Experimental Section

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Nuclear magnetic resonance spectra were obtained using a Jeolco minimar spectrometer. Tetramethylsilane was used as an internal standard. Infrared spectra were obtained using a Perkin-Elmer Model 137 G spectrophotometer. Gas–liquid chromatography (glc) was performed using a Hewlett-Packard Model 402 gas chromatograph with a hydrogen flame detector. A glass column (6 ft × 0.25 in. o.d.) bent in a U shape and packed with 3% SE-30 on 100/120 mesh GCQ at a column temperature of 270° with a helium flow rate of 90 ml/min was used for all glc analyses.

Dehydrobromination–Decarbomethylation of Bromo Ketone 1.—Bromo ketone **1** (500 mg, 1.27 mmol) was added to a solution of 1,5-diazabicyclo[5.4.0]undecene-5 (DBU) (390 mg, 2.56 mmol) and 1.51 ml of *o*-xylene. The temperature of the reaction solution was allowed to remain at 165° for 5 hr. The ether extract of the reaction mixture was acidified with 5% HCl and washed with 5% aqueous sodium carbonate and water, dried over anhydrous sulfate, and evaporated *in vacuo*. Crystallization of the residue from 20:1 methylene chloride–methanol solution yielded 299 mg (92%) of the white, crystalline compound **5**: mp 122.5–123.5° (lit.[16] mp 120–121°); λ_{max}^{KBr} 1650, 1600 cm^{-1}; δ^{CHCl_3} 1.41 (3 H, d, J = 6 cps), 1.73 (3 H), 4.33 (3 H), 6.91 (1 H, d, J = 1.8 cps), 7.39 (2 H, multiplet), 8.98 ppm (1 H, d, J = 9 cps). *Anal.* Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.90; H, 8.00.

Dehydrobromination of Bromo Ketone 1.—Bromo ketone **1** (500 mg, 1.27 mmol) was added to a solution of DBU (0.140 mg, 0.92 mmol) and 1.51 ml of *o*-xylene which was allowed to remain at 165° for 15 min. Following work-up in the manner described above, crystallization from aqueous methanol yielded 360 mg (90.5%) of the crystalline solid **3**: mp 175–177° (lit.[10] mp 173–175°); λ_{max}^{KBr} 1725, 1645, 1600, 1575 cm^{-1}; δ^{CHCl_3} 1.56 (3 H), 1.76 (3 H), 4.33 (3 H), 4.58 (3 H), 7.71 (1 H), 8.15 (2 H, multiplet), 9.58 ppm (1 H, d, J = 8 cps). *Anal.* Calcd for $C_{19}H_{22}O_4$: C, 72.50; H, 7.01. Found: C, 72.86; H, 7.14.

General Procedure for the *O*-Alkyl Cleavage of Methyl Esters. Methyl *O*-Methylpodocarpate, Methyl Mesitoate, and Methyl Triisophopylacetate, and Methyl Palmitate.—A solution of DBU (1.202 g, 8.30 mmol) and 0.83 mmol of the appropriate methyl ester was dissolved in 1.0 ml of *o*-xylene and the resulting mixture was allowed to remain at 165° for 48 hr. The usual work-up of the ether extract of the acidified carbonate layer yielded the corresponding acid, which was identical by ir, nmr, and mixture melting points with an authentic sample.

Attempted Cleavage of Acetate 9.—Acetate **9** (0.500 mg, 1.59 mmol) was dissolved in 1.9 ml of *o*-xylene and after the addition of DBU (2.42 g, 15.94 mmol) the solution was heated at 165° for 48 hr. The washed ether extract of the acidified reaction mixture yielded 0.489 mg (97.8%) of a white, crystalline material which was identical by glc, ir, nmr, and mixture melting points with an authentic sample of the starting material.

Selective Cleavage of Methyl 3β-Acetoxy-Δ^5-etienate.—Acetoxy ester (200 mg, 0.52 mmol) was added to a solution of DBU (740 mg, 4.86 mmol) in 0.62 ml of *o*-xylene and the resulting mixture was heated for 3.5 hr at 165°. The usual work-up yielded 154 mg of crude product. Glc comparison with authentic samples showed the product to be 50% of starting material, 41% of the desired acetoxy acid, 7% of the hydroxy acid resulting from hydrolytic loss of the acetate group, and 2% of the diene acid resulting from the loss of the acetate group.

Registry No.—**1**, 37931-64-9; **3**, 37931-65-0; **5**, 37931-66-1; DBU, 6674-22-2.

Acknowledgments.—We wish to thank the graduate school and the Biological and Physical Sciences Institute for partial financial support. We express our sincere appreciation to Dr. Ian K. Walker, Department of Scientific and Industrial Research, Wellington, New Zealand, for generous supplies of podocarpic acid.

(16) M. Ohta and L. Ohmori, *Chem. Pharm. Bull.*, **5**, 96 (1957).

Synthesis of Benzo[*b*]-1,4-diazabicyclo[3.2.1]octane

HOWARD C. CUNNINGHAM AND ALLAN R. DAY*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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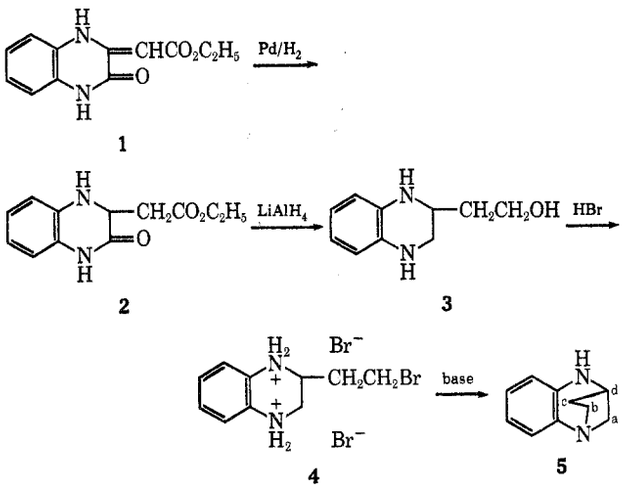
Benzo[*b*]1,4-diazabicyclo[3.2.1]octane (**5**), a new ring system, was prepared from 3-ethoxycarbonylmethylene-2-quinoxalone[1] as shown in Scheme I. Spectral data

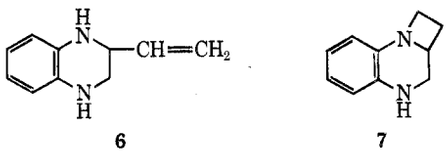
SCHEME I



support the keto structure shown above (**1**) rather than a tautomeric form. The infrared spectrum (KBr) shows conjugated ester carbonyl absorption at 1685 cm^{-1} and a lactam carbonyl at 1643 cm^{-1}, compared to the values 1705 and 1670 cm^{-1} for these bands in the dihydro compound **2**. The nmr spectrum of **1** (DMSO) showed a singlet at δ 5.55 which integrated for one proton. Protons on the α carbon atom of an α,β-unsaturated ester are known to absorb in this region.[2] Furthermore, no absorption was found in the region of δ 2.1 where protons in a methylene group adjacent to an ester group are known to absorb.[2] The uv spectrum (C_2H_5OH) was also in agreement with the assigned structure.

The free base corresponding to **4** could not be isolated due to the ease with which it undergoes cyclization to form **5**. The new compound (**5**) was formed by an intramolecular process as established by molecular weight determination.

Theoretically, two other compounds (**6** and **7**) might result from the treatment of compound **4** with bases.



6 **7**

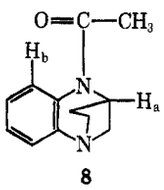
Compound **6** was ruled out for two reasons. The infrared spectrum showed no alkene absorption. Further-

(1) Y. J. L'Italien and C. K. Banks, *J. Amer. Chem. Soc.*, **73**, 3246 (1951).

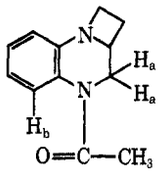
(2) L. M. Jackson, "Application of NMR Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp 53–57.

more, one would expect two N–H protons and three vinyl protons in the nmr spectrum of **6** but these were not observed. Thus, the choice is between **5** and **7**. One would expect the five-member ring to be more stable and hence the formation of **5** should be favored.

Comparison of the nmr spectrum of **5** or **7** with the nmr spectrum of the acetyl derivative **8** or **9** in $CDCl_3$



8

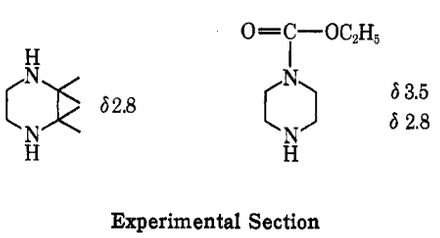


9

shows that the new ring compound has the structure shown as compound **5**. The nmr spectrum of **5** shows a multiplet at δ 2.06 (2 H, methylene protons at c in the bridge), a multiplet at 3.12 (4 H, methylene protons at a and b), a multiplet at 3.87 (1 H, bridgehead proton), a singlet at 4.15 (1 H, NH proton) and a multiplet at 6.8 (4 H, aromatic protons). When the nmr spectrum was determined in D_2O, the δ 4.15 peak disappeared.[3]

The nmr spectrum of the acetylated derivative showed some characteristic differences. The N–H proton peak disappeared and only three protons were found in the aromatic multiplet. One of the aromatic protons (H_b) was shifted downfield to δ 8.4 due to an anisotropic effect. More significant, the acetyl group would be expected to deshield the protons marked H_a. If the acetylated product were **9**, one would expect the multiplet for two protons to be shifted downfield and, if the acetylated product were **8**, the single H_a proton would be shifted downfield. Actually, it was the single proton at δ 3.87 that shifted to δ 4.83. It would appear therefore that structure **5** is correct and the product formed by intramolecular cyclization is benzo[*b*]-1,4-diazabicyclo[3.2.1]octane.

A similar shift has been observed in 1-carbethoxypiperazine.[4]



Experimental Section

Melting points were determined in a Thomas-Hoover melting point apparatus. Infrared spectra (KBr) were obtained with a Perkin-Elmer Model 521 spectrophotometer. Ultraviolet spectra were determined with a Cary 14 ultraviolet spectrophotometer. Nuclear magnetic spectra were obtained at 60 MHz with a Varian Associates Model A-60A spectrometer.

Ultraviolet Spectrum of 3-Ethoxycarbonylmethylene-2-quinoxalone (1).[1]—Obtained was uv (C_2H_5OH), λ_{max} (E_{max}), 201 (2.82×10^4), 226 (2.07×10^4), 283 (5.84×10^3), 344 (6.45×10^3).

3-Ethoxycarbonylmethyl-2-quinoxalone (2).—3-Ethoxycarbonylmethylene-2-quinoxalone[1] (23.2 g, 0.1 mol) was added to 125 ml of glacial acetic acid. The mixture was hydrogenated at 50° over 10% palladium on carbon. Hydrogenation was rapid and the starting material dissolved rapidly as hydrogenation occurred (20–30 min). After the catalyst was removed, the acetic acid was removed *in vacuo* on a steam bath. A little petroleum ether was added to the residue to facilitate complete crystallization. The product was recrystallized from petroleum ether (60–110°): yield 41%, yellow solid, mp 106–108°.

Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 6.03; N, 11.96. Found: C, 61.66; H, 5.85; N, 12.02.

2-(2-Hydroxyethyl)-1,2,3,4-tetrahydroquinoxaline (3).—3-Ethoxycarbonylmethyl-2-quinoxalone (18.5 g, 0.08 mol) was dissolved in 500 ml of dry tetrahydrofuran, and the solution was added dropwise to a stirred suspension of 9.5 g (0.25 mol) of lithium aluminum hydride. After the addition, stirring was continued for 2 hr and the mixture was then refluxed for 17 hr. The mixture was filtered and the inorganic salts were thoroughly extracted with tetrahydrofuran. The extract and filtrate were combined and dried ($MgSO_4$), and the solvent was removed *in vacuo*. The residual oil solidified on standing a short time with petroleum ether. The product was recrystallized from benzene–petroleum ether (bp 60–110°) with the aid of decolorizing carbon: yield 65%; colorless solid; mp 97–98°; ir (KBr, cm^{-1}) 3370 (m), 3305 (m), 2580–2950 (vs), 1590 (s), 1455 (s).

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.22; H, 7.94; N, 15.5.

2-(2-Bromoethyl)-1,2,3,4-tetrahydroquinoxaline Dihydrobromide (4).—2-(2-Hydroxyethyl)-1,2,3,4-tetrahydroquinoxaline (8.90 g, 0.05 mol) was added in small portions to 200 ml of 48% hydrobromic acid with stirring and some cooling. The mixture was refluxed for 8 hr. The mixture was reduced to a small volume by distillation and the dark, residual solid was washed with acetone to give a light gray solid (yield 69%). A colorless analytical sample was obtained by recrystallization from 48% hydrobromic acid with the aid of decolorizing carbon: mp >300°; ir (KBr, cm^{-1}) 2900–2100 (s), 1500 (s), 780 (s), 745 (s).

Anal. Calcd for $C_{10}H_{15}N_2Br_3$: C, 29.81; H, 3.75; N, 6.95; Br, 59.49. Found: C, 29.70; H, 3.81; N, 6.80; Br, 59.55.

Benzo[*b*]-1,4-diazabicyclo[3.2.1]octane (5).—2-(2-Bromoethyl)-1,2,3,4-tetrahydroquinoxaline dihydrobromide (10 g, 0.248 mol) was suspended in 50 ml of chloroform. A solution of 2.78 g (0.0496 mol) of potassium hydroxide in 100 ml of water was added and the mixture was stirred vigorously until solution was complete. The layers were then separated at once. The water layer was washed with chloroform and the extract and filtrate were dried ($MgSO_4$). The chloroform was removed on a steam bath leaving an oily residue which solidified on cooling. The product was recrystallized from benzene–petroleum ether (60–110°) with the aid of decolorizing carbon: yield 80%, colorless crystals, mp 131–134°.

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48; mol wt, 160. Found: C, 74.88; H, 7.50; N, 17.53; mol wt, 165 (Rast).

1-Acetylbenzo[*b*]-1,4-diazabicyclo[3.2.1]octane (8).—Compound **5** (1.60 g, 0.01 mol), 0.8 g (0.011 mol) of acetyl chloride, and 1.01 g (0.01 mol) of triethylamine were dissolved in 100 ml of chloroform, and the solution was refluxed for 3 hr. The chloroform was removed by distillation and the residue was treated with dry ether to precipitate the triethylamine hydrochloride which was removed by filtration. The precipitate was extracted with warm benzene. The ether filtrate and benzene extract were combined and evaporated. The slightly sticky solid, so obtained, was recrystallized from petroleum ether (bp 60–110°): yield 70%, colorless crystals, mp 117–120°.

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98; N, 13.85. Found: C, 71.36; H, 7.18; N, 13.81.

1-Benzoylbenzo[*b*]-1,4-diazabicyclo[3.2.1]octane (10).—This compound was prepared by the method used for **8**, using benzoyl chloride in place of acetyl chloride: yield 73%, colorless crystals, mp 158°.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.39; H, 6.01; N, 10.41.

1-Ethoxycarbonylbenzo[*b*]-1,4-diazabicyclo[3.2.1]octane (11).—The procedure for **10** was used again, using ethyl chloroformate in place of acetyl chloride: yield 30%, colorless crystals, mp 75–76°.

Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 67.09; H, 7.03; N, 11.93.

(3) The nmr spectrum of **5** with D_2O will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-1225. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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Registry No.—**1**, 30681-63-1; **2**, 37931-42-3; **3**, 37931-43-4; **4**, 37931-44-5; **5**, 27023-72-9; **8**, 37931-46-7; **10**, 37931-47-8; **11**, 37931-48-9.

Nitrogen Photochemistry. XI. Liquid Phase Irradiation of Primary Aliphatic Amines[1]

VIRGIL I. STENBERG,* N. KULEVSKY, AND CHIEN-HUA NIU

Department of Chemistry, The University of North Dakota, Grand Forks, North Dakota 58201

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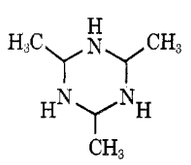
For some time, we have been studying the photochemistry of alkaloids and, as a direct consequence, it has been necessary to resolve some of the problems associated with amine photochemistry. The primary products from the liquid phase ultraviolet (uv) irradiation of several aliphatic amines have been isolated and identified to resolve existing questions on the probable (1) formation of imines and (2) existence of C–N bond cleavage in these photolyses.

Uncharacterized, unsaturated compounds are formed in equivalent amounts to hydrogen generated during the irradiation of hexane solutions of *n*-hexylamine and ethylmethylamine.[2] The irradiation of cyclohexylamine in cyclohexane produces exclusively cyclohexylcyclohexane in molar amounts.[3]

Pouyet reports that the irradiation of primary amines as 2-propylamine, *n*-butylamine, and isoamylamine in hexane provides hydrogen and 1-hexene in approximately equivalent amounts.[4,5] When the irradiation of primary amines is done in water, the corresponding alcohols and ammonia are formed.[4,6] Branching at the α carbon to the amino function enhances the reaction rate in both instances. Esr evidence has been given for presence of $CH_3CH{=}N\cdot$, $CH_3\dot{C}HNH_2$, and $CH_3CH_2\dot{N}H$ during the irradiation of ethylamine in an adamantane matrix while similar irradiations of *n*-propylamine and *n*-butylamine exhibit signals assigned to $RCH{=}N\cdot$ and $R\dot{C}HNH_2$.[7] At 77°K, Hadley and Volman have demonstrated that the irradiation of methylamine with 184.9-nm light gives esr signals for the $CH_3NH\cdot$ radical.[8]

In the vapor phase, irradiation of methylamine gives a trimer of methyl methylenimine, I, in addition to a polymer.[9–13] Mass spectrometric analysis of the gases has demonstrated the presence of a C_2H_5N compound which has been assigned the structure of ethylenimine.[10]



I

Experimental Section

Reagents.—The following lists the commercial sources of the chemicals used: Aldrich Chemical Co., cyclohexylamine, cyclopentylamine; Eastman, *n*-hexylamine, cyclohexylcyclohexane; and Chemical Samples Co., *n*-hexylcyclohexane, cyclopentylcyclopentane. Cyclohexane and cyclopentane were purified by known procedures.[14] *N*-1-(Hexylidene)hexylamine and *N*-cyclopentylidenecyclopentylamine were synthesized by the method of Campbell, *et al.*,[15] Dicyclopentylamine and *n*-hexylcyclohexylamine were prepared by reduction of the corresponding imines with excess 10% Pd/C in ethanol and vacuum distillation.

General Procedure for Products Accumulation Studies.—The irradiations were done in a quartz tube with a ground glass point using a 450-W medium-pressure Hanovia mercury arc lamp. Nitrogen gas free of oxygen was passed into the solution *via* a bubbler for 30 min prior to irradiation. The sample tube and the immersion well containing the lamp were placed in a 13.4 ± 0.1° water bath. Aluminum foil was placed around the upper part of the sample tube to avoid irradiating the vapors. The distance between the quartz tube and the edge of the immersion well was held constant at 3.5 cm. The reactions were monitored using a Beckman GC-5 equipped with flame ionization detectors, Disc integrator, and two 20 ft × 1/8 in. 5% KOH–20% Carbowax–Chromosorb W columns.[16] The cyclohexylamine study was done with 20 ft × 1/8 in. 18% Theed Chromosorb P columns. In order to restrict the number of products to a minimum, solvents with symmetrical molecules were employed.

General Procedure for Products Identification Studies.—The immersion well with lamp was surrounded by a Pyrex jacket containing *ca.* 1.5 g of sample in 300 ml of solvent. The solutions were irradiated for 4 hr with N_2 bubbling through and concentrated; the products were separated by an Aerograph A-700 glpc equipped with a 10 ft × 1/4 in. 5% KOH–20% Carbowax–Chromosorb W column. The product were identified by retention times and comparative nmr and ir spectra except for the air-oxidizable imine, *N*-cyclopentylidenecyclopentylamine. This imine was removed from its reaction solution by a 2 *N* HCl wash or hydrogenated to dicyclopentylamine with 10% Pd/C in ethanol. The latter compound was identified in the usual manner. Ammonia was trapped from the cyclohexylamine and *n*-hexylamine irradiation solutions by passing the effluent gas stream first through a NaCl–ice trap and subsequently through a Dry Ice trap. Ammonia was identified by its characteristic ir spectrum.[17]

Results

The products isolated and identified from the irradiations of cyclohexylamine, cyclopentylamine, and *n*-hexylamine are those represented in eq 1–3. The product accumulation data from these irradiations are illustrated in Tables I, II, and III.

Discussion

The four postulated cleavage patterns resulting from the irradiation of primary amines in the vapor phase are represented in eq 4a–d.[10] Pathway 4a is well ac-

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