**38** (3.2%), **39** (6.2%), quinoline (0.8–5.7%)
17	A	665	0.03		11.2	64.5	0.2	1.6	
	B (10.0)	690	0.6	2.6	12.8	50.7	0.2	1.0	
18	A	710	<0.001	1.7	3.8	68.4	1.1	3.5	
19	A	690	0.3		4.6	34.1	tr	0.4	
	B (25)	690	2.2		21.0	69.0	0.5	0.6	
	C	400	0.05		32.6	9.3	tr	16.3	
20	A	690	3.0	34.0	18.6		10.1	2.5	
	B (10.0)	690	0.8	8.9	88.1		3.9	1.6	
21	A	690	0.15		9.2	36.5	4.1	3.0	
	B (10.0)	690	0.75	5.2	19.3	12.9	0.5	1.4	
	C	400	0.2		12.8	3.8		3.2	
22	A	690	6.0		0.8			21.8	
	B (10.0)	690	0.5		3.8		3.8	21.8	
23	B (30)	450	2.0		23.4				**44** (tr), 11 other components
24	B (30)	450	2.0		10.4				

[a] Yields calculated on the basis of azide consumed. [b] A = static system; B = flow system (N_2 flow rate in mL/min); C = static system using a packed tube.

completely decomposed and no **44** was detected. None of the products formed have been identified to date.



44

As the results summarized in Table II show sultams are formed in all the cases studied, albeit in lower yields than on solution decomposition in Freon 113. The only major exception to this latter statement is in the case of 3-mesityl-1-propanesulfonyl azide (**20**) when FVP in a flow system at 690 °C gives an excellent yield of 7-membered sultam **34**. With this single exception, therefore, the preparative scale synthesis of the sultams is best achieved by solution decomposition of the sulfonyl azides in Freon 113. It is interesting to note also that the same product of chlorine migration (**33**) attendant upon cyclization is formed on FVP as is obtained on solution decomposition of the corresponding azide. Once again, no intramolecular C–H insertion into the propyl chain is observed, even in cases where the ortho positions are blocked.

A comparison of the yields of intramolecular cyclization of ((3-aryl-1-propyl)sulfonyl)- and of ((2-arylethyl)-sulfonyl)nitrenes[3] in Freon 113 shows that the former are uniformly higher, which may be attributed to the lesser strain involved in forming the 6-3-6 fused intermediate from the former than the 6-3-5 one from the latter. Another contrast, mentioned above, is the greater ease of formation of ring-transformation products from the latter under FVP conditions, with the consequent result that much more 1,2,3,4-tetrahydroquinolines are formed from the former at 650 °C than indolines are formed from the latter. Lastly, the former nitrene in Freon 113 appears to be less apt to undergo intermolecular hydrogen abstraction to yield the sulfonamide than is the latter under comparable conditions. This, however, might just be a reflection of the relative ease with which the ((3-aryl-1-propyl)-sulfonyl)nitrene undergoes intramolecular addition in non-hydrogen donor solvents, since intermolecular hydrogen abstraction and particularly solvent insertion become important in hydrocarbon solvents.

Experimental Section

Melting points are uncorrected. IR spectra were determined on Perkin-Elmer 257, 357, or Beckman Acculab 3 intruments and NMR spectra on a Varian Associates HA-100 or a Hitachi Perkin-Elmer R20B spectrometer with tetramethylsilane as internal standard. The mass spectra were determined on a CEC 21-104 or Hitachi Perkin-Elmer RMU-6M spectrometer and UV spectra on a Cary 14 sectrophotometer. Gas chromatographic analyses were carried out on a Varian-Aerograph Series 1800 gas chromatograph using helium as a carrier gas and a flame ionization detector.

Reagents and solvents were usually reagent grade and were fractionally distilled or recrystallized before use. Drying of organic extracts was effected with calcium chloride, magnesium sulfate, or molecular sieves (Davidson, type 4A, grade 514, 8-12 mesh). Petroleum ether refers to the fraction with bp 30–60 °C unless otherwise stated. Basic alumina for column chromatography was Alcoa (F-20) and neutral alumina was prepared by taking this basic alumina, boiling it with distilled water, neutralizing with acetic acid, rinsing with a large volume of distilled water, and activating by heating at 375 °C for 12 h, followed by cooling in a vacuum desiccator. Dry, oxygen-free nitrogen was obtained by passing commercial grade nitrogen through a train consisting of a basic solution of pyrogallol, then sulfuric acid, and finally anhydrous calcium chloride. Calculations of the thermolysis and FVP yields are based on unrecovered starting material.

Table III. New Sulfonyl Azides

sulfonyl azide	yield,[a] %	bp, °C (mmHg) or mp, °C
3-phenyl-1-propane-	75.4 (78.1)	mp 20 °C (petroleum ether)
3-phenyl-1-butane-	78.1 (94.4)	118 (<0.001)
3-methyl-3-phenyl-1-butane-	80.7 (98.4)	125 (<0.001)
3-(3,5-dimethylphenyl)-1-propane-	75.3	120 (<0.001)
3-mesityl-1-propane-	78.4 (95.2)	mp 56.5–58.2 (petroleum ether)
3-(2-chlorophenyl)-1-propane-	72.9 (99.0)	132 (<0.001)
3-(2,6-dichlorophenyl)-1-propane-	80.4 (92.0)	mp 46–47 (hexane)
2-phenoxyethane-	95	mp 64.5–65.5 (petroleum ether)
2-(4-methoxyphenoxy) ethane-	71.9	mp 62 (petroleum ether)
2-(4-chlorophenoxy)ethane-	72.1	mp 57 (petroleum ether)
2-(3-(trifluoromethyl)phenoxy)ethane-	63.4	mp 55–56

[a] With sodium azide. Yield in parentheses is that obtained with tetramethylguanidinium azide.

Table IV. New Sulfonamides

sulfonamide	yield, %	mp, °C
3-phenyl-1-butane-	90.6	90–91
3-methyl-3-phenyl-1-butane-	74.1	101–102
3-(3,5-dimethylphenyl)-1-propane-	56.9	93–94
3-mesityl-1-propane-	85.6	168.5–170
3-(2-chlorophenyl)-1-propane-	15.5	95.5–97.5
3-(2,6-dichlorophenyl)-1-propane-	54.3	134–135
N-*tert*-butyl-3-phenyl-1-propane-	31.9	61.5–62.5
N-cyclohexyl-3-phenyl-1-propane-	16.1	68–69
N-cyclohexyl-3-phenyl-1-butane-	40.2	70–71.5
N-cyclohexyl-3-methyl-3-phenyl-1-butane-	84.1	90–91.5
N-cyclohexyl-3-(3,5-dimethylphenyl)-1-propane-	69.5	92.5–94
N-cyclohexyl-3-mesityl-1-propane-	80.1	85–87
N-cyclohexyl-3-(2-chlorophenyl)-1-propane-	41.0	82–84
N-cyclohexyl-3-(2,6-dichlorophenyl)-1-propane-	80.3	79–80
N,3-diphenyl-1-butane-		liquid
N,3-diphenyl-3-methyl-1-butane-	20.9	41–42
3-(3,5-dimethylphenyl)-*N*-phenyl-1-propane-	52.4	61.5–62.5
3-mesityl-*N*-phenyl-1-propane-	43.7	68–69
3-(2-chlorophenyl)-*N*-phenyl-1-propane-	75.8	62–63.5
3-(2,6-dichlorophenyl)-*N*-phenyl-1-propane-	51.5	104–105
3-(2-chlorophenyl)-*N*-methyl-1-propane-	29.2	56–58
3-(2-bromophenyl)-*N*-methyl-1-propane-	42.8	45–46

Sulfonyl Azides. Sulfonyl azides were prepared from the corresponding sulfonyl chlorides which were prepared from disulfides or sulfonate salts by known reactions. The sulfonyl chlorides were also converted into sulfonamides by reaction with ammonia, cyclohexylamine, or aniline to obtain authentic samples of amides. Details of the procedures and characterization data for new compounds prepared are contained in supplementary pages following this article. New sulfonyl azides and sulfonamides are listed, respectively, in Tables III and IV.

Solution Thermolysis. The sulfonyl azide was dissolved in degassed solvent and thermolyzed in a glass-lined steel bomb with with stirring.[14] After cooling, the solvent was evaporated and the residue dissolved in ether. Preliminary analysis was carried out by TLC. Neutral alumina (1–3 g) was then added to the solution, the suspension was dried under vacuum, and the residue was placed on a column of neutral alumina and chromatographed. Products were identified by comparison with authentic samples wherever possible. The results are summarized in Table I.

Thermolysis of 3-Phenyl-1-propanesulfonyl Azide. (a) In Cyclohexane. The azide (2.88 g) in dry, degassed, oxygen-free cyclohexane (50 mL) was thermolyzed at 137 °C for 36 h. Chromatography on a column of neutral alumina using a series of solvents from petroleum ether to ethyl acetate–ethanol (85:15 v/v) gave the following: 3-phenyl-1-propanesulfonyl azide (27 mg, 0.9%) identical (IR) with an authentic sample; 3-phenyl-1-propanesulfonamide (72 mg, 2.9%), mp 59–60 °C (petroleum ether) (lit.[8] 60–61 °C), IR identical with that of an authentic sample; *N*-cyclohexyl-3-phenyl-1-propanesulfonamide (404 mg, 11.0%), mp 67.5–69 °C, identical with an authentic sample; 1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (48 mg, 1.9%) identical with an authentic sample: mp 172–173.5 °C (benzene); IR (KBr) 3190, 1280, 1120 cm^{-1}. Anal. Calcd for $C_9H_{11}NO_2S$: C, 54.80; H, 5.62. Found: C, 54.97; H, 5.72.

(b) In Benzene. The azide (903 mg) in dry, degassed, oxygen-free benzene was heated at 138 °C for 50 h. Chromatography as above gave recovered azide (99 mg, 10.9%), 3-phenyl-1-propanesulfonamide (18 mg, 2.6%), mp 59–61 °C, *N*,3-diphenyl-1-propanesulfonamide (704 mg, 71.2%), a yellow oil identical (IR) with an authentic sample, and **26** (X = R^1 = R^2 = H) (69.9 mg, 9.9%), mp 172–174 °C.

(c) In Freon 113. The azide (1.29 g) in dry, degassed, oxygen-free Freon 113 (35 mL) was heated for 36 h at 135 °C. Chromatography as above gave recovered azide (481 mg, 37.3%), 3-phenyl-1-propanesulfonamide (16 mg, 2.3%), and 1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (312 mg, 44.1%), all identical with authentic samples.

The results of the solution thermolyses of sulfonyl azides **17–19** and **21–23** are given in Table I. Below are given the properties of the sultams (**26**) isolated.

5-Methyl-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**26**; X = R^1 = H, R^2 = Me): mp 159.5–160 °C (benzene); IR (KBr) 3180, 1310, 1150 cm^{-1}. Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20. Found: C, 56.73; H, 6.30.

5,5-Dimethyl-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**26**; X = H, R^1 = R^2 = Me): mp 160–161 °C [pentane–benzene (3:1 v/v)]; IR 3180, 1320, 1150 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71. Found: C, 58.61; H, 6.74.

7,9-Dimethyl-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**26**; X = 7,9-Me_2, R^1 = R^2 = H): mp 183–184 °C (petroleum ether); IR (KBr) 3220, 1295, 1130 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22. Found: C, 58.87; H, 6.75; N, 5.95.

6-Chloro-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**26**; X = 6-Cl, R^1 = R^2 = H): mp 212–213.5 °C (benzene); IR (KBr) 3160, 1305, 1140 cm^{-1}. Anal. Calcd for $C_9H_{10}ClNO_2S$: C, 46.65; H, 4.35. Found: C, 46.63; H, 4.37.

6,9-Dichloro-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**33**): mp 194–195 °C (benzene); IR (KBr) 3180, 1320, 1140 cm^{-1}. Anal. Calcd for $C_9H_9Cl_2NO_2S$: C, 40.62; H, 3.41. Found: C, 40.65; H, 3.44.

2,3,4,5-Tetrahydrobenzo[*f*]-1,4,5-oxathiazepine 4,4-dioxide (**27**; X = H): mp 153–154 °C (petroleum ether–ethyl acetate); IR (KBr) 3180, 1325, 1260, 1130, 1020 cm^{-1}; NMR ($CDCl_3$) δ 7.11 (m, 4 H, Ar H), 6.44 (br s, 1 H, NH), 4.44 (t, 2 H, J = 5 Hz, OCH_2), 3.58 (t, 2 H, J = 5 Hz, CH_2SO_2). Anal. Calcd for $C_8H_9NO_3S$: C, 48.23; H, 4.55. Found: C, 47.96; H, 4.51.

7-Methoxy-2,3,4,5-tetrahydrobenzo[*f*]-1,4,5-oxathiazepine 4,4-dioxide (**27**; X = MeO): mp 165 °C (petroleum ether–ethyl acetate); IR (KBr) 3210, 1385, 1260, 1195, 1140, 1045, 1025 cm^{-1}; NMR ($CDCl_3$) δ 6.97 (s, 3 H, Ar H), 6.39 (br s, 1 H, NH), 4.43 (t, 2 H, J = 5 Hz, OCH_2), 3.78 (s, 3 H, OCH_3), 3.59 (t, 2 H, J = 5 Hz, CH_2SO_2). Anal. Calcd for $C_9H_{11}NO_4S$: C, 47.15; H, 4.84. Found: C, 47.12; H, 4.86.

7-Chloro-2,3,4,5-tetrahydrobenzo[*f*]-1,4,5-oxathiazepine 4,4-dioxide (**27**; X = Cl): mp 179 °C (petroleum ether–ethyl acetate); IR (KBr) 3230, 1365, 1260, 1140, 140 cm; NMR ($CDCl_3$) δ 7.10 (m, 3 H, Ar H), 6.43 (br s, 1 H, NH), 4.48 (t, 2 H, J = 5 Hz, OCH_2), 3.61 (t, 2 H, J = 5 Hz, CH_2SO_2). Anal. Calcd for $C_8H_8ClNO_3S$: C, 41.12; H, 3.45. Found: C, 41.23; H, 3.49.

Thermolysis of 3-Mesityl-1-propanesulfonyl Azide. The azide (1.51 g) in Freon 113 (50 mL) was heated at 124° C for 40 h. Chromatography as above gave starting azide (280 mg, 18.5%), mp 57–58 °C, identical with an authentic sample, and 6,8,9-trimethyl-1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**34**) (25 mg, 2.3%): mp 220–221 °C (benzene); IR (KBr) 3240, 1300, 1140 cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16. Found: C, 60.27; H, 7.16.

The results of thermolyses at higher temperatures are summarized in Table I.

1-Methyl-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-Dioxide (30). (a) 3-(2-Bromophenyl)-*N*-methyl-1-propanesulfonamide (**29**) (100 mg) in tetrahydrofuran (5 mL) was added to lithium 2,2,6,6-tetramethylpiperidide [prepared from *n*-butyllithium (0.75 mmol, 0.34 mL) and 2,2,6,6-tetramethylpiperidine (96 mg, 0.75 mmol in THF (5 mL)] and the solution boiled under reflux for 24 h. Water (2 mL) was added, the solution was evaporated in vacuo and the residue was extracted with $CHCl_3$ (4 × 25 mL). The dried ($MgSO_4$) extract was evaporated and the residue recrystallized from petroleum ether to give the *N*-methylsultam (**30**): mp 76.5–77.5 °C; IR (KBr) 1340, 1145 cm^{-1}; NMR ($CDCl_3$) δ 7.28 (m, 4 H, Ar H), 3.52 (t, 2 H, J = 6 Hz, CH_2SO_2), 3.39 (s, 3 H, CH_3), 2.96 (t, 2 H, J = 6 Hz, CH_2Ar), 2.24 (m, 2 H, $CH_2CH_2CH_2$). Anal. Calcd for $C_{10}H_{13}NO_2S$: C, 56.97; H, 6.16. Found: C, 57.00; H, 6.25.

(b) 1*H*-2,3,4,5-Tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (**26**; X = R^1 = R^2 = H) (500 mg) in ethanol (30 mL) was treated with thallous ethoxide (647 mg) and the precipitate formed was filtered (408 mg, 40.8%). It was suspended in toluene (50 mL), the suspension brought to boiling, and iodomethane (423 mg) in toluene (50 mL) added in one lot. The mixture was boiled under reflux for 22 h and filtered, and the solution was concentrated

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to give **30** (143 mg, 65.7% based on the crude thallium salt), mp 76.5–77.5 °C, identical with the authentic sample obtained as under a above.

Authentic 1*H*-2,3,4,5-Tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-Dioxide. 3-(2-Nitrophenyl)-1-propanesulfonyl chloride (5.0 g) was stirred with 10% aquous NaOH (20 mL) until the organic material had dissolved. The solution was then treated with 10% Pd-C (1.0 g) and reduced with H_2 at 50 psi for 5 min. The catalyst was filtered and the solution evaporated to dryness. The white residue was dried, powdered, and treated with acetyl chloride (100 mL). Phosphorus pentachloride (7.5 g) was added, the mixture was heated on a steam bath ($CaCl_2$ drying tube) for 15 min, the volatile materials were then distilled in vacuo, and the residue was stirred with cold water. The suspension was heated on a steam bath for 1 h and cooled, and the solid (A) was filtered. The aqueous layer was evaporated to give a dark brown liquid that was treated with 3 N HCl and extracted with $CHCl_3$ (4 × 100 mL). The organic layer was dried ($MgSO_4$) and evaporated to give a pale yellow solid. This was combined with solid A and recrystallized from benzene–pentane (1:3 v/v) to give 1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine (**26**; X = R^1 = R^2 = H) (1.05 g, 28.1%), mp 173–174.5 °C, identical in all respects to the product obtained from the azide thermolysis.

Flash Vacuum Pyrolysis. The experimental procedure was the same as that described earlier[3] except that, in the case of the 2-(aryloxy)ethanesulfonyl azides, it was found convenient to mix the finely ground solid azide with prewashed and dried sand. The mixture was placed in the preheater and a loose plug of glass wool was placed at the inlet of the pyrolysis tube, another at the exit. The liquid sulfonyl azides were added dropwise to the preheater where it vaporized immediately and the undecomposed vapor was then passed through the pyrolysis zone. The pyrolysate was quenched on a cold finger (dry ice/acetone for the arylpropanesulfonyl azides, liquid N_2 for the (aryloxy)ethanesulfonyl azides) and dissolved in ethyl acetate and the solution was filtered. The products were resolved by column chromatography on neutral alumina and eluted as before by using a series of solvents from petroleum ether to ethyl acetate–ethanol (85:15 v/v). A sample decomposition is given below.

Flash Vacuum Pyrolysis of 3-Phenyl-1-propanesulfonyl Azide. (a) Static System (A in Table II). The azide (2.24 g) was pyrolyzed at 360 °C (0.25 mm). Column chromatography gave the following: 1,2,3,4-tetrahydroquinoline (70 mg, 5.3%), bp 130–132 °C (0.5 mm) (lit.[15] mp 249–250 °C), identical (IR, NMR) with an authentic sample; allylbenzene (43 mg, 3.7%), bp 81–85 °C (25 mm) (lit.[15] bp 156–157 °C), identical (IR, NMR) with an authentic sample; 1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (527 mg, 27%), mp 170–172.5 °C, identical with an authentic sample; 3-Phenyl-1-propanesulfonamide (22 mg, 1.1%), mp 59.5–61 °C (lit.[16] mp 60–61 °C), identical with an authentic sample.

(b) Flow System (B in Table II) (with W. M. Thompson). The sulfonyl azide (1.25 g) was pyrolyzed at 995 °C (0.05 mm) with a nitrogen flow rate of 1.5 mL/min. Gas chromatography of the reaction mixture (4 ft × 2 mm 5% Apiezon M on Gas Chrom Q (100–120 mesh) column, He carrier gas 30 mL/min; program: 75 °C, 2 min; 20 °C/min; 250 °C, 15 min) indicated the presence of at least 10 components. Column chromatography of the black oil (723 mg) obtained gave recovered azide (0.8%) and 1,2,3,4-tetrahydroquinoline (72.4%), both identical with authentic samples, 5,6,7,8-tetrahydroquinoline (6.2%) [bp 82–85 °C (1.5 mm) (lit.[17] bp 110 °C (13 mm)); NMR ($CDCl_3$) δ 8.1 (m, 1 H, H_2), 7.1 (m, 2 H, H_3 + H_4), 2.85 (m, 4 H, 2 CH_2), 1.8 m (m, 4 H, 2 CH_2)], identical with an authentic sample prepared by the catalytic hydrogenation (PtO_2/H_2O/50 psi) of quinoline in CF_3CO_2H at 0 °C,[17] allylbenzene (11.9%), 1*H*-2,3,4,5-tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-dioxide (0.4%), mp 170–172 °C, hydrocinnamonitrile (3.2%) [bp 255–260 °C (lit.[18] bp 261 °C); IR (film) 2240 cm^{-1} (C≡N); IR and NMR spectra identical to those of an authentic sample], and quinoline (0.8–5.7%): bp 235 °C (lit.[18] bp 238 °C), identical with authentic material.

The results of the other FVP studies are given in Table II. All the products, including substituted allylbenzenes and tetrahydroquinolines which were known compounds, were identified by direct comparison (IR, NMR) with authentic samples. Only in the case of the FVP (method B) of 3-(2,6-dichlorophenyl)-1-propanesulfonyl azide could the allylbenzene not be purified. A product, assumed to be 2,6-dichloroallylbenzene (21.8%) was isolated: IR 1605 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 3 H, Ar H), 5.90 (m, 1 H, CH=CH_2), 5.05 (m, 2 H, CH=CH_2), 3.30 (m, 2 H, CH_2). Attempted purification by distillation led to extensive decomposition.

Flash Vacuum Pyrolysis of 1*H*-2,3,4,5-Tetrahydrobenzo[*c*]-1,2-thiazepine 1,1-Dioxide. FVP of the sultam (1.5 g) at 360 °C (0.005 mm) followed by chromatography in neutral alumina gave recovered sultam (1.43 g, 95.5%), mp 171–172 °C, and 1,2,3,4-tetrahydroquinoline (29 mg, 2.9%), identical with an authentic sample. FVP of sultam (method B) (1.1623 g) at 650 °C (0.005 mm) gave sultam (59 mg, 5.1%), mp 170–172 °C, and 1,2,3,4-tetrahydroquinoline (647 mg, 86.9%), bp 254–250 °C.

FVP of **26** (X = 7,9-Me_2, R^1 = R^2 = H) (18 mg) at 690 °C (0.15 mm) (Method A) gave recovered **26** (7.7 mg, 23.5%), mp 182–184 °C (benzene), and 6,8-dimethyl-1,2,3,4-tetrahydroquinoline (17 mg, 94.9% based on sultam consumed), bp 82–85 °C (0.75 mm) (lit.[19] bp 137 °C (11 mm)), identical with an authentic sample prepared by Dibal-H reduction of 6,8-dimethylquinoline in benzene.

Flash Vacuum Pyrolysis of 2,3,4,5-Tetrahydrobenzo[*f*]-1,4,5-oxathiazepine 4,4-Dioxide (27; X = H). The sultam (19 mg) was pyrolyzed at 450 °C (1 mm) to give an oil (18 mg). This was subjected to gas chromatography on an 8 ft × $^1/_8$ in. column of OV-217 (6%, w/v) on Gas Q (100–120 mesh), programmed from 65–250 °C at 40 °C/min. Starting sultam (52 %) and 1,4-benzoxazine (trace) were detected (identification by IR). 1,4-Benzoxazine was recovered (94 %) when subjected to the same FVP conditions.

Acknowledgment. We thank the National Science Foundation (CHE 78-04805) and the National Institutes of Health (NS-15606) for support of this work. We are grateful to Dr. W. M. Thompson for repeating and confirming the results obtained in the FVP of 3-phenyl-1-propanesulfonyl azide at 995 °C.

Registry No. **8** (Ar = 4-$MeOC_6H_4$), 5394-57-0; **8** (Ar = 2-ClC_6H_4), 1892-43-9; **8** (Ar = 3-$CF_3C_6H_4$), 52073-64-0; **8** (Ar = 4-$NO_2C_6H_4$), 16365-27-8; **9** (Ar = Ph, X = Br), 589-10-6; **9** (Ar = 4-$MeOC_6H_4$), 3383-74-2; **9** (Ar = 4-ClC_6H_4), 13001-28-0; **9** (Ar = 3-$CF_3C_6H_4$), 90220-78-3; **9** (Ar = 4-$NO_2C_6H_4$), 3383-72-0; **10** (Ar = Ph), 3384-00-7; **10** (Ar = 4-$MeOC_6H_4$), 90220-79-4; **10** (Ar = 4-ClC_6H_4), 90220-80-7; **10** (Ar = 3-$CF_3C_6H_4$), 90220-81-8; **11** (Ar = Ph), 3384-01-8; **11** (Ar = 4-$MeOC_6H_4$), 90220-74-9; **11** (Ar = 4-ClC_6H_4), 88107-03-3; **11** (Ar = 3-$CF_3C_6H_4$), 88107-04-4; **12** (Ar = 3-$CF_3C_6H_4$), 88106-90-5; **13** (Ar = Ph; R, R′ = H), 90220-25-0; **13** (Ar = Ph; R = H; R′ = CH_3), 90220-26-1; **13** (Ar = Ph; R, R′ = CH_3), 90220-27-2; **13** (Ar = 3,5-$Me_2C_6H_3$; R, R′ = H), 90220-28-3; **13** (Ar = 2,4,6-$Me_3C_6H_2$; R, R′ = H), 90220-29-4; **13** (Ar = 2-ClC_6H_4; R, R′ = H), 90220-30-7; **13** (Ar = 2,6-$Cl_2C_6H_3$; R, R′ = H), 90220-31-8; **14** (Ar = Ph; R, R′ = H), 90220-32-9; **14** (Ar = Ph; R = H; R′ = CH_3), 90245-51-5; **14** (Ar = Ph; R, R′ = CH_3), 90220-33-0; **14** (Ar = 3,5-$Me_2C_6H_3$; R, R′ = H), 90220-34-1; **14** (Ar = 2,4,6-$Me_3C_6H_2$; R, R′ = H), 90220-35-2; **14** (Ar = 2-ClC_6H_4; R, R′ = H), 90220-36-3; **14** (Ar = 2,6-$Cl_2C_6H_3$; R, R′ = H), 90220-37-4; **15** (Ar = Ph; R, R′ = H), 90220-38-5; **15** (Ar = Ph; R = H; R′ = CH_3), 90220-39-6; **15** (Ar = Ph; R, R′ = CH_3), 90220-40-9; **15** (Ar = 3,5-$Me_2C_6H_3$; R, R′ = H), 90220-41-0; **15** (Ar = 2,4,6-$Me_3C_6H_2$; R, R′ = H), 90220-42-1; **15** (Ar = 2-ClC_6H_4; R, R′ = H), 90220-43-2; **15** (Ar = 2,6-$Cl_2C_6H_3$; R, R′ = H), 90220-44-3; **16**, 80639-68-5; **16** (chloride), 63014-04-0; **16** (acid·Na), 90220-58-9; **17**, 90220-21-6; **17** (chloride), 90220-68-1; **17** (disulfide), 90220-64-7; **18**, 90220-22-7; **18** (chloride), 90220-69-2; **18** (acid·Na), 90220-60-3; **18** (alkyl bromide), 1197-97-3; **19**, 90220-23-8; **19** (chloride), 90220-70-5; **19** (acid·Na), 90220-59-0; **19** (alkyl bromide), 90220-57-8; **20**, 88106-86-9; **20** (chloride), 88107-01-1; **20** (acid·Na), 90220-61-4;

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20 (disulfide), 90220-82-9; **20** (alkyl bromide), 27644-98-0; **21**, 88106-85-8; **21** (chloride), 88107-00-0; **21** (acid·Na), 90220-62-5; **21** (disulfide), 90220-65-8; **21** (alkyl bromide), 54877-27-9; **22**, 90220-24-9; **22** (chloride), 90220-72-7; **22** (acid·Na), 90220-63-6; **22** (disulfide), 90220-73-8; **22** (alkyl bromide), 14573-25-2; **23**, 88106-87-0; **24**, 88106-89-2; **25**, 88106-88-1; **26** (X, R^1, R^2 = H), 80639-72-1; **26** (X, R^1 = H; R^2 = Me), 90220-45-4; **26** (X = H; R^1, R^2 = Me), 90220-46-5; **26** (X = 7,9-Me_2; R^1, R^2 = H), 90220-47-6; **26** (X = 6-Cl; R^1, R^2 = H), 90220-49-8; **26** (X, R^1, R^2 = H; Tl(I) salt), 90220-55-6; **27** (X = H), 90220-51-2; **27** (X = MeO), 90220-52-3; **27** (X = Cl), 90245-52-6; **28**, 90220-76-1; **29**, 90220-77-2; **30**, 90220-54-5; **31**, 80639-67-4; **31** (amine, acid), 90220-56-7; **33c**, 90220-50-1; **34**, 90220-48-7; **36a**, 300-57-2; **36b**, 934-10-1; **36c**, 18321-36-3; **36d**, 77446-17-4; **36e**, 4810-05-3; **36f**, 1587-07-1; **36g**, 90220-53-4; **37a**, 635-46-1; **37b**, 19343-78-3; **37c**, 20364-31-2; **37d**, 41910-65-0; **37f**, 72995-16-5; **38**, 645-59-0; **39**, 10500-57-9; **44**, 5735-53-5; 3,5-$Me_2C_6H_3(CH_2)_3OH$, 62343-68-4; 3,5-$Me_2C_6H_3(CH_2)_2CO_2H$, 42287-87-6; $(2\text{-}NO_2C_6H_4(CH_2)_3)_2S_2$, 90220-66-9; $2\text{-}NO_2C_6H_4(CH_2)_3Br$, 63307-45-9; $(2\text{-}BrC_6H_4(CH_2)_3)_2S_2$, 90220-67-0; $2\text{-}BrC_6H_4(CH_2)_3Br$, 1075-28-1; $2\text{-}BrC_6H_4(CH_2)_3SO_2Cl$, 90220-71-6; $Ph(CH_2)_3SO_2NHBu\text{-}t$, 90220-75-0; c-$C_6H_{11}NH_2$, 108-91-8; $PhNH_2$, 62-53-3; quinoline, 91-22-5; 1,1,3,3-tetramethylguanidinium azide, 56899-56-0.

Supplementary Material Available: Details of the synthesis of new alcohols, halides, sulfonate salts, disulfides, sulfonyl chlorides, and azides and characterization data (elemental analytical data, NMR spectral data, IR data, etc.) for new compounds (17 pages). Ordering information is given on any current masthead page.

Effects of Reagent Concentrations and Solvents on Reactions of Organomagnesium and Lithium Reagents with *o*-Quinol Acetates. Differing Reaction Paths from Polymeric Grignards and from Dialkylmagnesiums or Monomeric Grignards

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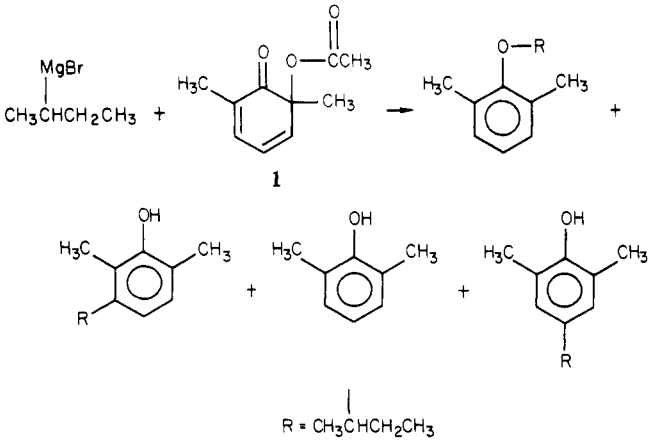
Received February 1, 1984

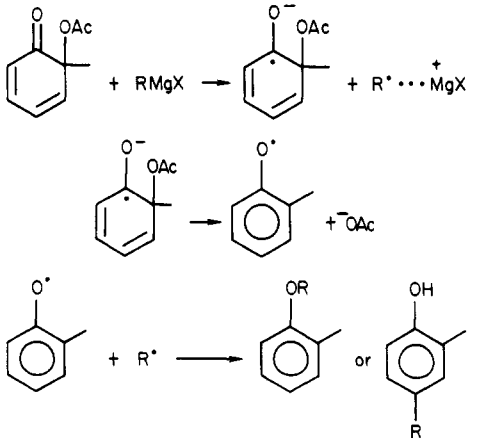
Studies of the reaction of 6-acetoxy-2,4,6-trimethylcyclohexa-2,4-dien-1-one (**2**) with isopropylmagnesium bromide showed that decreases in Grignard concentrations resulted in marked reductions in yields of the conjugate addition product, 3-isopropylmesitol (**5**), and increases in yields of isopropyl mesityl ether (**3**) and mesitol (**4**). Similar, though less pronounced, effects were observed with isopropylmagnesium chloride. Reaction of **2** with diisopropylmagnesium or diethylmagnesium resulted in large reductions in yields of **5** or of 3-ethylmesitol. Reactions with dialkylmagnesium reagents or with isopropyllithium were not significantly affected by changes in concentration. It is concluded that electron transfers from dialkylmagnesium reagents are the principal initial steps leading to formation of ethers and reduction products from reactions of *o*-quinol acetates with Grignard reagents, while non-electron-transfer reactions with the Grignards yield normal and conjugate addition products.

Alkyl Grignard and lithium reagents react with *o*-quinol acetates (6-acetoxycyclohexa-2,4-dien-1-ones) to yield aryl alkyl ethers in addition to the expected products of conjugate and direct addition to the unsaturated carbonyl groups.[1] Reduction of the quinol acetates to their parent phenols always accompanies ether formation and addition reactions. When para positions of the cyclohexadienone rings are unsubstituted, para-substituted phenols may also be obtained. The four products shown below, for instance, were obtained from reaction of *sec*-butylmagnesium bromide with the quinol acetate **1**:[1a]



1

The yields of ethers and *p*-alkyl[1a] (or *p*-benzyl)[1b] phenols from these reactions were found to increase significantly with increasing electron-donating abilities of the organometallic reagents. It was therefore proposed[1] that electron donations from the Grignard or lithium reagents to the quinol acetates were the initial steps in formation of ethers and para-substituted phenols. Electron transfer was followed by the reaction sequence shown below:



Our earlier work appeared to indicate that the concentrations of the Grignard solutions did not affect the nature or relative yields of the products. We have since observed, however, that when a wider range of Grignard reagent concentrations is employed the relative yields of products *do* depend on the concentrations of the Grignard reagents.[2]

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