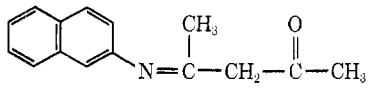


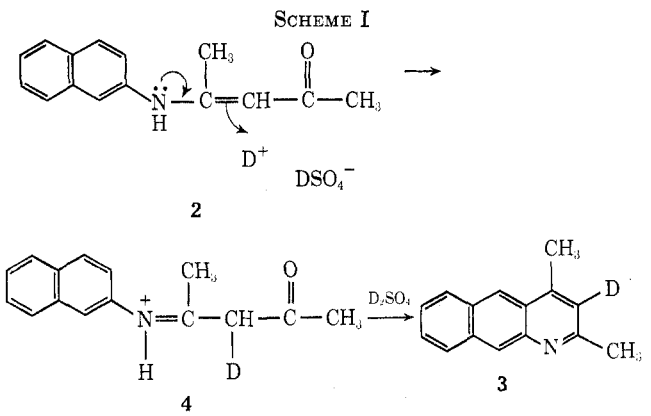
1

has proposed that the enamine **2** is protonated at the one position of the aromatic ring to block the formation of angular products.

The structure of the condensation product of acetylacetone and 2-aminonaphthalene is the enamine **2** as indicated by Huisgen's isolation of 2-acetylaminonaphthalene from the permanganate oxidation of **2**, the nmr spectra of **2**, and the comparison of the uv spectra of **2** with those of other known enamines of the same general structure. The treatment of **2** with D_2SO_4 produced 3-deuterio-2,4-dimethylbenzo[*g*]quinoline (**3**) which was identical except for the H_3 signal with a sample prepared with H_2SO_4. The assignment of the chemical shifts of protons H_3 (δ 6.94), H_5 (8.43), and H_{10} (8.60) is based on electron densities reported for benzo[*g*]quinoline[4,5] and the accepted assignment of chemical shifts in various quinolines.

The lack of incorporation of deuterium into the 10 position of **3** clearly indicates that Huisgen's proposed mechanism is not correct. The formation of **3** most likely proceeds by the mechanism shown in Scheme I. The protonation of **2** to give **4** lends credence to

SCHEME I



Johnson's rationalization of the formation of benzo[*g*]quinolines *via* the Combes reaction.

Experimental Section[6]

2-(2-Naphthyl)amino-2-penten-4-one (**2**).—2-Aminonaphthalene and acetylacetone were condensed as described by Johnson:[1] mp 99° (lit. mp 99°); nmr δ ($CDCl_3$) 2.04 (s, 6 H), 5.1 (s, 1 H), 7.45 (m, 7 H), 12.7 (b s, 1 H); $\lambda_{max}^{i\text{-PrOH}}$ 337 nm (ε 23,000).

2,4-Dimethylbenzo[*g*]quinoline.—The enamine **2** was treated with H_2SO_4 as described by Johnson:[1] mp 92° (lit. mp 93°); nmr δ ($CDCl_3$) 2.62 (s, 3 H), 2.67 (s, 3 H), 6.94 (s, 1 H), 7.43 (m, 2 H), 7.95 (m, 2 H), 8.31 (s, 1 H), 8.56 (s, 1 H).

3-Deuterio-2,4-dimethylbenzo[*g*]quinoline (**3**).—**2** (1 g, 0.044 mol) was treated with 3 g of D_2SO_4 as described by Johnson.[1] The crude material was dried and chromatographed on Brinkman silica gel, eluting with $CHCl_3$. The material so obtained was recrystallized from petroleum ether to give 52% **3**: mp 92° (lit. mp 93°); nmr δ ($CDCl_3$) 2.58 (s, 3 H), 2.65 (s, 3 H), 7.44 (m, 2 H), 7.96 (m, 2 H), 8.31 (s, 1 H), 8.56 (s, 1 H).

Registry No.—**3**, 35666-88-7.

(4) M. J. S. Dewar and G. J. Glecher, *J. Chem. Phys.*, **44**, 759 (1966).
(5) K. Nishimoto and L. S. Foster, *Theor. Chim. Acta*, **4**, 155 (1966).
(6) Melting points were taken with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Nmr spectra were obtained with a Perkin-Elmer R-12A spectrometer and are reported relative to TMS. Uv spectra were recorded using a Perkin-Elmer-Coleman 124 spectrophotometer.

The Synthesis of Azetidine-3-carboxylic Acid[1,2]

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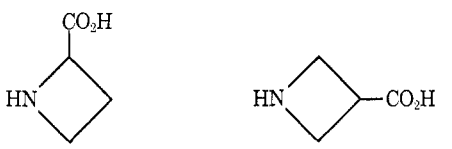
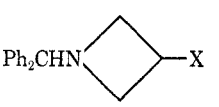
Received June 8, 1972

L-Azetidine-2-carboxylic acid (**1**) occurs in nature.[3] It has been shown to inhibit the growth of *E. coli* cultures and various seedlings[4] and to cause abnormalities in growing embryos.[5] The X-ray structure showed the ring to be 11° out of plane and it was postulated that the incorporation of **1** in a polypeptide chain could cause the direction of successive amide bonds in the α helix of the peptide tertiary structure to change by 16°.[6] As an extension of studies on azetidines,[7] it was therefore of interest to synthesize the isomeric azetidine-3-carboxylic acid (**2**).



1 **2**

Chatterjee and Triggle[8] had reported the preparation of the hydrochloride of 1-benzhydrylazetidin-3-ol (**3**) from epichlorohydrin and benzhydrylamine, but gave no experimental details or yields. Application of the procedure described by Gaertner[9] to this reaction gave 60-65% yields of the salt of **3**. Tosylation of **3** gave only 39% of the corresponding ester **4**, and reaction with



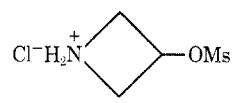
3, X = OH
4, X = OTs
5, X = OMs
6, X = OMe
7, X = OEt
8, X = Br
9, X =
10, X = CN
11, X = CO_2H
12, X = CH_2NH_2

(1) Presented in part at the 25th Annual Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 1970, Organic Chemistry Abstracts, No. 131, 1970, p 74.
(2) From the Ph.D. thesis of Roger Lok, University of Washington, 1971. Supported in part by the Graduate Research Fund, University of Washington.
(3) L. Fowden, *Biochem. J.*, **64**, 323 (1956); L. Fowden, *Advan. Enzymol.*, **29**, 89 (1967).
(4) L. Fowden and M. H. Richard, *Biochem. Biophys. Acta*, **71**, 459 (1963); E. J. Hewitt and B. A. Notton, *Phytochemistry*, **6**, 1329 (1967).
(5) D. J. Cummings, V. A. Chapman, S. S. Delong, and L. Mondale, *J. Virol.*, **1**, 193 (1967).
(6) H. M. Berman, E. L. McCandy, J. W. Burgner, II, and R. L. Van Etten, *J. Amer. Chem. Soc.*, **91**, 6177 (1969).
(7) A. G. Anderson, Jr., and M. T. Wills, *J. Org. Chem.*, **33**, 3046 (1968), and references cited therein.
(8) S. S. Chatterjee and D. J. Triggle, *Chem. Commun.*, 93 (1968).
(9) V. R. Gaertner, *Tetrahedron Lett.*, 4691 (1966).

chlorosulfonic acid afforded only a moderate yield (50%) of impure sulfate ester, but the mesylate derivative **5** formed in high yield.

It was noted that loss of material occurred when **4** was recrystallized from hot methanol, and the supposition that this was due to alcoholysis was confirmed when heating **4** and methanol under reflux gave 51% of the methyl ether **6**. Analogously, treatment of **5** with ethanol or sodium bromide formed **7** (37%) and **8** (85%), respectively. It was envisioned that carboxylation of the Grignard reagent of **8** followed by hydrogenolysis of the benzhydryl group would give **2**, but the Grignard reaction gave a low yield of dimeric product **9** and unchanged **8**. Reaction of **5** with sodium cyanide afforded 75% of the nitrile **10** and hydrolysis of this gave the carboxylic acid **11** in 75–86% yield.

It remained to remove the benzhydryl group by hydrogenolysis. An attempt to effect this operation at an earlier stage (on the hydrochloride of **5**) using 5% Pd/C in methanol gave unchanged starting material. Pearlman[10] has reported the debenzylation of amines catalyzed by palladium hydroxide on carbon, and this method gave **13** in nearly quantitative yield.[11] Application of this procedure to **11** gave **2** in essentially



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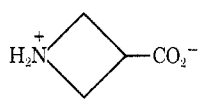

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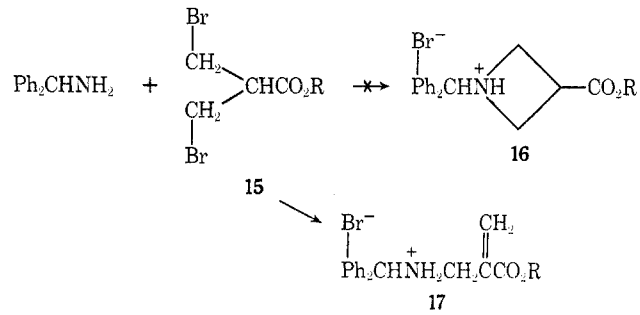
quantitative yield. It was found, in contrast, that under these conditions the hydrochloride of **10** underwent selective reduction of the cyano group to give a low yield of a product identified by its pmr and mass spectra as **12**. Subsequently **12** was also obtained from the lithium aluminum hydride reduction of **10**.

The pK_a values of **2** (3.2 ± 0.1 and 10.3 ± 0.1) were similar to those of β-proline. An X-ray structural analysis of crystalline **2** showed it to exist as the dipolar ion **14** and that the ring was puckered by less than 1°.[12] This new amino acid is undergoing testing for biological activity.

An alternative route to **2** was investigated based on the finding by Cromwell and coworkers[13] that treatment of 1-*tert*-butylamino-2-benzoyl-3-bromo-3-phenylpropane with *tert*-butylamine effected cyclization to the azetidine. In the proposed sequence benzhydrylamine would participate in a double displacement on the dibromo ester **15** to form **16**. Esters with the structure of **15** having R = ethyl and benzyl were prepared from the corresponding acid,[14] but reaction of these with benzhydrylamine gave only monodisplacement, monoelimination products (**17**).



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17

Experimental Section

All pmr spectra were recorded on Varian A-60 or T-60 spectrometers and are reported in parts per million (τ) relative to internal TMS. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer. Mass spectra were recorded on an Associated Electrical Industries MS-9 spectrometer with the assistance of George Tsou, Peter Wade, and William Howald and with perfluorotributylamine (70 eV) as the reference standard. pK_a values were determined with an automatic titrator Radiometer, type TTTlc. Melting points and boiling points are uncorrected. Elemental analyses were performed by Dr. A. Bernhardt, Elbach über Engelskirchen, Germany, and Chemalytics, Inc., Temple, Ariz. Organic solutions were dried over $MgSO_4$. Solvents were reagent grade. THF and ether were dried by distillation from $LiAlH_4$. Pyridine was distilled from BaO. Pentane was distilled from concentrated sulfuric acid. DMF was distilled from BaO. Hydrochloride salts of amines were prepared by passing dry HCl into an ethereal solution of the amine.

1-Benzhydrylazetidin-3-ol (3).—A mixture of 46.3 g (0.5 mol) of epichlorohydrin, 91.6 g (0.5 mol) of benzhydrylamine, and 200 ml of methanol was allowed to stand protected from light for 3 days and then refluxed for 3 days.[9] The methanol was removed (reduced pressure) and the residue was washed with acetone. The residue from the washes was refluxed with methanol and the solvent was then removed. The combined solids (85–90 g) were partitioned between ether and 6 *N* NaOH and removal of the solvent from the dried ethereal solution gave 75 g (61%) of **3** as a colorless solid, mp 107–110°. A sample sublimed at 80° (1 mm) had mp 113° (lit.[8] mp 115°); ir ($CHCl_3$) 3640 cm^{-1} (OH); pmr ($CDCl_3$) τ 7.13 (t, 2, J = 7 Hz, CHNCH), 6.55 (t, 2, J = 7 Hz, CHNCH), 6.02 (s, 1, OH), 5.7 (s, 1, Ph_2CH), 5.66 (m, 1, CHOH), and 2.75 (m, 10, ArH).

Anal. Calcd for $C_{16}H_{17}NO$: C, 80.31; H, 7.16; N, 5.85. Found: C, 80.50; N, 7.03; N, 6.02.

1-Benzhydryl-3-*p*-toluenesulfonatoazetidine (4).—To 2.51 g (10.5 mmol) of **3** in 15 ml of dry pyridine was added 2 g (10.5 mmol) of *p*-toluenesulfonyl chloride at −10° with stirring. The mixture was kept cold for 1.5 hr and then poured into an ice–water mixture. The oil which formed was separated. It solidified on standing (refrigerator) and amounted to 1.6 g (39%) of **4**, mp 101–104°. Extraction of the pyridine solution (saturated with K_2CO_3) with ether gave 1 g of unchanged **3**. A sample of **4** after recrystallization from methanol had mp 106–107°; ir ($CHCl_3$) 1360 cm^{-1} (SO); pmr (CCl_4) τ 7.74 (s, 3, $ArCH_3$), 7.02 (t, 2, J = 7 Hz, CHNCH), 6.65 (t, 2, J = 7 Hz,CHNCH), 5.75 (s, 1, Ph_2CH), 5.21 (p, 1, J = 6 Hz, CHOTs), and 2.35–2.81 (m, 14, ArH).

Anal. Calcd for $C_{23}H_{23}NO_3S$: C, 70.21; H, 5.85; N, 3.56; S, 8.14. Found: C, 70.06; H, 5.82; N, 3.37; S, 8.21.

1-Benzhydryl-3-methanesulfonatoazetidine (5).—To a solution of 71.7 g (0.3 mol) of **3** in 600 ml of anhydrous pyridine maintained at −20° was added slowly with stirring 51.75 g (0.45 mol) of methanesulfonyl chloride. Stirring was continued for 1 hr and the mixture, protected from moisture, was allowed to stand in a refrigerator overnight. The mixture was then poured into ice and H_2O. The collected, dried precipitate of crude **5** amounted to 104.3 g (110%),[15] mp 100–110°. A sample purified by extraction with *n*-pentane (Soxhlet) was obtained as colorless crystals: mp 113–114°; ir (CS_2) 1360 and 1180 cm^{-1} (SO); pmr ($DCCl_3$) τ 7.23 (s, 3, SCH_3), 6.45 (t, 2, J = 7.5 Hz, CHNCH), 6.88 (t, 2, J = 7.5 Hz, CHNCH), 5.63 (s, 1, Ph_2CH), 4.97 (p, 1, J = 6 Hz, CHOMs), and 2.69 (m, 10, ArH).

Anal. Calcd for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.43; S, 10.1. Found: C, 64.19; H, 5.82; N, 4.60; S, 9.97.

1-Benzhydryl-3-methoxyazetidine (6).—A mixture of 0.317 g (0.76 mmol) of **4**, 2 ml of anhydrous methanol, and 0.2 g of anhydrous sodium carbonate was refluxed for 4 hr and then filtered. The residue from the filtrate was partitioned between

(10) W. M. Pearlman, *Tetrahedron Lett.*, 1663 (1967).

(11) N. H. Cromwell and R. M. Rodebaugh, *J. Heterocycl. Chem.*, **6**, 435 (1969), had found this catalyst to be superior to the usual Pd/C for an analogous reaction in the synthesis of azetidine-2-carboxylic acid.

(12) Performed by S. Smith. The details will be published separately.

(13) N. H. Cromwell, J. L. Imbach, E. Doomes, and R. P. Rebman, *J. Org. Chem.*, **32**, 78 (1967).

(14) A. F. Ferris, *ibid.*, **20**, 780 (1955).

(15) Yields of crude **5** ranged from 90 to *ca.* 100% for eight runs.

$HCCl_3$ and aqueous sodium carbonate. The residue of crude **6**, mp 50–53°, obtained from the separated, dried organic layer amounted to 0.1 g (51%). A sample purified by sublimation at 50° (0.05 mm) had mp 55–57°; pmr (CCl_4) 7.2 (t, 2, J = 6.5 Hz, CHNCH), 6.9 (s, 3, OCH_3), 6.58 (t, 2, J = 6.5 Hz, CHNCH), 6.1 (p, 1, J = 6 Hz, CHOMe), and 2.77 (m, 10, ArH).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.56; N, 5.53. Found: C, 80.47; H, 7.69; N, 5.39.

1-Benzhydryl-3-ethoxyazetidine (**7**).—From 0.317 g (1 mmol) of **5**, 2 ml of absolute methanol, and 0.2 g of anhydrous sodium carbonate treated as described for the preparation of **6** was obtained 0.1 g (37%) of **7**, mp 65–67°, after sublimation of the crude product at 60° (1 mm): pmr (CCl_4) 8.93 (t, 3, J = 7.5 Hz, CH_2CH_3), 7.22 (t, 2, J = 7 Hz, CHNCH), 6.73 (q, 2, J = 7.5 Hz, CH_2CH_3), 6.58 (t, 2, J = 7 Hz, CHNCH), 6.0 (p, 1, J = 6 Hz, CHOEt), 5.73 (s, 1, Ph_2CH), and 2.75 (m, 10, ArH); molecular ion at m/e 267.259 (calcd for $C_{11}H_{21}NO$: 267.1623).

1-Benzhydryl-3-bromoazetidine (**8**).—1-Benzhydryl-3-methanesulfonatoazetidine (**5**) (12.7 g, 40 mmol) was added to a solution of 6.2 g (60 mmol) of NaBr in 80 ml of diethylene glycol. The mixture was heated at 60–65° for 2.5 hr, cooled to room temperature, and extracted with CCl_4. Removal of the solvent from the combined washed (H_2O) and dried extracts left 10.3 g (85%) of **8**, mp 95–99°. A sample recrystallized from ethanol had mp 101–102°; pmr (CCl_4) 6.65 (t, 2, J = 7 Hz, CHNCH), 6.31 (t, 2, J = 7 Hz, CHNCH), 5.65 (m, 1, CHBr), 5.61 (s, 1, Ph_2CH), and 2.67 (10, m, ArH).

Anal. Calcd for $C_{16}H_{16}NBr$: C, 63.59; H, 5.34; Br, 26.44; N, 4.65. Found: C, 63.71; H, 5.47; Br, 26.43; N, 4.77.

3,3′-Bis-1-benzhydrylazetidine (**9**).—A solution of 3.02 g (10 mmol) of **8** in 30 ml of dry ether was stirred under reflux with 0.243 g (10 g-atoms) of Mg turnings until the Mg disappeared (10 hr). Stirring was continued while gaseous CO_2 was passed over the solution for 2 hr. The mixture was poured onto crushed, solid CO_2 and the whole was extracted with H_2O. No precipitate formed when the separated aqueous phase was brought to pH 5 with 6 N hydrochloric acid. Removal of the solvent from the dried ether layer and chromatography [tlc on silica gel with 4:1 petroleum ether (bp 30–60°)–ether] of the residue gave unchanged **8** (R_f 0.9) and a small amount of **9** (R_f 0.75): mp 176°; pmr ($CDCl_3$) τ 7.28 (m, 6, 2 CHNCHCH), 6.84 (m, 4, 2 CHNCH), 5.76 (s, 2, 2 Ph_2CH), and 2.73 (m, 20, 2 ArH); molecular ion at m/e 444.257 (calcd 444.2565).

Anal. Calcd for $C_{32}H_{32}N_2$: C, 86.44; H, 7.26; N, 6.30. Found: C, 86.26; H, 7.38; N, 6.34.

1-Benzhydryl-3-cyanoazetidine (**10**).—To a solution of 95.1 g (0.3 mol) of **5** in 600 ml of DMF was added a solution of 44.1 g (0.9 mol) of NaCN in 75 ml of H_2O. The mixture was heated at 65° with stirring for 24 hr, cooled, and poured into an ice–water mixture. The precipitate was collected and dissolved in 400 ml of dichloromethane. Filtration of the dried organic solution through tlc grade silica gel removed colored impurities. Evaporation of the solvent gave 55.3 g (75%) of **10**: mp 152–153°; ir ($HCCl_3$) 2260 cm^{-1} (C≡N); pmr (CCl_4) τ 6.75 (m, 5, CH_2-$CHCH_2$), 5.7 (s, 1, Ph_2CH), and 2.7 (m, 10, ArH).

Anal. Calcd for $C_{17}H_{16}N_2$: C, 82.23; H, 6.45; N, 11.25. Found: C, 82.16; H, 6.41; N, 11.45.

1-Benzhydrylazetidine-3-carboxylic Acid (**11**).—Solutions of 9.9 g (40 mmol) of **10** in 100 ml of monoethoxyethanol and 8.08 g (144 mmol) of KOH in 6 ml of H_2O were combined and heated at 90–95° for 24 hr, at which time NH_3 evolution had ceased. The cooled solution was poured into an ice–water mixture and the whole was acidified (*ca.* pH 5) with 6 N hydrochloric acid. The precipitate after collection and drying amounted to 9.2 g (86%) of **11**, mp 180–190°. A sample after sublimation at 80° (10^{-3} mm) had mp 198°; ir (KBr) 1670 and 1370 cm^{-1} (C=O); pmr (DMSO-d_6) τ 6.7 (m, 5, CH_2CHCH_2), 5.54 (s, 1, Ph_2CH), 4.2 (broad s, 1, ^+NH), and 2.64 (m, 10, ArH).

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.37; H, 6.36; N, 5.24. Found: C, 76.34; H, 6.56; N, 5.36.

Reduction of 1-Benzhydryl-3-cyanoazetidine (**10**). **A. Catalytic.**—A mixture of the hydrochloride of **10** (2.85 g, 10 mmol) dissolved in 200 ml of dry methanol and 0.32 g of $Pd(OH)_2 \cdot C^{10}$ was treated with H_2 at room temperature and *ca.* 60 psi until about 0.01 mol of H_2 was taken up. The mixture was filtered, the solvent was evaporated from the filtrate, and the residue was extracted with dry THF. Examination (pmr, tlc) of the residue (1.5 g) from the THF extract indicated it to contain **10** plus a small amount of diphenylmethane. The insoluble residue (1.5 g) was partitioned between 6 N NaOH and $HCCl_3$. The spectra of the solid obtained from the dried organic layer indicated it to be impure **12**: ir ($CHCl_3$) 3300 cm^{-1} (NH); pmr ($CDCl_3$) τ 8.83 (s, 2, NH_2), 7.58 (m, 1, $CHCH_2N$), 7.23 [m, 4, $(CH)_2CCH_2N$], 6.8 (t, 3, J = 7 Hz, CHCCH), 5.77 (s, 1, Ph_2CH), 2.77 (m, 10, ArH); pmr [$CDCl_3$, *ca.* 0.05 M Eu(fod)$_3$][16] 7.03 (m, 1, $CHCH_2N$), 6.8 (t, 2, J = 7 Hz, CHCCH), 6.5 (t, 2, J = 7 Hz, CHCCH), 6.13 (d, 2, J = 7 Hz, $CHCH_2N$), 5.57 (s, 1, Ph_2CH), 4.37 (s, 2, NH_2), and 2.67 (m, 10, ArH); molecular ion at m/e 251.158 [calcd for $C_{17}H_{19}N_2$ (M − 1), 251.1548].

B. With Lithium Aluminum Hydride.—A solution of 2.48 g (10 mmol) of **10** in 30 ml of dry THF was added slowly to a suspension of 1.4 g (35 mmol) of lithium aluminum hydride in 10 ml of dry THF and the mixture was stirred overnight and then refluxed for 3 hr. Excess hydride reagent was hydrolyzed by the careful addition, with cooling, of saturated aqueous ammonium chloride, the gelatinous mixture was filtered and the filter cake was washed repeatedly with THF. Evaporation of the solvent from the combined, washed (saturated aqueous NaCl), and dried filtrates left a viscous, yellow oil which gave, after molecular distillation (*ca.* 0.01 mm), 1.79 g (72%) of material identical (ir, pmr and tlc) with the product from A.

3-Methanesulfonatoazetidinium Chloride (**13**).—A solution of the hydrochloride salt (3.54 g, 10 mmol) of the mesylate derivative **5** in 75 ml of absolute methanol was treated with H_2 in the presence of 0.32 g of $Pd(OH)_2 \cdot C^{10}$ at 50 psi until H_2 uptake ceased (1 hr). The mixture was filtered, the solvent was evaporated from the filtrate, and the solid residue was extracted with benzene. From the benzene extract was obtained 1.69 g of diphenylmethane. The residual solid was washed with dichloromethane and then amounted to 1.94 g (104%) of impure **13**, mp 99–101°. A sample after recrystallization from absolute ethanol had mp 104–105°; pmr (D_2O) τ 7.20 (s, 3, SCH_3), 5.97 (m, 6, H_2O, H_2CNCH_2), 4.97 (p, 1, J = 6 Hz, CHOMs).

Anal. Calcd for $C_4H_{10}NO_3ClS$: 3, 25.61; H, 5.34; Cl, 18.95; N, 7.46; S, 17.07. Found: C, 25.43; H, 5.43; Cl, 18.80; N, 7.60; S, 16.98.

Azetidine-3-carboxylic Acid (**2**).—A solution of 1 g (3.74 mmol) of the N-benzhydryl acid **11** in 200 ml of absolute methanol was treated with H_2 for 2 hr as described for the preparation of **13**. The initial solid residue was washed with ether and then amounted to 0.37 g (99%) of **2**. Paper (Whatman No. 3) chromatography (12:3:5 butanol–acetic acid–H_2O) gave a spot at R_f 0.32[17] which became purple when sprayed with ninhydrin. The material gave an intense blue color with Feigl's test for imino compounds. Electrophoresis showed migration toward the positive electrode. A sample recrystallized from 90% ethanol had mp 230–275° dec: ir (KBr) 2700–2400 ($^+NH_2$), 1620–1550, and 1400 cm^{-1} (CO_2^-); pmr (H_2O) τ 6.47 (m, 1, CH_2CHCH_2), 5.87 (d, 4, J = 7 Hz, CH_2CCH_2), and 5.3 (s, 2, H_2O); mass spectrum m/e 101.0477 (calcd 101.0477); pK_a^1 = 3.2 ± 0.1 and pK_a^2 = 10.3 ± 0.1.

Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.93; N, 13.87. Found: C, 47.41; H, 6.94; N, 13.85.

Registry No.—**2**, 36476-78-5; **3**, 18621-17-5; **4**, 36476-80-9; **5**, 33301-41-6; **6**, 36476-82-1; **7**, 36476-83-2; **8**, 36476-84-3; **9**, 36476-85-4; **10**, 36476-86-5; **11**, 36476-87-6; **12**, 36476-88-7; **13**, 36476-89-8.

(16) Norell Chemical Co., Inc.

(17) The R_f values for proline and azetidine-2-carboxylic acid are 0.39 and 0.35, respectively, under these conditions.

Synthesis of 2-Benzazepine-1,3-diones and Corresponding 4,5-Dihydro Compounds

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Received June 9, 1972

Earlier we reported on the PPA closure of α′-cyano-*trans*-stilbene-*o*-carboxylic acids and *o*-(2-cyano-2-phenylethyl)benzoic acids to 4-aryl-2-benzazepine-1,3-di-