

## References and Notes

- (1) Supported by the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.
- (2) T. M. Brown and E. L. McCann, *Inorg. Chem.*, **7**, 1227 (1968); D. L. Keper and R. Mandyczewsky, *ibid.*, **7**, 2091 (1968); E. L. McCann and T. M. Brown, *Inorg. Synth.*, **12**, 181 (1970).
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- (4) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4285 (1965).
- (5) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 4293 (1965).
- (6) E. S. Huyser, *Synthesis*, **7** (1970), and references therein.
- (7) Although generally acknowledged as yielding trans substituted dichlorides, cis addition of molecular chlorine to phenanthrene (P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961)) and acenaphthalene (S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *J. Am. Chem. Soc.*, **78**, 4939 (1956)) has been noted. Cis addition is also suspected in the cases of 1-phenylpropene (R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965)) and stilbene (S. J. Cristol and R. S. Bly, *ibid.*, **82**, 142 (1960)). More recently the addition of chlorine to cyclopentadiene has been observed to produce, inter alia, a 24% yield of the dichloride *cis*-3,4-dichlorocyclopentene (V. L. Heasley et al., *J. Org. Chem.*, **39**, 736 (1973)). The reaction of iodobenzene dichloride with several olefins is also reported to produce *cis*-dichloroalkanes: H. J. Lucas and E. R. Kennedy, "Organic Syntheses", Coll. Vol. 3, Wiley, New York, N.Y., 1955, p 482, and references therein.
- (8) Tetrachloroethylene is reported to react with rhenium(V) chloride to produce hexachloroethane and rhenium(IV) chloride: A. Brignole and F. A. Cotton, *Chem. Commun.*, 706 (1971).
- (9) Halogenation of olefins with copper(II) bromide and chloride leads to trans substituted dihalides and apparently involves molecular halogens: W. C. Baird, Jr., J. H. Surridge, and M. Buza, *J. Org. Chem.*, **36**, 3324 (1971).
- (10) W. Hleber and E. Romberg, *Z. Anorg. Chem.*, **221**, 321 (1935).
- (11) Exxon Summer Research Fellow, 1974.

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## Anodic Oxidation of Aziridines

Sir:

Our extensive studies of the generation and reactions of nitrenium ions<sup>1</sup> have utilized various routes to this highly reactive, divalent, electron-deficient nitrogen species. In principle, removal of a hydride, or of a proton and two electrons from a secondary amine, should produce a nitrenium ion. The latter of these possibilities would appear to be theoretically feasible through electrochemical processes. However, electrochemical studies reported thus far on simple aliphatic amines indicated that various modes of reaction were found to occur, which did not necessarily require the intermediacy of nitrenium ions.<sup>2</sup> With these facts in mind, we undertook a study of the electrolysis of aziridines, in order to determine whether chemical behavior consistent with the intermediacy of a singlet nitrenium ion could be observed. We now wish to present a preliminary report of the results of this study.<sup>3</sup>

2-Phenyl-2-ethylaziridine (**1**)<sup>6</sup> was electrolyzed in anhydrous methanol at 0° under a nitrogen atmosphere in a divided cell utilizing platinum electrodes, sodium perchlorate as electrolyte, and sodium carbonate as buffer. Passage of 4 F of current per mole of starting material at an applied voltage of 10–15 V and a constant current of 0.5 amps gave **2** (50%), **3** (6%), **4** (12%), **5** (1%), and **6** (<1%). Workup of the electrolysis mixture with aqueous acid resulted in considerable hydrolysis of **2** and **4**. All of the products were isolated by preparative VPC and identified either *via* comparison with independently prepared samples (for **2**, **3**, and **6**) or through their spectral properties. The structure of **4** was assigned on the basis of its spectral and chemical properties. The ir spectrum of **4** showed strong absorptions at 5.98 (C=N) and 9.53 (C—O)  $\mu$ ; the NMR spectrum of **4** showed absorptions at  $\tau$  9.32 (3 H, t, H<sub>a</sub>), 8.18 (2 H, q,

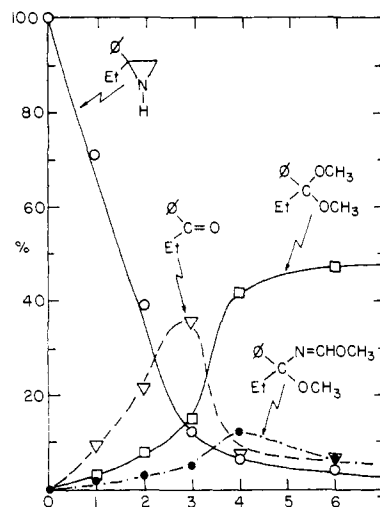
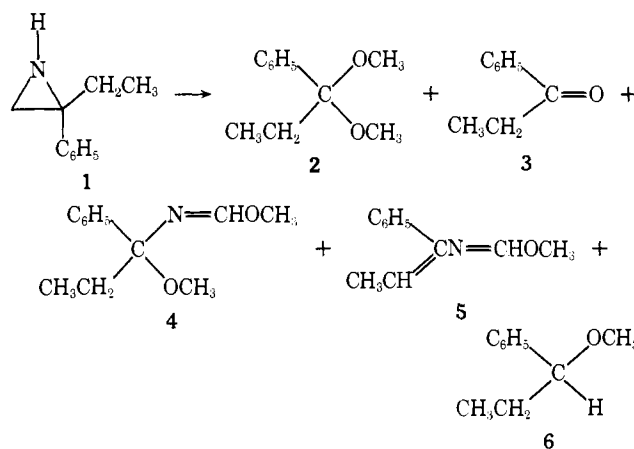
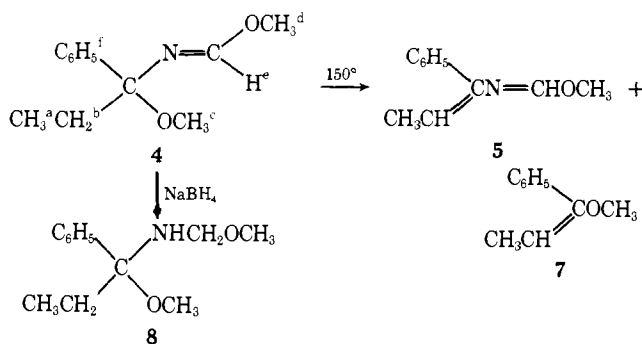


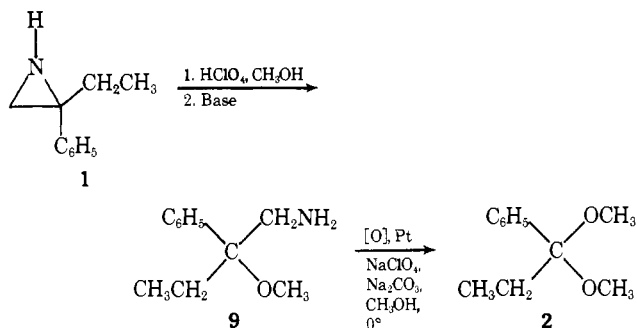
Figure 1. Plot of percentage composition (determined by VPC analysis) of the reaction mixture as a function of the number of faradays passed per mole of 2-phenyl-2-ethylaziridine.



H<sub>b</sub>), 7.10 (3 H, s, H<sub>c</sub>), 6.20 (3 H, d,  $J_{de} = 0.7$  Hz, H<sub>d</sub>), 2.40–3.00 (5 H, m, H<sub>f</sub>), and 2.32 (1 H, q,  $J_{de} = 0.7$  Hz, H<sub>e</sub>). Irradiation of the methoxyl group collapsed the quartet, observed for H<sub>e</sub>, to a singlet. The mass spectrum of **4** failed to show a parent peak. Instead it showed a base peak (and *apparent* parent peak) at  $m/e$  178 which represents the loss of the ethyl group from **4**.<sup>8</sup> In contrast to the failure of normal mass spectrometric methods to give the true parent ion, chemiionization mass spectrometry<sup>9</sup> established the molecular weight of **4** to be 207. Chemical evidence for the structure of **4** was obtained from its pyrolysis at 150° to give **5** (loss of CH<sub>3</sub>OH) and **7** (loss of HN=CHOCH<sub>3</sub>) in the ratio of 2:1. In the presence of sodium borohydride, **4** was reduced slowly to give a product, which was spectroscopically identified as **8**.



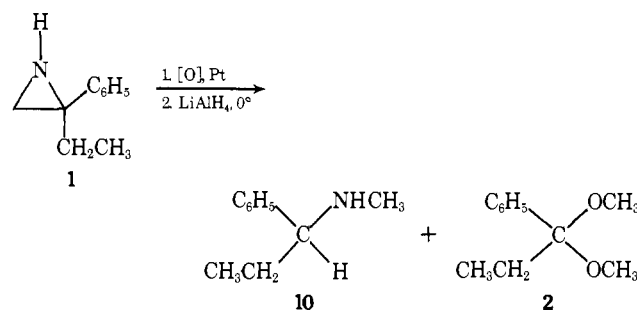
As a control experiment, we felt that it was important to demonstrate that **1** was not being opened in an acid-catalyzed process<sup>10</sup> to give **9**, followed by electrolysis of **9** to



give **2**. Superficially, this looked like a serious complication when we found that treatment of a methanolic solution of **1** with a small amount of perchloric acid followed by neutralization gave 84% of **9**. More seriously, electrolysis of **9** gave 96% of **2**. Fortunately, polarographic studies vs. a silver-silver perchlorate standard electrode showed that **1** had an  $E_{1/2}$  at 0.64 V, whereas **9** had an  $E_{1/2}$  at 1.82 V. Controlled potential electrolysis of a mixture of **1** and **9** showed that while **1** was converted to the previously observed products, **9** was recovered unchanged. These studies rule out **9** as an intermediate in the electrolysis of **1**.

In order to gain a greater insight into the electrochemical process whereby the major products, **2**, **3**, and **4**, were formed, we have carried out a detailed study of this electrolysis. Figure 1 shows a plot of product composition as a function of the number of faradays of electricity used in the electrolysis of **1**. An obvious anomaly in this plot was the buildup of propiophenone (**3**), which maximized at 3 F per mole of **1**, followed by its apparent rapid conversion to its dimethyl ketal, **2**, in an electrochemical reaction. Control reactions showed that under the reaction conditions propiophenone could be recovered unchanged. This indicated to us that the electrolysis of **1** was producing an unstable intermediate which was convertible under relatively mild conditions into propiophenone. Furthermore, it appeared that this intermediate was electrochemically converted to **2** and **4**. Additional evidence in support of this hypothesis was obtained by spectroscopic examination of the crude electrolysis mixture after 3 F per mole of **1** had been passed. Although VPC analysis indicated the presence of 35% of propiophenone, no trace of propiophenone could be detected by either ir or NMR spectroscopy. Instead, an absorption was noted in the ir spectrum at  $5.99 \mu$  characteristic of an N=C linkage.<sup>11</sup>

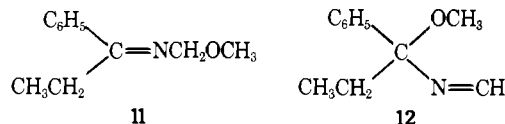
In order to learn more about the nature of this intermediate, the electrolysis was carried out until 3 F per mole of **1** had been passed, the solvent was removed at low temperature and pressure, and the residue was reduced with lithium aluminum hydride in ether at  $0^\circ$ . We obtained 31% of **10**,<sup>12</sup> 13% of **2**, and 10% of the starting aziridine **1**. No trace of



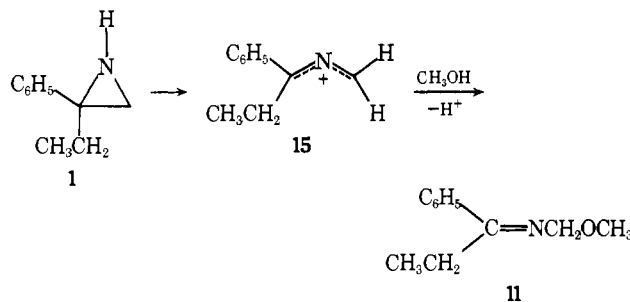
the reduction product of propiophenone, 1-phenylpropan-1-ol, could be detected. This indicated the absence of propiophenone in the electrolysis product mixture at this time.

The formation of **10** in the reduction<sup>13</sup> indicated that the electrochemically generated intermediate have either structure **11** or **12**. Numerous attempts to purify the intermediate resulted in only partial success. Under the best conditions, material of 60–70% purity could be obtained. This material gave a parent peak of  $m/e$  177.1154 (calcd  $m/e$  177.1157) consistent with either **11** or **12**. The ir spectrum showed a strong absorption at  $6.14 \mu$  indicative of a conjugated imine linkage. The NMR spectrum showed peaks at  $\tau$  8.90 (t,  $J = 7$  Hz,  $\text{CH}_3$  of ethyl group), 7.43 (q,  $J = 7$  Hz,  $\text{CH}_2$  of ethyl group), 6.60 (s,  $\text{OCH}_3$ ), 5.18 (s,  $\text{CH}_2$ ), and 3.2–2.1 (m, aromatic protons). In view of the low field position expected for the olefinic protons of **12**, it was felt that the spectral data were more consistent with the intermediate having structure **11**.<sup>11</sup>

An independent synthesis of **11** was accomplished in 20–30% yields through the reaction of propiophenone imine (**13**) with chloromethyl methyl ether (**14**) in the presence of triethylamine below  $0^\circ$  in *n*-hexane. This material (70% pure) showed ir and NMR spectral properties identical with the intermediate isolated from the electrolysis of **1**. Hydride reduction of this independently prepared material gave **10** (97% yield based on the amount of **11** present).



Although a variety of mechanistic paths to **11** can be proposed, an attractive possibility involves the loss of two electrons and of a proton from **1** in a stepwise process to give the azaallyl cation **15**. Collapse of **15** with solvent would be expected to yield **11**. The mechanistic steps involved in the subsequent electrochemical conversion of **11** into **2** and **4** are less clear and are currently under study.



The isolation of the highly unstable intermediate **11** represents the first capture of an azaallyl cation. Presumably, this is the same type of cation as is involved in the methanolysis of *N*-chloroaziridines.<sup>4</sup> In agreement with this suggestion is the observation that the *N*-chloro derivative of **1** solvolyzes in methanol-water to give propiophenone in 78% yield. This conversion is readily explained by addition of solvent to the solvolytically generated azaallyl cation **15**, followed by hydrolysis of the intermediate to give **3**. We are continuing to explore the oxidation of small nitrogen containing heterocyclic compounds.

**Acknowledgments.** We are indebted to the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this investigation.

## References and Notes

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- (2) C. K. Mann, *Anal. Chem.*, **36**, 2424 (1964); P. J. Smith and C. K. Mann, *J. Org. Chem.*, **34**, 1821 (1969); K. K. Barnes and C. K. Mann, *ibid.*, **32**, 1474 (1967); P. J. Smith and C. K. Mann, *ibid.*, **33**, 316 (1968); N. L. Weinberg and E. A. Brown, *ibid.*, **31**, 4058 (1966); L. C. Portes, V. V. Bhat, and C. K. Mann, *ibid.*, **35**, 2175 (1970); S. D. Ross, *Tetrahedron Lett.*, 1237 (1973), and references contained therein.
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- (8) Similarly, **2** failed to show a true parent peak on mass spectral analysis. Instead, it also showed a base peak and apparent parent peak resulting from loss of the ethyl moiety.
- (9) We wish to thank Dr. R. L. Foltz of Battelle Columbus Laboratories for obtaining the CI-MS measurements for us.
- (10) The generation of highly acidic localized sites in an electrolysis is an experimental possibility which should always be taken into consideration.
- (11) A range of 5.96–6.03  $\mu$  has been suggested for nonconjugated *N*-alkyl substituted imines: J. Fabian, M. Legrand, and P. Poirier, *Bull. Soc. Chim. Fr.*, 1499 (1956). For an alternate route to a closely related series of compounds see A. Padwa and J. Smolanoft, *J. Chem. Soc., Chem. Commun.*, 342 (1973).
- (12) The structure of **10** was established through comparison with an authentic sample of **10** prepared via the addition of ethyl Grignard to the imine derived from benzaldehyde and methylamine and subsequent hydrolysis.
- (13) For ample precedent see N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966).
- (14) Address correspondence concerning this study to Paul G. Gassman, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

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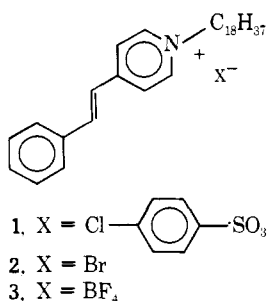
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### Medium Effects on Photochemical Reactions. Photochemistry of Surfactant Alkyl-4-stilbazole Salts in Solution, in the Solid State, and in Monolayer Assemblies

Sir:

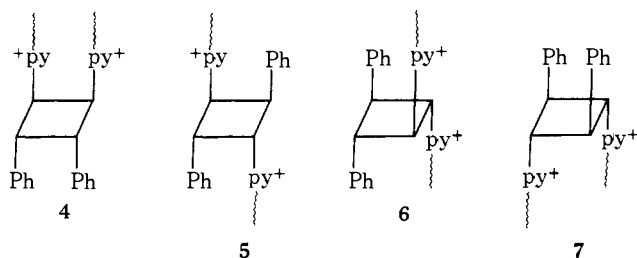
A recent interest in these laboratories has been the photochemistry of surfactant molecules in different media. Since many of these compounds may be readily incorporated into monolayers, our attention has been directed toward employing the oriented, semirigid environment of monolayer assemblies to direct or modify their photochemistry.<sup>1</sup> In the present communication we report an investigation in the photochemistry of the *p*-chlorobenzenesulfonate (**1**), bromide (**2**), and tetrafluoroborate (**3**) salts of *N*-octadecyl-*trans*-4-stilbazole.<sup>2</sup> These results indicate that environment



can play a major role in determining photoreactivity<sup>4</sup> and suggest that the amphipathic nature of these molecules may modify their solution or solid-state behavior relative to non-surfactant analogs.

Although essentially insoluble in aliphatic hydrocarbons (hexane and hexadecane) and water, **1–3** were moderately soluble in polar organic solvents. Acetonitrile solutions of these salts exhibit a long-wavelength absorption maximum at 345 nm ( $\epsilon$  23,600) and a weak fluorescence with a maximum at 430 nm. The photochemistry of **1–3** in acetonitrile solution is unexceptional and is well-represented by that of **1**. Irradiation of acetonitrile solutions of **1** at 366 nm results in *trans*  $\rightarrow$  *cis* isomerization and, eventually, establishment of a photostationary state. Upon prolonged irradiation of very dilute nondegassed solutions, slow disappearance of **1**, primarily due to cyclization, can be observed. By comparison, the properties of **1** are quite different from those of **2** and **3** in the solid state. Although excitation spectra are not significantly different, solid samples of **1** exhibit broad, intense yellow-green fluorescence with  $\lambda_{\text{max}}$  at 470 nm while solid samples of **2** and **3** fluoresce blue with  $\lambda_{\text{max}}$  at 430 nm. Irradiation (G.E. reflector flood lamp through 2 cm of H<sub>2</sub>O and a Corning 0-52 filter) of 0.2 g of **1** spread on a watch glass for 8 hr led to essentially quantitative conversion of the starting material to a white solid product. In contrast, **2** and **3** were recovered unchanged after irradiation under identical conditions.

The solid state photoproduct of **1** can be isolated in up to 70% yield by recrystallization from 2-propanol. The uv spectrum (CH<sub>3</sub>OH) exhibits maxima at 257 and 223 nm, and the formerly vinylic protons of **1** appear at  $\delta$  5.01 (br "d") and 4.75 (br "d") in the NMR (CDCl<sub>3</sub>) of the product. Irradiation of the solid photoproduct at 254 nm reversibly regenerates the yellow-green fluorescence of **1**, consistent with a photodimer structure.<sup>6</sup> Thus, the most reasonable assignments of the resonances at 5.01 and 4.75 are to cyclobutane ring protons adjacent to pyridinium and phenyl, respectively, in a *trans-1* + *trans-1* photodimer. Of the four possible dimers **4–7**, **5** and **6** could be obtained as viscous oils by bisalkylation of the corresponding 4-stilbazole dimers<sup>7</sup> with octadecyl *p*-chlorobenzenesulfonate. The cyclobutane ring protons of the *trans*-*cis*-*trans* dimer **5** appeared as a broad unresolved 4 H resonance centered at  $\delta$  4.97. In contrast, the corresponding protons of the *trans*-*trans*-*trans* dimer **6** appear at  $\delta$  4.18 (br "d", 2 H) and 3.96 (br "d", 2 H), an upfield shift compatible with the pseudo-equatorial disposition of the four aromatic rings.<sup>9</sup> These results clearly point to **4** as the structure of the solid state photoproduct of **1**.



Both stilbazole salts **1** and **2** form monolayers and, in mixtures with tripalmitin (TP), may be incorporated into monolayer assemblies by the usual techniques.<sup>10</sup> Assemblies incorporating **1** or **2** have a long-wavelength absorption maximum (345 nm) comparable to that in solution, but the band is quite broad on the long-wavelength side, tailing well out past 430 nm. Analogous to the solid state of **1**, these assemblies exhibit a green fluorescence with a maximum at about 490 nm. In contrast to the solid state, the photoreac-