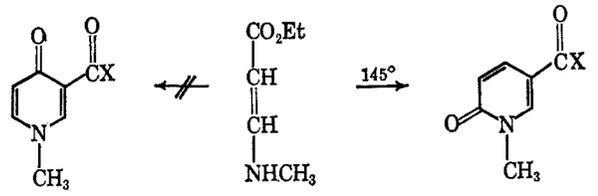
hydroxynicotinic acid[6,7] in a sealed tube with methyl iodide in alcoholic potassium hydroxide followed by conversion of the product to the amide. (See Scheme I.)

SCHEME I



1a, X = $NH_2$
b, X = OEt
c, X = OH

2

3, X = OEt
4, X = OH
5, X = $NH_2$

### Experimental Section[8]

**Ethyl β-Methylaminoacrylate (2).**—Methylamine gas (8 g) was absorbed while passing through a solution of 25 g of commercial ethyl propiolate in 150 ml of benzene with cooling by ice water to keep the temperature below 25°. The benzene solution was stirred for 1 hr at room temperature and refluxed for 2 hr. After the solvent had been removed, the reaction mixture was distilled to yield **2**, bp 83–90° (15 mm), 24.8 g (74.6%). Repeating the distillation gave a boiling point of 85–86° (17 mm). *Anal.* Calcd for $C_5H_{11}NO_2$: C, 55.80; H, 8.58; N, 10.84. Found: C, 55.07; H, 8.37; N, 10.99.

**Ethyl 1-Methyl-1,6-dihydro-6-oxonicotinate (3).**—Heating 7.8 g of **2** at 140–145° for 6 hr with stirring gave a solid product upon cooling. The reaction mixture was dissolved in 30 ml of 2-propanol, treated with active charcoal, and concentrated to 10 ml. The addition of *n*-hexane led to a good yield of colorless needles, mp 78–80° (lit.[9] mp 74°), 3.2 g (59%). *Anal.* Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.28; H, 5.82; N, 7.70.

**1-Methyl-1,6-dihydro-6-oxonicotinic Acid (4).**—Compound **3** (5.7 g) was hydrolyzed with potassium hydroxide in 95% ethanol. After the ethanol was removed *in vacuo* the residue was dissolved in 300 ml of water and passed through a column (17.8 × 3.2 cm) of Dowex 2 formate ion-exchange resin.[10] After the column was washed with 1 l. of water, **4** was eluted with 1 l. of 6 *N* formic acid. The eluate was concentrated *in vacuo* and the residue was recrystallized from water to yield 3.8 g (78%) of colorless needles, mp 241–243° (lit.[10,11] mp 240–240.5°, 238–239°). The melting point of a mixture with an authentic sample[10] (mp 243°) was 240–243°. *Anal.* Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.80; H, 4.75; N, 9.15.

**1-Methyl-1,6-dihydro-6-oxonicotinamide (5).**—To a solution of 1.5 g of **4** in 20 ml of chloroform, 10 ml of tetrahydrofuran, and 2 g of triethylamine was added, dropwise, 2 g of ethyl chloroformate at −5°. After stirring the solution for 1 hr, 30 ml of 15 *N* ammonium hydroxide was added to the solution which was then stirred for 2 hr more at room temperature. After the solvent was removed *in vacuo*, the residue was dissolved in 300 ml of water and applied to a column (12.7 × 3.2 cm) of Dowex 2 formate ion-exchange resin. The column was washed with 600 ml of water. From the combined effluent and wash water, 0.55 g (36.1%) of **5** was obtained, mp 211° (lit.[12] mp 212–215°). An admixture of **5** with an authentic sample (mp 208.5–210°) melted at 211–214°. Unreacted **4** (0.3 g) was recovered by elution of the column with 6 *N* formic acid.

**4-Hydroxynicotinic Acid.**—3-Iodo-4-hydroxypyridine (mp 290–293° dec, 4.4 g)[6] and 5.4 g of cuprous cyanide were stirred and heated in 100 ml of dimethylformamide at 140–145° for 5 hr. The reaction mixture was filtered and concentrated *in vacuo*. The residual oil was refluxed in a solution of 12 g of potassium hydroxide in 40 ml of water for 6 hr. The reaction mixture was then diluted to 400 ml and filtered. The filtrate was passed through a column (10 × 3.2 cm) of Dowex 2 formate ion-exchange resin. After washing the column with 800 ml of water, the acid was eluted with 800 ml of 6 *N* formic acid. The eluate was evaporated *in vacuo* and the residue was recrystallized from water, mp 246–250° (lit.[7] mp 249–251°), 1.23 g (45.5%). Repeating the recrystallization gave a melting point of 250–252°, with a change in the crystal form from plates to pillows at about 220–230°.

**1-Methyl-1,4-dihydro-4-oxonicotinic Acid (1c).**—The above acid (0.5 g), 20 ml of 90% methyl alcohol containing 0.6 g of potassium hydroxide, and 10 ml of methyl iodide were heated at 100° for 44 hr in a sealed tube. The reaction mixture was evaporated *in vacuo*, and the residue was dissolved in 25 ml of 10% potassium hydroxide solution and refluxed for 1 hr. The cooled solution was diluted to 400 ml and passed through a column (10 × 3.2 cm) of Dowex 2 formate ion-exchange resin. After the column was washed with 800 ml of water, the acid **1c** was eluted with 800 ml of 6 *N* formic acid. The solvent was removed *in vacuo* and the residual white powder was recrystallized from 95% ethanol to give colorless needles, mp 245–247°, 0.196 g (35.7%). *Anal.* Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.19; H, 4.56; N, 9.07. The ultraviolet spectrum showed $\lambda_{max}$ 251.5 mμ (ε 1.099 × $10^4$) in water, $\lambda_{max}$ 262.5 mμ (ε 1.288 × $10^4$) in 1 *N* NaOH, and $\lambda_{max}$ 241.5 mμ (ε 8.74 × $10^3$) in 1 *N* HCl.

**1-Methyl-1,4-dihydro-4-oxonicotinamide (1a).**—The acid **1c** (0.2 g) was converted to the amide by the procedure used to convert **4** to **5**. The residue obtained from the effluent of the Dowex 2 formate column was extracted twice with 100 ml of boiling acetone and two recrystallizations from acetone gave **1a** as colorless pillows, mp 183–184° (lit.[2,4] mp 181–182°, 179–181°), 0.092 g (43%). *Anal.* Calcd for $C_7H_8N_2O_2 \cdot 0.5H_2O$: C, 52.17; H, 5.63; N, 17.38. Found: C, 52.05; H, 5.80; N, 17.36. The ultraviolet spectrum[13] gave $\lambda_{max}$ (water) 257.5 mμ (lit.[2] 256 mμ) (ε 1.063 × $10^4$), 285 mμ (ε 4.36 × $10^3$); $\lambda_{max}$ (1 *N* NaOH) 258 mμ (ε 1.186 × $10^4$), 285 mμ (ε 4.98 × $10^3$); $\lambda_{max}$ (1 *N* HCl) 239.5 mμ (ε 7.48 × $10^3$). Elution of the column with 600 ml of 6 *N* formic acid recovered 0.02 g of **1c**.

**Registry No.**—**1a**, 769-49-3; **1c**, 10561-89-4; **2**, 10561-90-7; **3**, 10561-91-8; **4**, 3719-45-7; **5**, 701-44-0; 4-hydroxynicotinic acid, 609-70-1.

(6) F. W. Broekman and H. J. C. Tendeloo, *Rec. Trav. Chim.*, **81**, 107 (1962).

(7) F. W. Broekman, A. van Veldhuizen, and H. Janssen, *ibid.*, **81**, 792 (1962).

(8) All melting points were obtained with a Kofler micro hot stage apparatus. Elemental analyses were done by Huffman Microanalytical Laboratories, Wheatridge, Colo.

(9) C. Räth and F. Schiffmann, *Ann.*, **487**, 127 (1931).

(10) G. E. Lindenblad, M. Kaihara, and J. M. Price, *J. Biol. Chem.*, **219**, 893 (1956).

(11) H. Meyer, *Monatsh. Chem.*, **26**, 1311 (1905).

(12) W. E. Knox and W. I. Grossman, *J. Biol. Chem.*, **166**, 391 (1946).

(13) The ultraviolet spectra were identical with those reported in water, 0.1 *N* NaOH, and 1 *N* HCl.[4]

## Acid-Catalyzed Rearrangement of Cyclopropylphenylglycolic Acid[1a,b]

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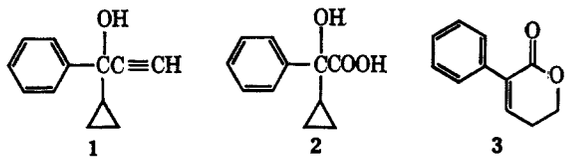
*Received January 25, 1967*

In the course of a study of the ozonolysis of 3-cyclopropyl-3-phenyl-1-propyn-3-ol (**1**) in attempts to prepare cyclopropylphenylglycolic acid (**2**), it was observed that when a method of isolation of product was employed in which sulfuric acid was added to the ozonolysis mixture, a compound was isolated which was neither the starting material **1** nor the anticipated glycolic acid **2**. A communication from this labora-

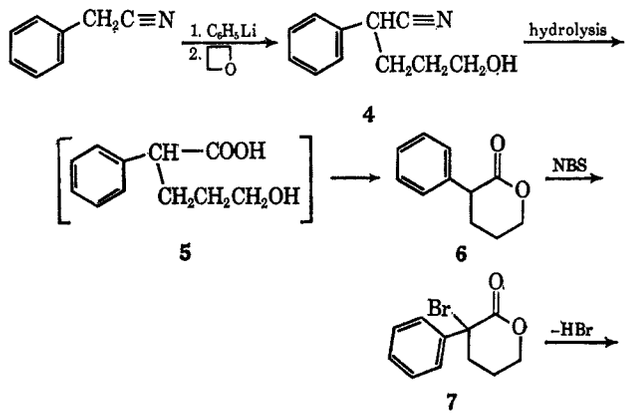
(1) (a) A preliminary report of this work appeared in *Tetrahedron Letters*, 423 (1966). (b) The investigation was supported in part by Grant MH-07775 from the National Institutes of Health. Abstracted in part from a portion of a thesis submitted by L. L. D. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, University of Iowa, 1966. (c) To whom all correspondence should be addressed.



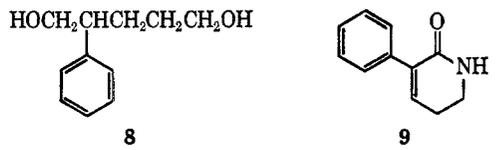
1 2 3

tory[2] proposed a structure for the anomalous product, but it was suggested by Roberts[3] that structure **3** is more consistent with the nmr data. This compound, 3-phenyl-5,6-dihydro-2-pyrone, was prepared according to Scheme I. The compound **4**, which was prepared by

SCHEME I



a modification of a method employed by Reinecke and Kray[4] in the pyridine series, could be converted to **6** by either acidic or alkaline hydrolysis. However, the product of the acid-catalyzed hydrolysis was always contaminated with unchanged nitrile which could not be removed by distillation. The hydroxy acid **5** could not be isolated by either procedure.[5] Treatment of **6** with N-bromosuccinimide gave 3-bromo-3-phenyltetrahydro-2-pyrone (**7**). Attempted distillation of **7** resulted in loss of hydrogen bromide and formation of **3**; however, careful recrystallization of **7** from ethanol permitted retention of the bromine atom. The bromo lactone **7** was best dehydrohalogenated by heating with pyridine. That **3**, the final product of Scheme I, is indeed the correct structure for the anomalous product reported previously was verified by comparison of infrared spectra, which were identical. Reduction of **3** and of the anomalous product with lithium aluminum hydride resulted in (±)-2-phenyl-1,5-pentanediol **8**, a known compound.



8 9

When cyclopropylphenylglycolic acid **2** was refluxed with aqueous sulfuric acid, **3** was formed in good yield. Cyclobutylphenylglycolic acid[6] was refluxed with aqueous sulfuric acid for a prolonged time; an essentially quantitative recovery of starting material resulted. Cyclopropylphenylglycine was refluxed with aqueous sulfuric acid; an almost quantitative amount of starting material was recovered. However, when a solution of cyclopropylphenylglycine in excess aqueous sulfuric acid was treated with sodium nitrite then permitted to stand for some time, a moderate yield of **3** was obtained. Cyclopropylphenylglycolic acid **2** was rearranged to **3** in benzene solution by use of boron trifluoride etherate. However, the yield of **3** was low and considerable intractable oily material was formed.

The inertness of cyclopropylphenylglycine toward aqueous sulfuric acid is taken as evidence that attack by the Lewis acid occurs at the alcoholic hydroxyl group of cyclopropylphenylglycolic acid, not on the cyclopropane ring.

It was speculated that treatment of cyclopropylphenylglycolamide with acid might lead to the pyridone system **9**. Treatment of cyclopropylphenylglycolamide with aqueous sulfuric acid led to a good yield of the 2-pyrone **3**. Reaction with boron trifluoride etherate in benzene resulted in a complex rearrangement which will be the subject of a future communication; **9** was apparently not produced. It is concluded that aqueous sulfuric acid hydrolyzes the amide link of cyclopropylphenylglycolamide more rapidly than it induces rearrangement. The cyclopropylphenylglycolic acid thus generated *in situ* is immediately converted into **3** by the sulfuric acid.

### Experimental Section[7]

**2-Phenyl-5-hydroxy-*n*-pentanenitrile** (**4**).—Bromobenzene (314 g, 2 moles) in 100 ml of anhydrous ether was added dropwise with stirring to 27 g (4 g-atoms) of lithium wire suspended in 2 l. of anhydrous ether. When all of the lithium had dissolved (approximately 2 hr), phenylacetonitrile (234 g, 2 moles) was added, with stirring, at a rate to maintain refluxing. The mixture was stirred for 1 hr after the phenylacetonitrile had been added, then trimethylene oxide (116 g, 2 moles, Aldrich Chemical Co.) in 200 ml of anhydrous ether was added over 1 hr to the ice-cooled reaction mixture. After refluxing for 16 hr, water was added, and the ether layer was extracted with water until the washings were neutral. The ether solution was dried ($MgSO_4$) and filtered, and the solvent was removed from the filtrate under reduced pressure. The residue distilled at 150° (0.7 mm) to yield 175 g (51%) of a colorless oil: $n^{25}D$ 1.5214; infrared absorption (film) at 2.86 (OH), 4.42 (C≡N), and 6.2 and 6.7 μ (phenyl); nmr peaks ($CDCl_3$) at δ 7.32 (5 H, singlet), 3.84 (2 H, triplet), 3.60 (1 H, triplet), 2.58 (1 H, singlet), and 1.84 (4 H, unresolved).

*Anal.* Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99; mol wt, 175. Found: C, 74.89; H, 7.45; N, 7.78; mol wt (cryoscopic in $CHCl_3$, Crobaugh Laboratories), 175.

**3-Phenyltetrahydro-2-pyrone** (**6**).—Sodium hydroxide (36 g, 0.9 mole) in 150 ml of distilled water was added slowly to 80 g (0.456 mole) of **4** with stirring, and the resulting mixture was refluxed for 20 hr. The cooled reaction mixture was extracted repeatedly with ether, and the aqueous solution was acidified with 50% $H_2SO_4$. A yellow oil separated, and the mixture was extracted repeatedly with ether. The combined ethereal extracts were dried ($MgSO_4$) and filtered, and the ether was removed from the filtrate under reduced pressure. The oily residue was distilled at 144° (0.35 mm) to yield 29 g (36%) of a viscous oil: $n^{25}D$ 1.5454; infrared absorption (film) at 5.85 (C=O) and 6.2 and 6.7 μ (phenyl); nmr peaks ($CDCl_3$) at δ 7.24 (5 H, singlet), 4.32 (2 H, triplet), 3.72 (1 H, triplet), and 2.00 (4 H, unresolved).

(2) J. G. Cannon and L. L. Darko, *J. Org. Chem.*, **29**, 3419 (1964).

(3) J. D. Roberts, personal communication. The authors acknowledge with thanks Professor Roberts' interest and assistance in the problem.

(4) M. G. Reinecke and L. R. Kray, *J. Org. Chem.*, **29**, 1736 (1964).

(5) It is inferred that the acid produced by L. Westman [*Arkiv Kemi*, **11**, 431 (1957)] by hydrolysis of the addition product of allylphenylacetic acid and HBr is not the same as our material.

(6) S. B. Kadin and J. G. Cannon, *J. Org. Chem.*, **27**, 240 (1962).

(7) All melting points are corrected and boiling points are uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Crobaugh Laboratories, Charlestown, W. Va. Infrared spectra were recorded on a Beckman IR5-A spectrophotometer. Nmr spectra were recorded on a Varian A-60 instrument using tetramethylsilane as the internal reference.

*Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.79; H, 6.91.

**3-Bromo-3-phenyltetrahydro-2-pyrone (7).**—Compound **6** (9.4 g, 0.0534 mole) in 25 ml of reagent grade $CCl_4$ was added to 9.5 g (0.0534 mole) of N-bromosuccinimide suspended in 25 ml of $CCl_4$. The mixture was heated to boiling on a steam bath and 0.1 g of freshly recrystallized benzoyl peroxide was added. The reaction mixture was refluxed for 2 hr, during which time the originally colorless solution turned reddish. The cooled mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The residual caramel-colored oil solidified on standing overnight at room temperature. Recrystallization from ethanol yielded 7.0 g (52%) of white needles: mp 85.5–86.5°; infrared absorption ($CHCl_3$) at 5.85 (C=O) and 6.2 and 6.7 $\mu$ (phenyl); nmr peaks ($CDCl_3$) at $\delta$ 7.4 (5 H, multiplet), 4.38 (2 H, multiplet), 2.72 (2 H, quartet), and 1.9 (2 H, unresolved).

*Anal.* Calcd for $C_{11}H_{11}BrO_2$: C, 51.78; H, 4.35; Br, 31.32. Found: C, 51.76; H, 4.35; Br, 31.06.

**3-Phenyl-5,6-dihydro-2-pyrone (3). Method A.**—A mixture of 1.0 g (0.0052 mole) of **2**[6] and 15 ml of 5% $H_2SO_4$ was refluxed for 3 hr, after which it was cooled and extracted with ether. This extract was dried ($Na_2SO_4$) and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual oil was dissolved in hot Skellysolve B and upon cooling, white crystals appeared: mp 98–100°; yield, 0.60 g (66%); infrared absorption ($CHCl_3$) at 5.83 (C=O) and 6.7 $\mu$ (phenyl); nmr absorption ($CDCl_3$) at $\delta$ 7.35 (5 H, singlet), 6.96 (1 H, triplet), 4.44 (2 H, triplet), and 2.60 (2 H, sextet).

*Anal.* Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; mol wt, 174. Found: C, 75.91; H, 6.04; mol wt, 175.[8]

**Method B.**—A mixture of 15 ml of sodium hydroxide dried pyridine, 5 ml of anhydrous ethanol, and 2.0 g (0.0078 mole) of **7** was refluxed for 12 hr. The solvents were removed from the deep brown solution under reduced pressure; the oily residue was dissolved in $CHCl_3$ and this solution was extracted with two 25-ml portions of water. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual, brown oil was taken up in hot Skellysolve B and upon cooling, 1.1 g (70%) of white crystals separated, mp 98–100°. The infrared spectrum ($CHCl_3$) was identical with that of the product of method A.

**Deamination of *dl*-Cyclopropylphenylglycine.**—To an ice-chilled solution of 10 g (0.052 mole) of *dl*-cyclopropylphenylglycine (Pierce Chemical Co., Rockford, Ill.) in 250 ml of 50% $H_2SO_4$ was added 6.9 g (0.1 mole) of $NaNO_2$ in 15 ml of water. The mixture was stirred in an ice bath for 42 hr, then 30 ml of 10% sulfamic acid solution was added to decompose the excess nitrite. The resulting mixture was diluted to a convenient volume with water and was extracted with four 50-ml portions of ether. The combined ethereal extracts were washed with 5% $Na_2CO_3$, then with water, dried ($Na_2SO_4$), and filtered, and the solvent was removed from the filtrate under reduced pressure. The yellow residue was taken up in hot Skellysolve B and on cooling, 3.5 g (38%) of white crystals appeared, mp 96–97°. An infrared spectrum ($CHCl_3$) of this material was superimposable upon a similar spectrum of an authentic sample of **3**.

**(±)-2-Phenyl-1,5-pentanediol (8).**—Compound **3** (25 g, 0.144 mole) in 100 ml of anhydrous ether was added slowly to 12 g (0.316 mole) of lithium aluminum hydride suspended in 200 ml of anhydrous ether. The resulting mixture was refluxed for 24 hr, water was added slowly to the ice-cooled solution, and the resulting mixture was poured over ice. Sulfuric acid (200 ml of 10%) was added; two layers separated, and the ether layer was washed with 5% $Na_2CO_3$ then with water, dried ($MgSO_4$), and filtered. The filtrate was evaporated under reduced pressure leaving a colorless oil which distilled at 144–145° (0.1 mm): yield, 15 g (57%) of a colorless oil [lit.[9] bp 150–155° (1.0 mm)]; infrared absorption (film) at 2.8 and 3.0 (OH) and 6.2 and 6.7 $\mu$ (phenyl).

*Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; O, 17.75. Found: C, 73.46; H, 8.98; O, 17.09.

A di(*p*-toluenesulfonate) of **8** was prepared according to the method of Kawazu and Fujita[9] and was recrystallized from methanol, mp 88–89° (lit.[9] mp 89–90.5°).

**Cyclopropylphenylglycolamide.**—A mixture of 5.4 g (0.026 mole) of methyl cyclopropylphenylglycolate[6] and 150 ml of liquid $NH_3$ was permitted to stand in a bomb at room temperature for 36 hr. The excess $NH_3$ was permitted to evaporate, leaving a tan, crystalline solid which was recrystallized several times from $CHCl_3$ (charcoal), to yield 1.0 g (20%) of a white, crystalline solid: mp 120–122°; infrared absorption ($CHCl_3$) at 2.93 and 3.0 (OH, NH) and at 6.0 $\mu$ (amide).

*Anal.* Calcd for $C_{11}H_{11}NO_3$: C, 69.1; H, 6.80; N, 7.33. Found: C, 68.78; H, 6.74; N, 7.24.

**Rearrangement of Cyclopropylphenylglycolic Acid (2) with Boron Trifluoride Etherate.**—A mixture of 1.0 g (0.052 mole) of **2**, 2 ml of boron trifluoride etherate (Eastman White Label), and 40 ml of sodium-dried benzene was refluxed for 3 hr and then was permitted to stand at room temperature for 24 hr. The reaction mixture was washed with six 25-ml portions of water, dried ($Na_2SO_4$), and filtered, and the solvent was removed from the filtrate under reduced pressure. The residual, deep amber oil was taken up in a minimum amount of hot ethanol and on cooling, crystalline material separated which was recrystallized from ethanol to yield rosettes of needles: mp 97–98.5°, yield 0.28 g (31%). The infrared spectrum ($CHCl_3$) of this material was identical with a similar spectrum of an authentic sample of **3**. The mother liquor from the first crystallization was diluted with water; an amber oil separated whose infrared spectrum ($CHCl_3$) showed a broad band between 3.2 and 3.6 $\mu$ and peaks at 5.7, 5.82, and 5.92 $\mu$. Column chromatographic treatment of this oil gave rise to no identifiable material.

**Treatment of Cyclopropylphenylglycolamide with Aqueous Sulfuric Acid.**—Cyclopropylphenylglycolamide (1.3 g, 0.0068 mole) was heated under reflux for 6 hr with 13 ml of 5% $H_2SO_4$. The cooled reaction mixture was extracted repeatedly with ether; the combined extracts were washed with water until the washings were neutral, then the ether was removed on a steam bath. An off-white solid remained which recrystallized from ethanol to yield 0.6 g of needles, mp 98–100°. From the mother liquor was isolated an additional 0.1 g of material, mp 98–100°. Total yield was 0.7 g (58%). A sodium fusion indicated the absence of nitrogen. An infrared spectrum ($CHCl_3$) was identical with a spectrum of an authentic sample of **3**.

**Registry No.**—**2**, 1460-46-4; **3**, 13019-35-7; **4**, 13019-36-8; **6**, 13019-37-9; **7**, 13019-38-0; **8**, 13019-39-1; cyclopropylphenylglycolamide, 13019-40-4.

(8) Mass spectroscopic determination was by Varian Associates, Palo Alto, Calif.

(9) K. Kawazu and T. Fujita, *J. Am. Chem. Soc.*, **81**, 932 (1959).

## The Synthesis of Pentacyclo[4.3.0.0$^{2,4}$.0$^{3,8}$.0$^{5,7}$]nonane[1]

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*Received December 27, 1966*

In the course of our investigations on the behavior of polycyclic carbonium ions, it became desirable to prepare the interesting and symmetrical hydrocarbon pentacyclo[4.3.0.0$^{2,4}$.0$^{3,8}$.0$^{5,7}$]nonane (**4c**). Our first thought was to build on the successful photoisomerization of *exo*-tricyclo[3.2.1.0$^{2,4}$]octene-6 (**1**) to tetracyclo[3.3.0.0$^{2,8}$.0$^{4,6}$]octane (**2**) which we have recently reported.[2] The addition of a methano bridge connecting C-3 and C-8 in structure **1** produces ring skeleton **3c** (deltacyclene),[3] and a photoisomerization of delta-

(1) This work was supported in part by the National Science Foundation, Grant GP-6228.

(2) P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Letters*, 3301 (1965). For similar photoisomerizations of the *anti*-3,6,7-tricarbomethoxy and *anti*-3,6,7-tricarboxylic acid derivatives of **1**, see H. Prinzbach, W. Eberbach, and G. von Veh, *Angew. Chem. Intern. Ed. Engl.*, **4**, 436 (1965).

(3) The name "deltacyclene" has been suggested for structure **3c** and "deltacyclane" for the related saturated tetracyclononane **5d** by A. Nickon and H. R. Kwasnik, private communication, and ref 4b.

(4) (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613 (1965); **87**, 1615 (1965); (b) H. R. Kwasnik, Ph.D. Thesis, Johns Hopkins University, 1966.