sulfonate salt gave $\alpha_{DMF}^{5461\,Å}$ = +26° and the urea from the tartrate salt gave $\alpha_{DMF}^{5461\,Å}$ = −28°. A second crystallization of the salts gave ureas with $\alpha_{DMF}^{5641\,Å}$ = +40° and $\alpha_{DMF}^{5641\,Å}$ = −40°. For preparation of optically active azo compounds various batches of +(−) ureas having specific rotation from +(−)23 to +(−)40° were used.

N-Phenyl-*N'*-2-bromo-9-methyl-9-fluorenylurea (IIa).—To 1.98 g of 2-bromo-9-methyl-9-aminofluorene in 40 ml of benzene was added 0.79 ml of phenyl isocyanate. The solution was heated to boiling on a steam bath and allowed to cool, and 2.4 g of colorless crystals was collected, mp 269.5–270°, after two crystallizations from acetone.

Anal. Calcd for $C_{21}H_{17}BrN_2O$: C, 64.13; H, 4.36; N, 7.12. Found: C, 64.67; H, 4.41; N, 7.09.

2-Bromo-9-methyl-9-fluorenylazobenzene (IIIa).—Potassium *tert*-butoxide (2.70 g) was dissolved in 430 ml of *tert*-butyl alcohol, 9.65 g of *N*-phenyl-*N'*-2-bromo-9-methyl-9-fluorenylurea was added, and the resulting slurry was stirred for 15 min at room temperature. *tert*-Butyl hypochlorite (4.58 ml) was added dropwise from a syringe over 2 min. The reaction mixture became bright yellow and the temperature rose to 30°. Stirring was continued for 15 min and the mixture poured onto ice and water and extracted with ether until the water was colorless. Some unreacted urea remained suspended at the interface. The ether was thoroughly washed with water (2 l.) to remove the *tert*-butyl alcohol. (Since emulsions result from shaking while extracting, it is better to pour the water through the ether and not to shake it.) The ether is filtered from 2.7 g of unreacted urea and dried with K_2CO_3 and evaporated leaving a red oil. This was chromatographed using a cold dry column of alumina eluting with 20% benzene in petroleum ether (bp 30–60°).[10] The fractions of the chromatograph were monitored by tlc. The first few fractions contained two faster running compounds in addition to the yellow azo compound and these fractions were discarded. The yield of azo compound was 1.5 g (23% based on recovered urea). This material could be crystallized with difficulty from petroleum ether, mp 67–73° dec. However, the oil and crystals had identical infrared and nmr, and the elemental analyses of the oil and the solid were identical. The nmr spectrum ($CDCl_3$) showed δ 1.85 (s, CH_3) and 7.26–8.05 (m, aromatic H's), and the uv spectrum of the oil showed λ^{EtOH} 404 nm (ε 202).

Anal. Calcd for $C_{20}H_{15}BrN_2$ (oil): C, 66.12; H, 4.16; N, 7.71. Found: C, 66.34; H, 4.24; N, 7.63.

The azo compound prepared from the partially resolved ureas gave $\alpha_{EtOH}^{5461\,Å}$ = +(−)150°. The optical purity of the azo compound was not determined. However, when attempts were made to recrystallize the partially resolved material it was found that the racemate crystallized leaving a more highly resolved oil in the mother liquors. Hence the oil was used without crystallization.

[(α-Phenyl-α-methyl)propyl]azobenzene (IIIb).—To 2.36 g of IIb[11] in 100 ml of *tert*-butyl alcohol was added 1.06 g of potassium *tert*-butoxide. This was stirred for 15 min at room temperature and 2.04 ml of *tert*-butyl hypochlorite was added dropwise over 2 min. After the addition was complete the reaction mixture was poured into 120 ml of cold water and extracted with petroleum ether. The petroleum ether extracts were washed well with water, then dried, and evaporated. The petroleum ether soluble portion of the residue was chromatographed over neutral alumina and 0.6 g of a yellow oil was eluted with petroleum ether. Nmr showed this material to be a 1:3 mixture of an unidentified compound and azo compound IIIb. The analytical sample was prepared by fractional molecular distillation: nmr (CCl_4) δ 0.77 (t, 3 H, J = 7 Hz, CH_2CH_3), 1.57 (s, 3 H, CH_3), 2.12 (q, 2 H, J = 7 Hz, CH_2CH_3); uv λ_{vis}^{EtOH} 410 nm (ε 120).

Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.38; N, 11.65. Found: C, 80.22; H, 7.82; N, 11.59.

Registry No.—IIa, 32659-22-6; (±)-IIa, 32659-23-7; (+)-IIIa, 32659-24-8; (−)-IIIa, 32659-25-9; IIIb, 32722-87-5; 2-bromo-9-methyl-9-azidofluorene, 32670-62-5; 2-bromo-9-methyl-9-aminofluorene, 32659-26-0.

(10) The alumina used for the dry column (240 g) was deactivated by the addition of 7 ml of water to 380 g of neutral alumina and heating the resulting mixture at ~50° for 1 hr on the rotary evaporator. The jacketed chromatograph column (1.2 × 14 in.) was cooled with an ice–water mixture.

(11) M. Thiel, W. Schafer, and F. Asinger, *Justus Liebigs Ann. Chem.*, **613**, 128 (1958).

The Synthesis of 3-Alkyl-2-pyrazinyl Methyl Ketones and Related Compounds

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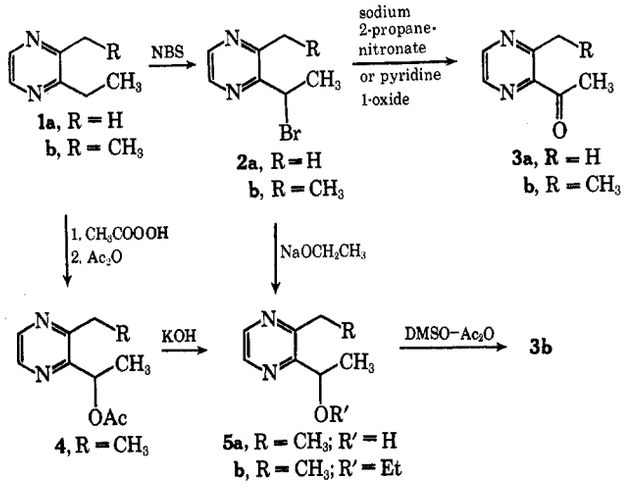
Received September 2, 1971

Acetylpyrazines, which are important flavoring materials,[1a–d] are not readily available. The literature contains no convenient synthetic route involving less than four steps.

We now report a simple two-step synthesis of acetylpyrazines from the corresponding alkylpyrazines. Monobromoalkylpyrazines, obtained by treatment of alkylpyrazines with *N*-bromosuccinimide (NBS),[2,3] are readily oxidized to the corresponding ketones by either sodium-2-propanenitronate[4] or pyridine 1-oxide.[5] Thus, 2-ethyl-3-methylpyrazine (**1a**) on treatment with NBS in the presence of benzoyl peroxide gave 2-(1-bromoethyl)-3-methylpyrazine (**2a**) (≈100%) which in turn was converted to ketone **3a**[1c] by both sodium 2-propanenitronate and pyridine 1-oxide in 66 and 25% overall yield, respectively. Similarly, 2-(1-bromoethyl)-3-ethylpyrazine (**2b**), obtained from 2,3-diethylpyrazine (**1b**), was converted to ketone **3b** in 54% overall yield with sodium 2-propanenitronate. When bromide **2b** was treated with excess sodium ethoxide in ethanol, ethyl ether **5a** was obtained in 43% yield.



In another experiment ketone **3b** was prepared from **1b** using the *N*-oxide rearrangement.[6] Treatment of **1b**

(1) (a) D. L. Roberts, to R. J. Reynolds Tobacco Co., U. S. Patent 3,402,051 (Sept 17, 1968); *Chem. Abstr.*, **72**, 11496*d* (1970); (b) M. Winter, F. Gautschi, I. Flament, and M. Stoll, to Firmenich et Cie., French Patent 1,530,436 (June 28, 1968); *Chem. Abstr.*, **71**, 90131*m* (1969); (c) Polak's Frutal Works, U. S. Patent Application 666,980; (d) V. K. Smith, Jr., P. River, and S. Kushner, to American Cyanamid Co., U. S. Patent 2,677,686 (May 4, 1954).

(2) *N*-Chlorosuccinimide has previously been used for the chlorination of 2,3-dimethylpyrazine: R. A. Pages and P. E. Spoerri, *J. Org. Chem.*, **28**, 1702 (1963).

(3) For bromination of methylpyrimidine derivatives with *N*-bromosuccinimide, see M. Hasegawa, *Pharm. Bull.*, **1**, 387 (1953); *Chem. Abstr.*, **49**, 10970*g* (1955).

(4) H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, **71**, 1767 (1949); *Org. Syn.*, **30**, 99 (1950).

(5) W. Feely, W. L. Lehn, and V. Boekelheide, *J. Org. Chem.*, **22**, 1135 (1957).

(6) G. Kobayashi and S. Furukawa, *Pharm. Bull.*, **1**, 347 (1953); *Chem. Abstr.*, **49**, 10948*e* (1955); V. Boekelheide and W. J. Linn, *J. Amer. Chem. Soc.*, **76**, 1286 (1954); B. Klein, J. Berkowitz, and N. E. Hetman, *J. Org. Chem.*, **26**, 126 (1961).

with 1 mol of peracetic acid and excess acetic anhydride gave acetoxypyrazine **4** (42%) which was saponified to hydroxypyrazine **5a** (77%) and oxidized to ketone **3b** by the acetic anhydride–dimethyl sulfoxide method.[7] It should be mentioned that our attempts to oxidize alcohol **5a** to ketone **3b** with either the Jones reagent[8] or chromium trioxide–pyridine[9] were unsuccessful.

Experimental Section

Vapor phase chromatographic (vpc) analyses were performed on an F & M 810 instrument using 5% Carbowax 20M and 5% silicone SE-30 packed stainless steel columns (1/4 in. × 25 ft). The following spectrometers were used: infrared (ir), Beckman IR-5A and IR-4; nuclear magnetic resonance (nmr), Varian A-60 and HA-100 (TMS as internal standard); mass spectrometer, CEC Model 21-103C and AEI MS9. Mass spectral major fragmentation peaks are listed in decreasing order of intensity except for the molecular ion peak which is listed first. Five per cent deactivated silicic acid (Grace, 100–200 mesh), made by adding 5 ml of water to 95 of silicic acid, and acid alumina (activity I, Fisher Scientific, 80–200 mesh) were used for column chromatography. Anhydrous magnesium sulfate was used as drying agent.

2-(1-Bromethyl)-3-methylpyrazine (2a).—A solution of **1a** (24.4 g, 0.2 mol) in carbon tetrachloride (400 ml) containing NBS (35.6 g, 0.2 mol) and benzoyl peroxide (0.5 g) was refluxed for 90 min, cooled, filtered, and solvent stripped under reduced pressure to give 40.5 g (~100%) of crude orange-brown oil. Vpc (Carbowax) indicated the complete conversion of **1a** to bromide **2a**. Pure bromide was isolated by vpc (silicone): ir (neat) 3.3, 3.4, 3.45, 5.85, 6.55, 6.95, 7.12, 7.3, 7.55, 7.95, 8.4, 8.55, 8.85, 9.22, 9.45, 9.61, 10.3, 11.5, 11.75, 12.7, 13.2, 13.7 μ; nmr ($CDCl_3$) δ 2.07 (d, 3, $-CHBrCH_3$), 2.6 (s, 3, C-3 methyl H), 5.2 (q, 1, $-CHBrCH_3$), 8.3 (s, 2, C-5 and C-6 H); mass spectrum *m/e* 200 (molecular ion), 121, 39, 93, 42, 52.

Anal. Calcd for $C_7H_9BrN_2$: *m/e* 199.9949. Found: *m/e* 199.9954.

3-Methyl-2-pyrazinyl Methyl Ketone (3a). A. With Sodium 2-Propanenitronate.—2-Nitropropane (18.7 g, 0.21 mol) was added to a solution of sodium ethoxide, prepared by the reaction of sodium (4.6 g, 0.2 g-atom) with absolute ethanol (200 ml). After the mixture was stirred for 30 min at room temperature, crude bromide **2a** (40.5 g) was added and the resulting slurry, which gradually thinned out and darkened during heating, was refluxed for 2 hr. The mixture was cooled and the solid was filtered. Removal of solvent under reduced pressure yielded 36.1 g of residue which was distilled, giving 18.1 g (66.5%) of pale yellow oil **3a**: bp 56° (0.5 mm); ir (neat) 3.3, 3.4, 3.45, 5.92 (>C=O), 6.48, 6.55, 6.95, 7.09, 7.19, 7.3, 7.41, 7.82, 8.05, 8.42, 8.6, 9.23, 9.45, 9.7, 9.9, 10.2, 10.6, 11.7 μ; nmr ($CDCl_3$) δ 2.7 (s, 3, $-C(=O)CH_3$), 2.8 (s, 3, methyl H), 8.5 and 8.6 (two d, 2, C-5 and C-6 H); mass spectrum *m/e* 136 (molecular ion), 43, 94, 93, 42.

Anal. Calcd for $C_7H_8N_2O$: *m/e* 136.0636. Found: *m/e* 136.0641.

B. With Pyridine 1-Oxide.—A solution of crude **2a** (40.5 g) and pyridine 1-oxide (38 g) in acetonitrile (300 ml) was refluxed for 5 hr and then cooled. The solvent was stripped under reduced pressure leaving a dark residue behind, to which 10% aqueous potassium hydroxide solution (150 ml) was added. The aqueous layer was extracted with ether. The organic extract was dried, concentrated, and distilled to afford a fraction (8.9 g), bp 57–64° (3–5 mm), which was further purified by column chromatography (100 g silicic acid): 20–50% ether in hexane (500 ml) eluted 6.8 g (25%) of ketone **3a**.

2-(1-Bromoethyl)-3-ethylpyrazine (2b).—A solution of **1b** (68.1 g, 0.5 mol) in carbon tetrachloride (1 l.) containing NBS (89 g, 0.5 mol) and benzoyl peroxide (1 g) was refluxed for 90 min, cooled, filtered, and solvent stripped under reduced pressure to give 108.3 g (~ 100%) of crude bromide **2b**. Pure bromide was isolated by vpc (silicone): ir (neat) 3.3, 3.35, 3.42, 3.5, 6.52, 6.85, 6.9, 6.93, 7.1, 7.29, 7.5, 7.6, 7.9, 8.1, 8.39, 8.62, 8.89, 9.2, 9.42, 9.6, 9.73, 10.3, 11.65, 13.8 μ; nmr ($CDCl_3$) δ 1.35 (t, 3, $-CH_2CH_3$), 2.1 (d, 3, $-CHBrCH_3$), 2.75 (q, 2, $-CH_2CH_3$), 5.39 (q, 1, $-CHBrCH_3$), 8.0 (s, 2, C-5 and C-6 H); mass spectrum *m/e* 214 (molecular ion), 135, 39, 119, 52, 54, 136.

Anal. Calcd for $C_8H_{11}BrN_2$: *m/e* 214.0006. Found: *m/e* 214.0009.

3-Ethyl-2-pyrazinyl Methyl Ketone (3b).—2-Nitropropane (62.3 g, 0.7 mol) was added to a solution of sodium ethoxide, prepared by the reaction of sodium (12.7 g, 0.55 g-atom) with absolute ethanol (600 ml). After the mixture was stirred for 30 min, crude bromide **2b** (108.3 g) was added and the resulting slurry, which gradually thinned out, was refluxed for 2 hr. After the usual work-up and distillation, 40.5 g (54%) of pale yellow oil **3b** was obtained: bp 55° (1.1 mm); ir (neat) 3.3, 3.39, 3.41, 5.5, 5.9 (>C=O), 6.05 (very weak), 6.45, 6.55, 6.85, 7.09, 7.14, 7.4, 7.6, 7.85, 8.02, 8.45, 8.6, 8.7, 9.2, 9.3, 9.45, 9.72, 10.3, 10.5, 11.65 μ; nmr ($CDCl_3$) δ 1.28 (t, 3, $-CH_2CH_3$), 2.69 (s, 3, $-C(=O)CH_3$), 3.15 (q, 2, $-CH_2CH_3$), 8.44 and 8.61 (two d, 2, C-5 and C-6 H); mass spectrum *m/e* 150 (molecular ion), 43, 107, 52, 79, 27.

Anal. Calcd for $C_8H_{10}N_2O$: *m/e* 150.0793. Found: *m/e* 150.0799.

3-Ethyl-α-methyl-2-pyrazinemethanol Acetate (4).—To a solution of **1b** (27.2 g, 0.2 mol) in acetic acid (100 ml) was added slowly 40% peracetic acid (38 g, 0.2 mol) at 75–80°. After stirring for 1 hr at 75° the acetic acid was stripped under reduced pressure, acetic anhydride (150 ml) was added to the residue, and the reaction mixture was refluxed for 4 hr. The acetic anhydride was removed under reduced pressure to obtain a dark residue which was taken up in ether and poured into water. The ether extract was washed with sodium bicarbonate and sodium chloride solutions, dried, evaporated, and distilled to yield 16.5 g (42.5%) of colorless oil **4**: bp 107–110° (0.4 mm); ir (neat) 3.3, 3.35, 3.41, 3.45, 5.75, 6.85, 7.05, 7.29, 7.59, 8.05, 8.6, 8.75, 9.2, 9.35, 9.45, 9.75, 9.9, 10.25, 10.55, 11.6, 11.75 μ; nmr ($CDCl_3$) δ 1.3 (t, 3, $-CH_2CH_3$), 1.56 (d, 3, $-OCHCH_3$), 2.06 (s, 3, $-OOCCH_3$), 2.9 (q, 2, $-CH_2CH_3$), 6.1 (q, 1, >CHOAc), 8.4 (m, 2, C-5 and C-6 H); mass spectrum *m/e* 194 (molecular ion), 43, 151, 152, 134, 133, 135.

Anal. Calcd for $C_{10}H_{14}N_2O_2$: *m/e* 194.1055. Found: *m/e* 194.1058.

3-Ethyl-α-methyl-2-pyrazinemethanol (5a).—To a solution of **4** (11.7 g, 0.06 mol) in methanol (75 ml) was added slowly 20% aqueous potassium hydroxide (30 ml) and the solution was stirred for 2 hr at room temperature. The reaction mixture was poured into water and extracted with ether. The dried extract was concentrated to give 9.7 g of crude material which was distilled to afford 7.1 g (77.7%) of colorless oil **5a**: bp 70–71° (1.5 mm); ir (neat) 3.0 (–OH), 3.3, 3.39, 3.41, 3.49, 6.51, 6.9, 7.1, 7.3, 7.6, 7.9, 8.6, 9.2, 9.7, 9.85, 10.3, 11.1, 11.7, 12.2, 12.7, 13.7 μ; nmr ($CDCl_3$) δ 1.33 (t, 3, $-CH_2CH_3$), 1.45 (d, 3, $-OCHCH_3$), 2.82 (q, 2, $-CH_2CH_3$), 5.05 (q, 1, >CHOH), 8.34 and 8.45 (two d, 2, C-5 and C-6 H); mass spectrum *m/e* 152 (molecular ion), 137, 107, 52, 45, 80.

Anal. Calcd for $C_8H_{12}N_2O$: *m/e* 152.0949. Found: *m/e* 152.0953.

3-Ethyl-2-pyrazinyl Methyl Ketone (3b). DMSO–Ac_2O Method.—A solution of **5a** (2.28 g, 0.015 mol) in dimethyl sulfoxide (27 ml) and acetic anhydride (18 ml) was allowed to stand at room temperature for 24 hr. The reaction mixture was poured into water and basified with 10% aqueous hydroxide solution. The mixture was extracted with methylene chloride. The organic extract was dried and concentrated to give a residue which was dissolved in hexane, washed with water, and dried. Removal of solvent gave 1.75 g of oil which showed one major peak by vpc (Carbowax) due to **3b**.

3-Ethyl-2(1-ethoxyethyl)pyrazine (5b).—Crude bromide **2b**, obtained by reacting **1b** (13.6 g, 0.1 mol), NBS (17.8 g, 0.1 mol), and benzoyl peroxide (0.2 g) in carbon tetrachloride in the usual manner, was added to a solution of sodium ethoxide (4.6 g, 0.2 g-atom of sodium in 250 ml of dry ethanol) and refluxed for 1 hr. The reaction mixture was cooled, filtered, and distilled to obtain 7.75 g (43%) of colorless oil **5b**: bp 44–50° (0.5 mm); ir (neat), 3.3, 3.4, 3.42, 3.49, 5.72, 6.5, 6.85, 7.1, 7.29, 7.45, 7.58, 7.89, 8.0, 8.62, 9.05, 9.3, 9.4, 9.9, 10.3, 10.6, 11.65 μ; nmr ($CDCl_3$) δ 1.2 (t, 3, $-OCH_2CH_3$), 1.3 (t, 3, $-CH_2CH_3$), 1.5 (d, 2, $EtOCHCH_3$), 2.94 (q, 2, $-CH_2CH_3$), 3.4 (m, 2, $-OCH_2-CH_3$), 4.76 (q, 1, $EtOCHCH_3$), 8.4 (s, 2, C-5 and C-6 H); mass spectrum *m/e* 180 (molecular ion), 136, 45, 73, 121, 133, 27.

(7) J. D. Albright and L. Goldman, *J. Amer. Chem. Soc.*, **87**, 4214 (1965).
(8) K. Bowden, I. M. Heilbron, E. R. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).
(9) K. Biemann, G. Büchi, and B. H. Walker, *J. Amer. Chem. Soc.*, **79**, 5558 (1957).

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.

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

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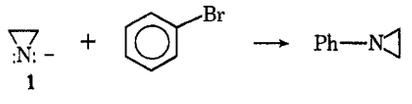
Received May 11, 1971

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]



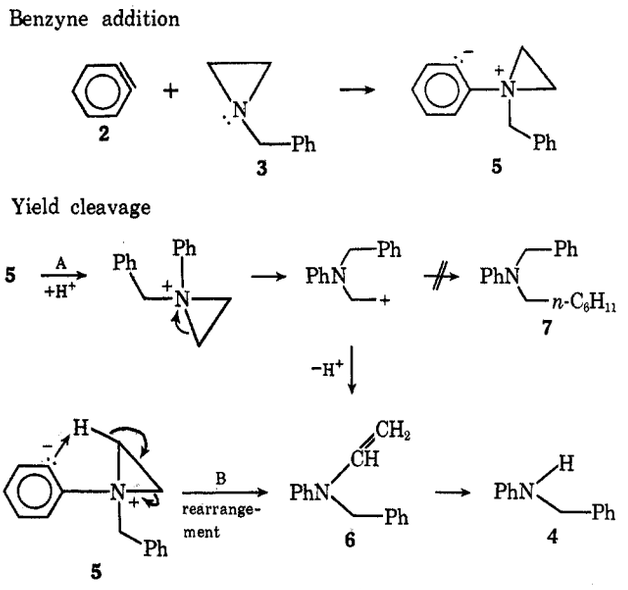
1

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 SN1 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

(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 SN2 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).