*Anal.* Calcd for $C_{10}H_{16}N_2O$: *m/e* 180.1262. Found: *m/e* 180.1265.

**Registry No.**—**2a,** 32974-89-3; **2b,** 32974-90-6; **3a,** 23787-80-6; **3b,** 32974-92-8; **4,** 32974-93-9; **5a,** 32974-94-0; **5b,** 32974-95-1.

**Acknowledgment.**—The authors express their appreciation to Dr. W. I. Taylor for his interest in this project. We also thank Mr. W. Ledig for his technical assistance and Messrs. H. Bondarovich and M. Jacobs for doing high-resolution mass spectrometric analyses and nmr analyses.

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# New Deamination in a Benzyne Addition to *N*-Benzylaziridine

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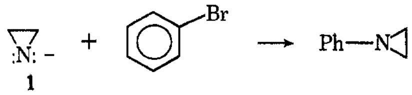
Aziridine chemistry is receiving widening attention since the recent discovery[1] of an economic access to the parent compound in 1963. However, the only likely aryne reaction reported in the literature is a simple amide elimination–addition of **1** to bromobenzene.[2]

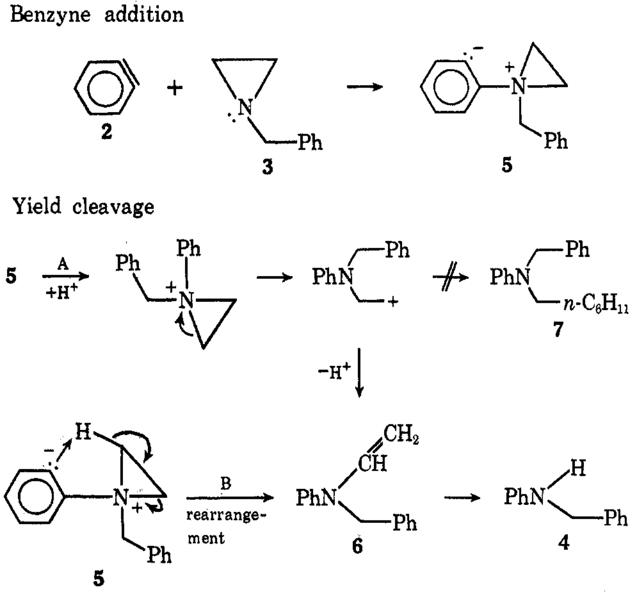


In a continuing interest in the chemistry of ammonium ylides, we endeavored to add benzyne (**2**), generated *in situ* by the fluorobenzene–butyllithium route,[3] to *N*-benzylaziridine (**3**) in the hope of producing α-ylides, whose subsequent fate might have been of definite synthetic interest.

Surprisingly, the addition reaction followed quite a different course, the main product being *N*-benzylaniline (**4**) to the exclusion of amounts larger than 0.1% of the theoretical yield of rearranged products.[4] Amine **4** was identified by glc retention time ratio *vs.* a known standard, enhancing technique, by mass spectrometry, and, on a separated analytical sample, by ir and pmr spectroscopy.

The obvious rationalization of this unexpected product is a benzyne addition to the tertiary aziridine **3**, followed by the formal elimination of ethylene from the activated amine ring. Two mechanisms may be envisaged for the latter reaction (Scheme I, A and B). Both routes lead to a common intermediate **6** from the initial ortho ylide **5**; **6** should in turn eliminate acetylene.[5] Route A involves a less likely[6] ring opening of the $S_N1$ type of the aziridinium ion **5**; in this context it is rather strange that no substitution product, *i.e.*, *N*-(*n*-hexyl)-*N*-benzylaniline (**7**), was formed. Thus, route B, a one-step concerted Hofmann elimination, appears at this time a more satisfactory alternative.[7]

SCHEME I



Interestingly, all known deamination reactions of aziridines are thermal dissociation[8] of tertiary aziridines bearing activating nitrogen substituents and a photochemical dissociation of a highly substituted aziridine;[9] all these reactions yielded an olefin product.

Research is now under way in our laboratory in order to elucidate the reaction mechanism of this new deamination and widen the scope of the reaction.

## Experimental Section

Glc analyses were performed with a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector, using the internal standard method for qualitative and quantitative determinations. Calibration factors (area/weight coefficients) as well as authentic retention time ratios were evaluated with genuine pure samples. Ratio agreements were within 0.5%. The ideal column for these analyses was found to be a 0.5 × 200 cm column packed with 5% SF-96 on Chromosorb P (80–100 mesh) operating between 80 and 220°. Ir spectra were recorded with a Beckman IR-5 spectrometer (neat compound for

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(1) "Ethylenimine," Dow Chemical Co., 1965, p 3.

(2) R. G. Kostyanovskii and O. A. Pan'shin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1554 (1964).

(3) This method afforded reasonable yields of ylides, as deduced from cleavage and rearrangement products of the reaction between dimethylbenzylamine and benzyne: A. G. Giumanini and A. R. Lepley, *Bull. Chem. Soc. Jap.*, **42**, 2359 (1969).

(4) "Expected" rearranged products are those from Stevens (ring enlargement and benzyl group migration), Sommelet, and perhaps 1,3 shift (to the aniline ring with ring enlargement or benzyl migration).

(5) A. Lattes and M. Rivière, *C. R. Acad. Sci.*, **262**, 1797 (1966), found that *N*-(β-chloroethyl)-*N*-methylaniline, treated with *n*-butyllithium, gave *N*-methylaniline. No mechanism was advanced for this reaction, which should involve the sequential steps of a dehydrohalogenation and devinylation. Devinylation by excess of a strongly basic reagent is simply the reverse reaction for the synthesis of *N*-vinylamines from acetylene and secondary amines in the presence of a trace of a basic catalyst: C. E. Schildkneckt, "Vinyl and Related Polymers," Wiley, New York, N. Y., 1952, pp 653, 654.

(6) An excellent presentation of the available evidences for the mechanism of aziridine ring opening is given in the book by O. C. Dormer and G. E. Ham, "Ethylenimine and Other Aziridines," Academic Press, New York, N. Y., 1969, p 206 ff. Carbon unsubstituted aziridines open the ring according to an $S_N2$ mechanism.

(7) J. P. N. Brewer, H. Heaney, and J. M. Jablonski, *Tetrahedron Lett.*, 4455 (1968), observed benzyne reactions of ethers and tertiary amines leading to C–O and C–N bond cleavage, respectively, which were rationalized in terms of an analogous sequence, *i.e.*, addition followed by internal β-proton abstraction with simultaneous alkene elimination. For other pertinent references, see A. R. Lepley and A. G. Giumanini, "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1971.

(8) Reference 5, p 293 ff.

(9) A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, **89**, 102 (1967).

liquid samples, KBr pellet for solids). Pmr spectra were recorded with a JEOL 60 spectrometer. Mass spectra were recorded with a low-resolution Perkin-Elmer 270 instrument equipped with gas chromatographic eluate direct inlet into the ion source, with target temperatures ranging from 100 to 220°, electron energy 75 eV, and acceleration potential 2 kV. Ten highest peaks are reported (*m/e* values, relative intensity, and eventual ion interpretation are given in brackets).[10]

Aziridine was purchased from Fluka (Switzerland). *N*-Benzylaniline was prepared in 60% yield according to a method described in the literature:[11] ir 3310 m, 3010 m, 2830 w, 1603 s, 1500 s, 1455 s, 1430 m, 1360 m, 1320 s, 1265 s broad, 1180 m, 1155 m, 1095 m, 1075 m, 1060 m, 1030 m, 985 m, 865 w, 745 s broad, and 690 $cm^{-1}$ s; mass spectrum (glc inlet, target 220°) 91 (100, $C_7H_7$), 183 (52, parent peak), 182 (19, immonium ion), 106 (18, loss of $C_6H_5$, methylene immonium ion), 77 (17, $C_6H_5$), 65 (17), 92 (9), 104 (9), 184 (8), and 51 (8).

***N*-Benzylaziridine.**—Aziridine (386 mmol) was added dropwise under stirring below 0° to a hexane solution of *n*-butyllithium (0.96 *N*, 386 mmol) in an atmosphere of dry argon. To this mixture in the same conditions benzyl chloride (386 mmol) was added dropwise. The resulting mixture was stirred during 12 hr at room temperature, then chilled to −10°, and treated with cold brine, and the organic layer separated. The organic layer was extracted with 15% hydrochloric acid at −15°, the separated aqueous extract was dropped carefully into 40% aqueous KOH kept at −10°, and the mixture extracted with ether, dried over sodium sulfate, and vacuum distilled. **3** was obtained as a colorless liquid: bp 87–89° (12 Torr);[12] yield 46.8%; glc homogeneous; ir 3080 m, 3000 m, 2850 w, 2680 w, 1500 w, 1460 m, 1275 m, 1160 w, 1032 w, 1010 m, 821 w, 778 s, 695 $cm^{-1}$ s; pmr ($CCl_4$, $\tau$ values in ppm from TMS) 2.74 (m, 5 Ar H), 6.77 (s, 2 H), 8.38 (def t, 2 cis-H), and 9.02 (def t, 2 trans H); mass spectrum (glc inlet, target 100°) 42 (100, $C_2H_4N$), 91 (60, $C_7H_7$), 65 (15, $C_5H_5$), 132 (14, loss of H, immonium ion), 51 (12), 105 (10, $C_7H_7N$), 77 (8, $C_6H_5$), 39 (8, $C_3H_3$), 133 (7, parent peak), and 103 (5, $C_7H_5N$).

**Benzyne Addition to *N*-Benzylaziridine.**—*n*-Butyllithium (1.13 *M* in hexane, 76 mmol) was added dropwise at −13° to a well-stirred solution of fluorobenzene (23 mmol) in the amine (38 mmol) under argon. The reaction appeared slightly exothermic and the mixture promptly acquired a lively red color which eventually faded to pale yellow. The mixture was kept at −13° during 15 hr and then quenched with cold water. Hydrochloric acid (15%, 2 equiv) chilled at −15° was used to extract the amines from the organic solution chilled at −10°; the aqueous solution with the amine salts was immediately carefully added to a solution of 40% potassium hydroxide (4 equiv) in water at −15° and the resulting mixture was extracted with ether. The hexane solution containing the neutral compounds revealed only little *n*-butylbenzene at the glc analysis. It was quickly identified by mass spectrometry.[13] Glc analysis of the amine solution showed unreacted **3** (28% recovery) and *N*-benzylaniline (**4**) (14%). At higher glc temperature an amine of apparent mol wt 266 (highest *m/e* peak in its mass spectrum)[14] in *ca.* 2% yield was detected. The identifications of **3** and **4** were made on the basis of glc enhancing technique, the mass spectra, and ir and pmr spectra on samples of sufficient purity obtained by distillation.

Attempts to prepare the assumed intermediate **6**, *N*-benzyl-*N*-vinylaniline, a hitherto unknown compound, met with failure.[15]

**Registry No.**—**2,** 462-80-6; **3,** 1074-42-6; **4,** 103-32-2.

**Acknowledgment.**—This work was supported in part by the Italian National Research Council (CNR) under Contract No. 7000143/03.

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(10) We are indebted to Mrs. Armida B. Giumanini of the Center for Mass Spectrometry of this University for recording the spectra.

(11) F. G. Wilson and T. S. Wheeler, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1948, p 102.

(12) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5203 (1958), reported bp 86–88° (12 Torr).

(13) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 455 ff.

(14) The mass spectrum of this compound is inducive of a structure dimeric of **3** with peaks at the following *m/e* values: 91 (100), 120 (100), 175 (100), 266 (45), 134 (54), 92 (41), 146 (41), 65 (39), 132 (39), 119 (31), 42 (28), and 104 (27).

(15) Complete details will be reported at a later time.

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# Disproportionation of 2-Iodothiophene in Dimethyl Sulfoxide

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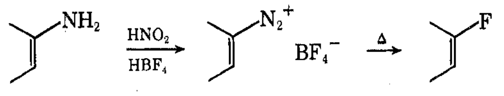
Fluorination of aromatic and heteroaromatic compounds is vested with both a theoretical and a practical interest. The method of choice for the introduction of fluorine into such structures is the two-step sequence of the preparation of a diazonium fluoroborate followed by its decomposition (Schiemann).



This method suffers from two serious drawbacks: the starting amine may not be readily available and not always do diazotation and decomposition follow the desired course.[2] A different access to fluorinated heteroaromatics in particular would therefore be desirable and with this goal we attempted to prepare 2-fluorothiophene[3] (**1**).

We attempted to make use of a nucleophilic displacement of the iodide ion by the fluoride ion in DMSO at near reflux temperature, treating 2-iodothiophene (**2**) with ammonium fluoride. To our surprise, no evidence of even trace amounts of **1** was found by gas chromatography–mass spectrometry, but a few new higher boiling compounds were formed together with some thiophene (**3**) and dimethyl sulfide. The two major higher boiling components were identified on the basis of their mass spectra as 2,5-diiodothiophene (**4**, 25%) and 5-iodo-2-thiophenaldehyde (**5**, 1.5%). Vpc–mass spectrometric inspection of other minor components of the reaction mixture ruled out the presence of isomeric diiodothiophenes and of other polyiodothiophenes. Since the spectra of the four isomeric diiodothiophenes show very similar fragmentation patterns with only tiny intensity differences, the 2,4 and 3,4 isomers were ruled out on the basis of vpc retention time ratios (Table I) and enhancing technique. Final identification of **4** was achieved by ir and pmr on an analytical sample. Vpc properties and mass spectral fragmentation of **5** were identical with those of a sample prepared by an independent route. Two well-separated minor vpc peaks eluted at much higher temperature had an identical mass spectrum fitting the elemental composition and the expected fragmentation pattern for *x,x′*-diiododithienylmethanes (**6**).

The formation of **4** may be rationalized either according to a radical mechanism (Scheme I, route A) or an

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(1) (a) Work supported in part by CNR Contract 7000143-03. (b) Chemistry student.

(2) A. Roe, *Org. React.*, **5**, 194 (1949).

(3) All fluorinated thiophenes are known, but their syntheses are very costly and difficult. Compound **1** was prepared in 10–15% yield by chlorine–fluorine exchange with $SbF_3$ [R. T. Van Vleck, *J. Amer. Chem. Soc.*, **71**, 3256 (1949)] or by reaction of the dangerous $FClO_3$ with 2-thienyllithium at −72° in 52% yield [R. D. Shuetz, D. D. Taft, J. P. O'Brien, J. L. Shea, and H. M. Mork, *J. Org. Chem.*, **28**, 1420 (1963)]. The latter method, also used to prepare the 3 isomer, gives an inseparable mixture of the desired compound with thiophene and is therefore impractical.