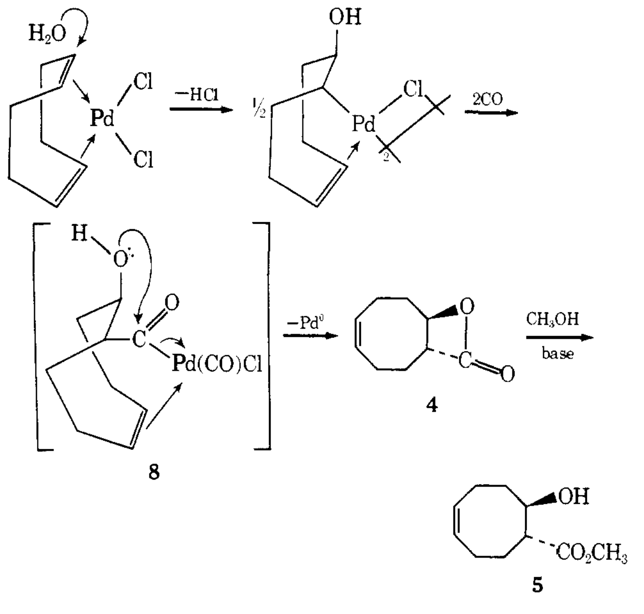
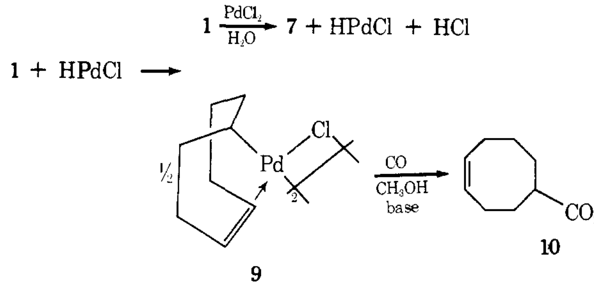
Scheme II



Scheme III



molecule of cyclooctadiene to form the hydride addition complex **9**. Carbonylation of **9** yields methyl 4-cyclooctenecarboxylate (**10**).

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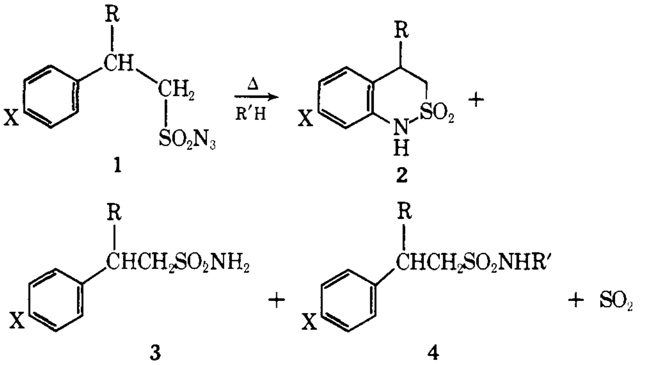
Flash Vacuum Pyrolysis of β-Arylethylsulfonyl Azides. Dihydropyrindine Formation

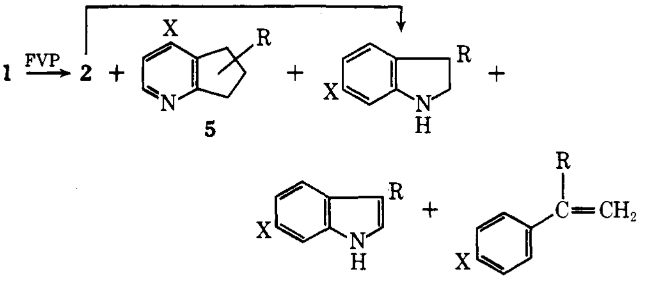
Sir:

Intramolecular cyclization of sulfonyl azides has been shown to be a useful approach to interesting cyclic sulfonamides.[1] In contrast, decomposition of α-toluenesulfonyl azide in solution gave none of the desired cyclization product and this was attributed[1] to strain in the required fused benzaziridine intermediate. Support for this comes from the fact that thermolysis of β-phenethylsulfonyl azide (**1a**) in diglyme at 149° gave 3,4-dihydro-2,1-benzothiazine 2,2-dioxide (**2a**) (6%), β-phenethylsulfonamide (**3**) (30.6%), and SO_2 (10%), while in *n*-tetradecane at 149°, **2a** (6–8%), **3** (6–7%), and a mixture of isomeric *N*-tetradecyl-β-phenethylsulfonamides (**4a**) (47%) were isolated. In cyclohexane, similar results were obtained, and the main product was (**4a**, R′ = C_6H_{11}) (44.5%).[2]



In the hope of improving the yield of **2** by decreasing or eliminating the opportunity for intermolecular reactions of the nitrene the flash vacuum pyrolysis (FVP) of **1a** was studied. The highest yield of **2a** (12.8%) was obtained at 300° (3 mm). In addition, however, there was obtained a 6.9% yield of dihydropyrindine (**5a**). At 400°, the yield of **2a** dropped slightly (11.3%) but that of **5a** rose to 32.7%, and traces of indole, indoline, and styrene were detected by GLC/mass spectrometry. FVP of **1a** at 650° (3 mm) (N_2 carrier gas) gave **5a** (64.8%), indoline (11.2%), indole (1.5%), and styrene (8.2%), but no **2a**.

Dihydropyrindine (**5**) and styrene are not formed from **2** on FVP, and indeed the latter is stable at 300°. The possibility was considered that indoline arose from phenethylnitrene formed in the gas phase by a Wolff-type rearrangement of the sulfonylnitrene followed by loss of SO_2. This was shown not to be the case by FVP of β-phenethyl azide when, as expected,[3] no intramolecular substitution occurred and only tars were formed. The indole and indoline arise from the FVP of **2a**: at 650° (N_2 carrier gas) the latter gave

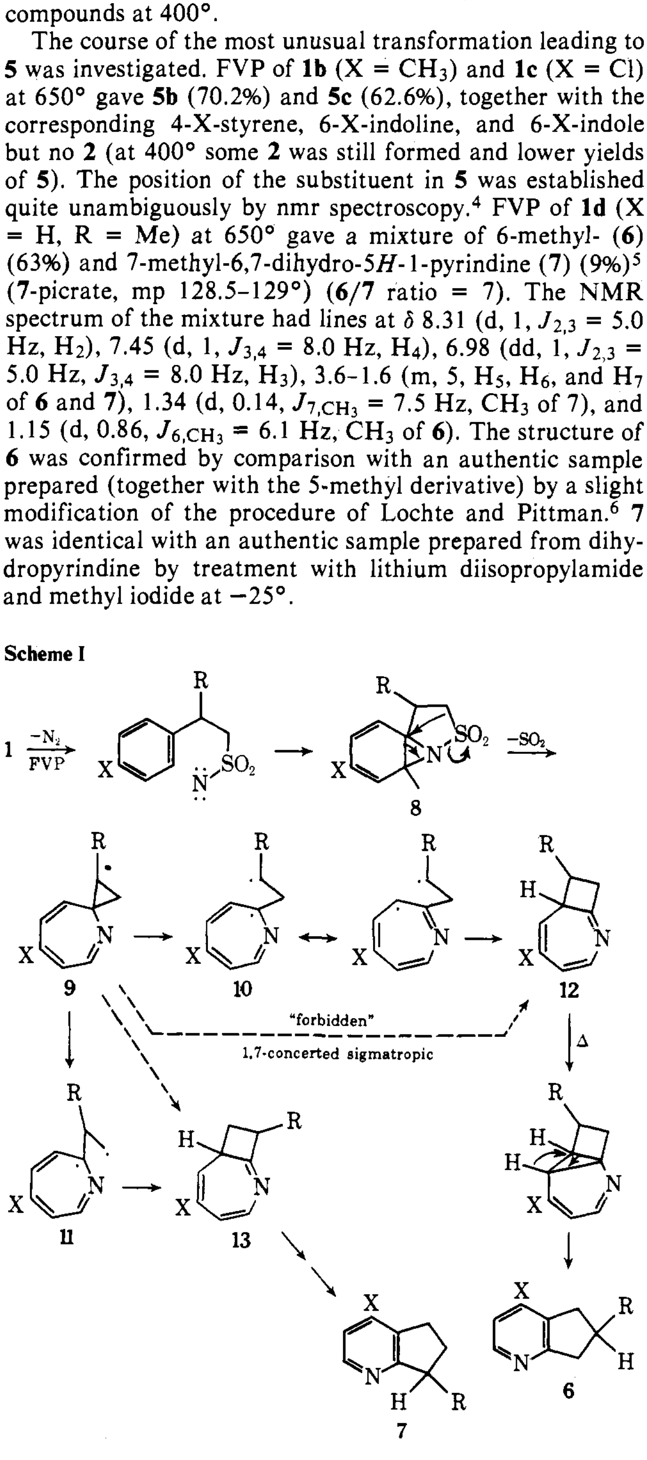


a, X = R = H
b, X = CH₃; R = H
c, X = Cl; R = H
d, X = H; R = CH₃

indoline (75%) and indole (7.7%) but only traces of these compounds at 400°.

The course of the most unusual transformation leading to **5** was investigated. FVP of **1b** (X = CH_3) and **1c** (X = Cl) at 650° gave **5b** (70.2%) and **5c** (62.6%), together with the corresponding 4-X-styrene, 6-X-indoline, and 6-X-indole but no **2** (at 400° some **2** was still formed and lower yields of **5**). The position of the substituent in **5** was established quite unambiguously by nmr spectroscopy.[4] FVP of **1d** (X = H, R = Me) at 650° gave a mixture of 6-methyl- (**6**) (63%) and 7-methyl-6,7-dihydro-5*H*-1-pyrindine (**7**) (9%)[5] (**7**-picrate, mp 128.5–129°) (**6**/**7** ratio = 7). The NMR spectrum of the mixture had lines at δ 8.31 (d, 1, $J_{2,3}$ = 5.0 Hz, H_2), 7.45 (d, 1, $J_{3,4}$ = 8.0 Hz, H_4), 6.98 (dd, 1, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 8.0 Hz, H_3), 3.6–1.6 (m, 5, H_5, H_6, and H_7 of **6** and **7**), 1.34 (d, 0.14, J_{7,CH_3} = 7.5 Hz, CH_3 of **7**), and 1.15 (d, 0.86, J_{6,CH_3} = 6.1 Hz, CH_3 of **6**). The structure of **6** was confirmed by comparison with an authentic sample prepared (together with the 5-methyl derivative) by a slight modification of the procedure of Lochte and Pittman.[6] **7** was identical with an authentic sample prepared from dihydropyrindine by treatment with lithium diisopropylamide and methyl iodide at −25°.

Scheme I



The above results indicate that C_4 in **1** becomes C_4 in **5**, while C_β in **1** becomes mainly C_6 in **5**, though some "scrambling" occurs and C_β appears to a small extent as C_7 in **5**. A number of reaction sequences can be envisioned to explain these observations, but the one we favor is presented in Scheme I. The first step is the loss of nitrogen to give the nitrene followed by addition to the adjacent benzene ring to give the benzaziridine (**8**).[7] At the lower temperatures and in solution this can ring-open to **2**. At higher temperatures, elimination of SO_2 (which could occur concertedly as shown or *via* a diradical intermediate) gives **9**. This can rearrange to the cyclobutane derivatives **12** and **13** *via* a diradical process as shown. The allowed concerted thermal 1,7-shift requires an inversion at the migration center, and this seems sterically prohibited in this 1-methylspiro[2.6]azanona-4,6,8-triene system.[8,9] A "forbidden" 1,7-suprafacial concerted process[11] cannot be excluded, however. The predominant formation of **6** rather than **7** tends to speak for the diradical process in which a secondary radical (**10**) is formed more readily than the primary one (**11**). Electrocyclic 6π-ring closure followed by cyclopropane ring opening and hydrogen migration leads to the final products.

We have adapted the above FVP to the preparation of gram quantities of the dihydropyrindines and are continuing our studies of the mechanism of their formation.

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(2) The best yields of **2** can be obtained by using an "inert" solvent, such as Freon-113 at 135° for 36 hr in these thermolyses: **2a** (28%); **2b** (38.1%), **2c** (1–2%).

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A Model Dehydrogenase Reaction. Charge Distribution in the Transition State

Sir:

Nonenzymatic reductions by nicotinamide coenzymes in aqueous solutions may serve as models for the action of the NAD⁺-dependent dehydrogenases. We report here the ef-