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FLASH VACUUM PYROLYSIS OF 3,5-DISUBSTITUTED β-PHENETHYLSULFONYL AZIDES

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(Submitted in honor of Prof. T. Nozoe's 77th birthday)

Flash vacuum pyrolysis of 3,5-dimethyl-β-phenethylsulfonyl azide at 650° gives appreciable quantities of the normal nitrene cyclization products as well as some 2-cyclopropyl-3,5-dimethylpyridine. 3-Chloro-(5H)- and (7H)-pyrindine are obtained from 3,5-dichloro-β-phenethylsulfonyl azide. Possible mechanisms are proposed to account for the results.

The flash vacuum pyrolysis (FVP) of a number of β-phenethylsulfonyl azides has been reported and a tentative mechanism proposed for the formation of dihydropyrindines.[1] We now describe the results obtained from the FVP of some 3,5-disubstituted β-phenethylsulfonyl azides (**1**) which necessitate some refinement in the proposed mechanism. In the final step of the latter a hydrogen migration [**2**(R = H) ⟶ **3**(R = H)] occurred from the position originally *meta* to the ethyl side

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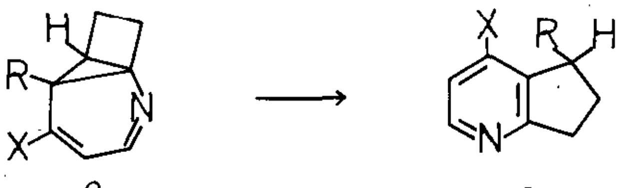
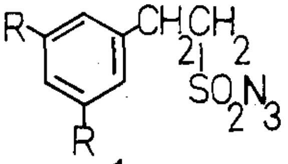
≠ Present address: Department of Chemistry & Geology, Clemson University, Clemson, SC 29631, USA chain to the carbon that now became C_5 in the dihydropyrindine (3).



2 3

It was of interest, therefore, to determine whether or not such a migration would occur if the meta positions were blocked and, if not, what pathway would be followed.

3,5-Dimethyl-β-phenethylsulfonyl azide (1; R = Me)[2] underwent FVP at 400°C in a nitrogen flow (10mm Hg pressure) to give 6,8-dimethyl-3,4-dihydro-2,1-benzothiazine-2,2-dioxide (4; R = Me)[3] (46%), mp 187-188°, 3,5-dimethylstyrene (5; R = Me) (3.8%)[3], and 5,7-dimethylindoline (6; R = Me) (trace). As expected,[1] FVP of 1 at 650° gave a lower yield of 4 (20.5%) and a corresponding larger amount of 6 (14.8%). In addition, however, a new type of product was obtained, namely 2-cyclopropyl-3,5-lutidine (7; R = CH_3) (2.9%), bp 45-48°/0.05 mm; picrate, mp 154-156°(EtOH); identical with a sample prepared (49% yield) from 3,5-lutidine and cyclopropyllithium in boiling toluene. No pyrindine derivative 3 was detected.



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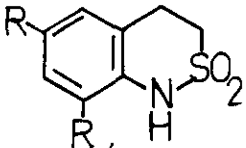

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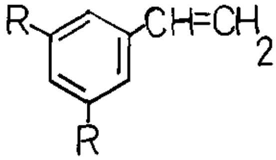

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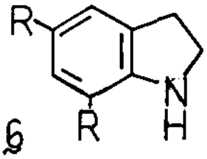

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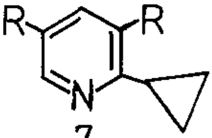

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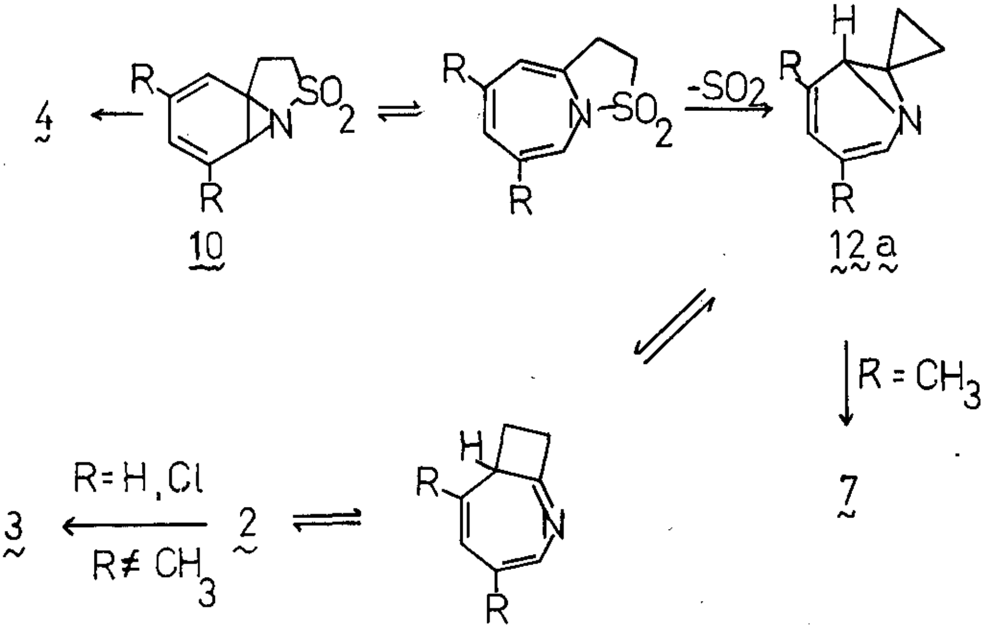
Cyclopropylpyridine **7** (R = CH_3) was stable under the FVP conditions. Reinvestigation of the FVP of β-phenethylsulfonyl azide (**1**; R = H) at 650° gave rise to a trace of a compound with the same retention time as authentic 2-cyclopropylpyridine (**7**; R = H) but the quantity formed was too small to permit collection from the g.l.c. and thus positive identification could not be made. A similar result was obtained by carrying out the FVP at 750°. **7** (R = H) too was stable at 650° and did not rearrange to dihydropyrindine under FVP conditions.

In contrast, FVP of 3,5-dichloro-β-phenethylsulfonyl azide (**1**; R = Cl), mp 79-80° (aq. EtOH), at 650° gave **5** (R = Cl)[4] (2.4%), **4** (R = Cl) (4.8%), mp 156-157° (benzene), **6** (R = Cl) (2.7%), and a mixture of 3-chloro-(5*H*)-(**8**) and 3-chloro-(7*H*)-1-pyrindine (**9**), mp 58-59° (43.9% yield).[5] No cyclopropylpyridine derivative (**7**) could be detected by g.l.c..

8 **9**

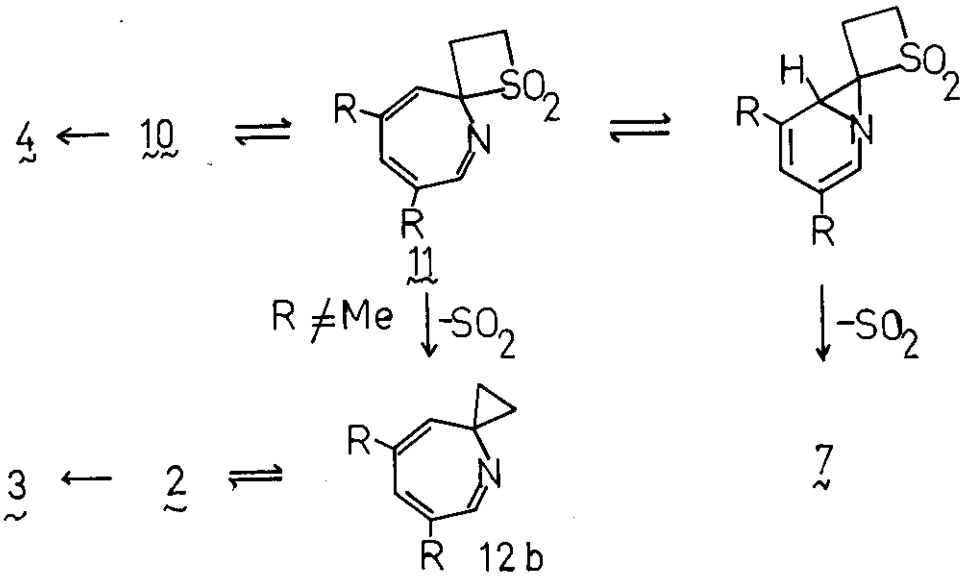
In the tentative mechanism proposed earlier[1] the proton migration step [**2** ⟶ **3** (R = H)] occurs at the end of the reaction sequence, long after the SO_2 is eliminated. The formation of appreciable quantities of **4** (R = Me) [and the product **5** of its thermal decomposition[1]] at 650°[7] when migration [**2** ⟶ **3** (R = Me)] is apparently not feasible suggests that either the 3,5-dimethyl groups stabilize the intermediate sultam considerably, thus diverting the reaction towards formation of **4** (R = Me), or loss of SO_2 occurs much later in the sequence with all the preceding steps being reversible. In the former case, the proposed[1] scheme would have to be refined somewhat as in Scheme I below. If the latter case obtains then a possible explanation might

SCHEME I

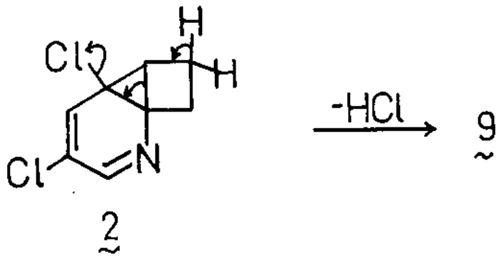


be that outlined in Scheme 2, though again it would be necessary to assume that loss of SO_2 from **11** is rendered more difficult when R = CH_3. An intermediate such as **12** (**a** or **b**) is required by the observation that both α- (present work)[8] and β-methyl-β-phenethylsulfonyl azides[1] give the same ratio of 6- to 7-methyldihydropyrindines.

SCHEME 2



3-Chloro-(7H)-1-pyrindine (9) may arise directly from 2 (R = Cl).



ACKNOWLEDGEMENT. We are grateful to the National Science Foundation (Grant #CHE-75-09309) for the support of this work.

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1. R. A. Abramovitch and W. D. Holcomb, J. Am. Chem. Soc., **97**, 676 (1975).

2. All new compounds were completely characterized by microanalysis and infrared, nmr, and mass spectrometry.

3. R. A. Abramovitch and W. D. Holcomb, unpublished results.

4. C. S. Marvel, C. G. Overberger, R. E. Allen, H. W. Johnson, J. H. Saunders, and J. D. Young, *J. Am. Chem. Soc.*, **68**, 861 (1946).

5. Nmr ($CDCl_3$) δ 8.39 and 8.28 (2 d, $J_{2,4}$ = 2.5 Hz, 1H, H_2), 7.65 and 7.53 (2 d, $J_{2,4}$ = 2.5 Hz, 1H, H_4), 7.07-6.67 (m, 2H, vinylic H), 3.60 - 3.30 (m, 2H, CH_2). The ratio of the peaks at δ 8.39 and 8.28, and at δ 7.65 and 7.53 changes from 3.9:1 to 1.5:1 on keeping the $CDCl_3$ solution with the δ 8.39 and 7.65 peaks decreasing in intensity and those at δ 8.28 and 7.53 increasing. This shows that **9** initially formed tautomerizes to **8** in solution, as reported for other (5*H*)-1-pyrindines.[6]

6. M. M. Robinson, *J. Am. Chem. Soc.*, **80**, 6254 (1958). C.B. Reese, *ibid*, **84**, 3979 (1962). G. Bergson and A.-M. Weidler, *Acta Chem. Scand.*, **16**, 2464 (1962). A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron Lett.*, 2579 (1966).

7. Under these conditions, no **4** (R = H) is isolated from **1** (R = H).[1]

8. Sodium 1-phenyl-2-propanesulfonate, mp >310°; 1-phenyl-2-propanesulfonyl chloride, bp 81-83°/0.1 mm; 1-phenyl-2-propanesulfonyl azide, bp 90-93°/0.1 mm.

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