Anal. Calcd. for $C_{19}H_{22}INO$: C, 46.57; H, 6.62; N, 4.18. Found: C, 46.70; H, 6.54; N, 4.43.

As described above for preparation of derivative V, a sample of the distilled mixture of amines IIe and IIIe, which had been shown to contain a considerable amount of a third isomer, was treated with methyl iodide and the resulting oil treated with picric acid. This treatment afforded a mixture of two types of crystals, which were separated mechanically. One type of crystals was recrystallized five times from 95% ethanol to give 5-fluoro-2-methylbenzyldimethylethylammonium picrate (VIIe), m.p. 134–135°.

Anal. Calcd. for $C_{18}H_{21}FN_4O_7$: C, 50.94; H, 4.99; N, 13.20. Found: C, 50.75; H, 4.87; N, 13.26.

The second type of crystals from this separation was assumed to be the picrate of the methiodide of the unidentified rearrangement product isomer. After two recrystallizations from 95% ethanol, it melted at 195.5–197°.

Anal. Calcd. for $C_{18}H_{21}FN_4O_7$: C, 50.94; H, 4.99; N, 13.20. Found: C, 50.81; H, 5.21; N, 13.27.

Independent Synthesis of Derivatives V, VIId, and VIIe.—Ortho substitution rearrangement of 2-methoxybenzyltrimethylammonium iodide as described[4] gave 3-methoxy-2-methylbenzyldimethylamine (VI), b.p. 78–80° at 0.7 mm., reported b.p. 111–113° at 9.5 mm.[4] This amine was treated overnight with excess ethyl iodide. The resulting oil was triturated with ether and treated with ethanolic picric acid to give quaternary picrate V which, after six recrystallizations from 95% ethanol, melted at 115.5–118°. A mixture of this material and the sample of picrate V obtained as described above melted at 117–119°. The infrared spectra of the two samples were superimposable.

Ortho substitution rearrangement of 4-methoxybenzyltrimethylammonium bromide as described[4] gave 5-methoxy-2-methylbenzyldimethylamine, b.p. 77–78.5° at 0.65 mm., reported b.p. 106–108.5° at 7.3 mm.[4] Treatment overnight with ethyl iodide afforded derivative VIId. After two recrystallizations from a mixture of acetonitrile and anhydrous ether, this material melted at 165–165.5°, undepressed on admixture with derivative VIId obtained as described above.

Ortho substitution rearrangement of 4-fluorobenzyltrimethylammonium chloride as described[5] gave 5-fluoro-2-methylbenzyldimethylamine (VIIIe), b.p. 77–78° at 6.2 mm., reported b.p. 57–60° at 3–4 mm.[5] Vapor phase chromatography of this amine on several columns gave no evidence of any isomeric impurity. This amine was treated overnight with ethyl iodide and the resulting oil treated with ethanolic picric acid. This treatment afforded quaternary picrate VIIe which, after three recrystallizations from 95% ethanol, melted at 134.5–135°, undepressed on admixture with derivative VIIe obtained as described above

Norsteroids. IV. The Benzilic Acid Rearrangement of 3-Hydroxy-5α-cholest-3-en-2-one and 2-Hydroxy-5α-cholest-1-en-3-one[1]

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Treatment of 3-hydroxy-5α-cholest-3-en-2-one or of 2-hydroxy-5α-cholest-1-en-3-one with potassium hydroxide in *n*-propyl alcohol gives a single benzilic acid rearrangement product, A-nor-5α-cholestan-2-ol-2-carboxylic acid. This product indicates a common intermediate for the rearrangement of the isomeric diosphenols. Further transformations of the hydroxy acid are described.

Of the various ring contraction methods available for the preparation of ring-norsteroids, the benzilic acid rearrangement of diosphenols is particularly useful because of its stereospecificity. Thus, the 2,3-diosphenol derived from bismethylenedioxyprednisone rearranged to a single A-nor-2-hydroxy-2-carboxylic acid, which was then converted to A-norcortisone.[2]

Similarly, treatment of 2-bromolanosta-1,8-diene-3-one with alcoholic potassium hydroxide presumably led to the corresponding diosphenol (which was not isolated) which then rearranged to give a single ring contraction product, A-norlanost-8-en-2-ol-2-carboxylic acid.[3] The reaction of 2,2-dibromocholestan-3-one with aqueous or alcoholic alkali also probably proceeded through the diosphenol (spectroscopic evidence was obtained for its presence) to give A-norcholestan-2-ol-2-carboxylic acid, which was not characterized but was directly cleaved with lead tetraacetate to A-norcholestan-2-one.[4]

The rearrangement of 2,2-dibrom-4,4-dimethylcholestan-3-one and of 2,2-dibrom-3-oxotrinordammara-24:20 ξ_2-olide to the corresponding A-nor-2-hydroxy-2-carboxylic acids has also been reported.[5] In all of the above examples of the rearrangement only a single hydroxy carboxylic acid was isolated, and no evidence was given for the presence of isomers.

The work reported here describes a study of the rearrangement of the isomeric diosphenols, 3-hydroxy-5α-cholest-3-en-2-one (I), Diosphenol A, and 2-hydroxy-5α-cholest-1-en-3-one (II), Diosphenol B. These diosphenols had previously been prepared and characterized by several groups.[6] This work[6] also established the fact that the two diosphenols and the diketone were interconvertible in the presence of acid or base,

(1) Grateful acknowledgment is made to the National Science Foundation for grant NSF-G5926, which financed this study.

(2) R. Hirschmann, G. A. Bailey, R. Walker, and J. M. Chemerda, *J. Am. Chem. Soc.*, **81**, 2822 (1959).

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(4) T. Rull and G. Ourisson, *Bull. soc. chim. France*, 1573 (1958).

(5) R. Hanna, C. Sandris, and G. Ourisson, *ibid.*, 1454 (1959).

(6) (a) E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, 353 (1938); (b) L. Ruzicka, Pl. A. Plattner, and M. Furrer, *Helv. Chim. Acta*, **27**, 524 (1944); (c) J. C. Sheehan and W. F. Erman, *J. Am. Chem. Soc.*, **79**, 6050 (1957).

and it was therefore of interest to determine the product of the rearrangement from each diosphenol.

When Diosphenol A (I) was treated with a hot solution of potassium hydroxide in aqueous *n*-propyl alcohol, rearrangement proceeded readily to give A-nor-5α-cholestan-2-ol-2-carboxylic acid (IV, R = H) in yields of 92–99.6% (Fig. 1). In order to establish that only a single product was formed, the crude hydroxy acid was chromatographed on a silica gel–Supercel mixture and eleven fractions were collected. Each fraction was crystalline and none of them depressed the melting point of a constant melting analytically pure sample of the hydroxy acid. While it is conceivable that no separation of diastereomers was achieved by this treatment, it appears unlikely in view of the number of identical fractions eluted and of the melting point behavior of the various fractions and of the crude material on recrystallization.

Rearrangement of Diosphenol B (II) under the same conditions gave the same hydroxy acid (IV, R = H) in quantitative yield. The fact that both diosphenols gave the same rearrangement product provides evidence that the rearrangement proceeds *via* an intermediate common to both diosphenols. This is plausible in view of the fact that the two diosphenols and the α-diketone are interconvertible, especially in basic solution.[6a] On the basis of the studies by Georgian and Kundu[7] and Wendler, Taub, and Graber[8] it appears that the rearrangement proceeds through the conformationally more stable hydroxide addition intermediate. Four hydroxide addition intermediates, I, II, III, and IV, (Fig. 2) are possible for the 2,3-diketone, and of these III should be the most stable, since repulsion forces due to both 1,3-diaxial interactions and oxygen–oxygen dipoles are minimized. This intermediate would then give rise to 2β-hydroxy-2α-carboxy-A-nor-5α-cholestane. No direct evidence is available at present to support this configurational assignment.

Therefore, it appears that when isomeric diosphenols are subjected to the conditions of the benzilic acid rearrangement, only one product, arising from the conformationally most stable hydroxide intermediate, will be obtained, unless, of course, there is little difference in stability between the various possible intermediates.

Treatment of the hydroxy acid IV (R = H) with lead tetraacetate resulted in cleavage to A-norcholestan-2-one (V) in high yield (97%), thus establishing the position of the hydroxyl and carboxyl groups in the hydroxy acid.[8b] The hydroxy acid IV (R = H) was converted to the methyl ester by treatment with either diazomethane or

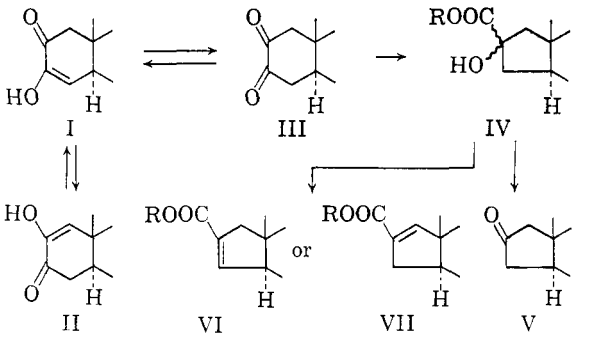

Fig. 1—Benzilic acid rearrangement of isomeric diosphenols

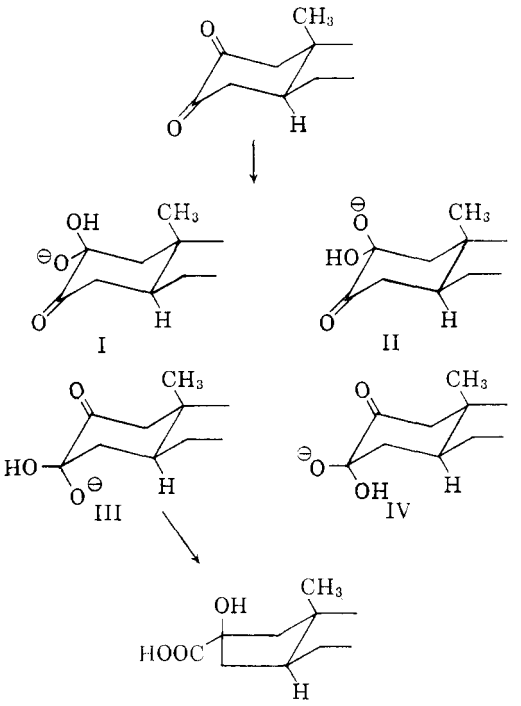

Fig. 2.—Possible intermediates in the benzilic acid rearrangement.

methanolic hydrogen chloride, and the ester was readily hydrolyzed back to the acid in alkaline solution.

Pyrolysis of the hydroxy acid IV (R = H) at 265° resulted in dehydration to an α,β-unsaturated acid (58%), either VI or VII, which was converted to the methyl ester with diazomethane. The same unsaturated acid was also obtained (44% yield) by treatment with phosphorus pentoxide in boiling decalin.

The position of the double bond is assigned to the 1-position (VII, R = H) on the basis of two independent lines of evidence. First, the unsaturated acid was extremely resistant to pyrolytic decarboxylation. It has been shown[9] for other α,β-unsaturated carboxylic acids that the pyrolytic decarboxylation was relatively facile if isomeriza-

(7) V. Georgian and N. Kundu, *Chem. Ind.* (London), 1322 (1958).

(8)(a) N. L. Wendler, D. Taub, and R. P. Graber, *Tetrahedron*, **7**, 173 (1959); N. L. Wendler and D. Taub, *Chem. Ind.* (London), 415 (1958). (b) E. J. Bailey, D. H. R. Barton, J. Elks, and J. F. Templeton, *J. Chem. Soc.*, 1578 (1962), have recently reported the oxidation of this hydroxy acid to A-norcholestan-2-one by means of sodium dichromate in acetic acid.

(9) R. T. Arnold, O. C. Elmer, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 4359 (1950).

tion of the double bond to the β, γ-position was possible. Conversely, if this isomerization was not possible, decarboxylation was difficult and high temperatures were necessary.

Second, the n.m.r. spectrum of the unsaturated acid showed a singlet band at 2.86 τ (tetramethylsilane reference), due to the olefinic proton. While this band was somewhat broadened, it definitely was not split, suggesting that there were no adjacent protons available for spin–spin coupling, as would be the case for the 2-olefin, VI.[10,11]

Experimental[12]

3-Hydroxy-5α-cholest-3-ene-2-one (I) (Diosphenol A) and 2-Hydroxy-5α-cholest-1-ene-3-one (II) (Diosphenol B).—The two diosphenols were prepared essentially as described by Stiller and Rosenheim.[6a] Diosphenol A had m.p. 144–145.5°, $[\alpha]_D$ +80.8° (8.8% in $CHCl_3$), $\lambda_{max}^{CCl_4}$ 2.92, 5.86 (w), and 5.98 μ, $\lambda_{max}^{CHCl_3}$ 274 mμ (log ϵ 3.79); reported[6a]: m.p. 144–145°, $[\alpha]_D$ +79.1° (1% in $CHCl_3$), λ_{max}^{EtOH} 272 mμ (log ϵ 3.70).

Diosphenol B had m.p. 178–179°, $[\alpha]_D$ +54.2° (3.2% in $CHCl_3$), $\lambda_{max}^{CCl_4}$ 2.92, 5.99 μ, $\lambda_{max}^{CHCl_3}$ 272 mμ (log ϵ 3.93); reported[6a]: m.p. 168–169°, $[\alpha]_D$ +57.2° (1% in $CHCl_3$), λ_{max}^{EtOH} 270 mμ (log ϵ 3.93).

A-Norcholestan-2-ol-2-carboxylic Acid (IV, R = H). (a) From "Diosphenol A."—A solution of 304 mg. (0.76 mmole) of diosphenol A and 2.8 g. of potassium hydroxide in 6 ml. of water and 80 ml. of *n*-propyl alcohol was boiled under reflux for 20 hr. and then diluted with 100 ml. of water and acidified with hydrochloric acid. The resulting mixture was extracted with one 50-ml. and two 30-ml. portions of ether, and this ether extract was washed with five 10-ml. portions of water after which the wash was neutral. The ether solution was then extracted with eleven 10-ml. portions of half-saturated potassium bicarbonate solution, when no more flocculent material appeared at the interface of the mixture when it was cooled in ice–water for several minutes. The bicarbonate extracts and insoluble salts were combined, 50 ml. of ether was added, and the mixture was acidified with hydrochloric acid. The ether layer was then removed, the aqueous layer was extracted with 20 ml. more of ether, and the combined ether extract was washed with water, dried over anhydrous sodium sulfate, and the ether was removed to give 294 mg. (92%) of brown needles, m.p. 242–245° dec. In various runs the yield ranged between 92 and 99.6%. One recrystallization from acetone gave m.p. 257–258° dec., $[\alpha]_D$ +24.5° (0.94% in dioxane), $\lambda_{max}^{CCl_4}$ 2.92, 3.50, and 5.87 μ. The analytical sample was obtained by one more recrystallization from acetone and had m.p. 257–259° dec.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.46; H, 11.08. Found: C, 77.46; H, 10.81.

In order to establish that no isomers were present, a 302-mg. sample of the hydroxy acid, obtained as described above, and not recrystallized, was taken up in 30 ml. of benzene and 15 ml. of petroleum ether (b.p. 30–60°) and chromatographed on a column composed of a mixture of 3 g. of silica gel and 6 g. of Supercel. The first 90 ml. of eluate gave 46 mg. of material which proved to be a mixture of diosphenol and the product. Then eleven eluates of approximately 40 ml. each were collected, using solvents of increasing polarity as follows: benzene, 10% ether in benzene, 50% ether in benzene, 10% methanol in ether, 50% methanol in ether,methanol, and 0.5% acetic acid in methanol. Each of the eluates yielded crystalline material on evaporation of the solvent, with the melting point ranging between 236 and 252°. A mixture melting point was taken with each fraction and a sample of analytically pure material, m.p. 257–259°. In each case, the melting point of the mixture was higher than that of the material from the chromatogram. The total weight of material recovered from the column was 286 mg. (95%). The fractions containing only the product, 240 mg., were combined and recrystallized twice from acetone to give 79 mg., m.p. 256.5–257.5°.

(b) From "Diosphenol B".—A solution of 101 mg. (0.252 mmole) of Diosphenol B in 3 ml. of aqueous potassium hydroxide solution (5.6 g. in 10 ml. of water) and 40 ml. of *n*-propyl alcohol was boiled under reflux for 20 hr., then poured into 100 ml. of water and acidified with concentrated hydrochloric acid. The resulting mixture was extracted with one 50-ml. and one 40-ml. portion of ether. The ether extract was washed four times with water, dried over anhydrous sodium sulfate, and the ether removed to give 107 mg. (101%) of needles, m.p. 247–249°. One recrystallization from 12 ml. of acetone gave 52 mg. (49%), m.p. 257.5–258.5° dec., $\lambda_{max}^{CCl_4}$ 2.92, 3.50, and 5.87 μ, m.m.p. with A-norcholestan-2-ol-2-carboxylic acid from Diosphenol A, 257.5–258.5°.

Further concentrations of the mother liquors gave an additional 7 mg., m.p. 254.5–257°, and 11 mg., m.p. 250–252°. The melting point of both crops was raised when they were mixed with pure acid.

Methyl A-Norcholestan-2-ol-2-carboxylate (IV, R = CH_3).—A solution of diazomethane in ether was added in portions to an ice cold solution of 59 mg. (0.14 mmole) of A-norcholestan-2-ol-2-carboxylic acid (m.p. 254–255.5°) in 5 ml. of ether until no more nitrogen was evolved. Then 15 ml. of ether was added, the solution was washed once with dilute hydrochloric acid and twice with water, dried over anhydrous sodium sulfate, and evaporated to give 57 mg. (93%) of needles, m.p. 76–78.5°, $[\alpha]_D$ +20° (1.7% in $CHCl_3$). Two recrystallizations from ethanol–water gave 49 mg. (80%), m.p. 82.5–83.5°, $[\alpha]_D$ +22° (1.4% in $CHCl_3$).

Anal. Calcd. for $C_{28}H_{48}O_3$: C, 77.72; H, 11.18. Found: C, 77.03; H, 10.82.

The methyl ester was also obtained by boiling under reflux a solution of the acid in methanolic hydrogen chloride for 24 hr.

A solution of 14 mg. of the ester and 500 mg. of potassium hydroxide in 1 ml. of water and 9 ml. of methanol was allowed to stand at room temperature for 30 hr. Then the solution was concentrated to 4 ml. under reduced pressure, acidified with dilute hydrochloric acid, and cooled to give 11 mg. (81%) of acid, m.p. 251–253° dec. One recrystallization gave 5 mg., m.p. 257–258° dec., m.m.p. with the acid described above, 257–258°.

Δ^1- or Δ^2-A-Norcholesten-2-carboxylic Acid (VI or VII, R = H) by Pyrolysis.—A 131-mg. (0.313 mmole) sample of A-norcholestan-2-ol-2-carboxylic acid in an evacuated tube was heated at 265° for 16 min., after which gas evolution had ceased. The product was dissolved in petroleum ether and the solution was treated with decolorizing charcoal and then cooled in Dry Ice to give 73 mg. (58%), m.p. 213.5–214°. Recrystallization from an ether–petroleum ether mixture gave 52 mg. (42%) m.p. 219.5–220°, $[\alpha]_D$ +50° (1.5% in $CHCl_3$), $\lambda_{max}^{CHCl_3}$ 2.92, 5.98, and 6.27 μ, λ_{max}^{MeOH} 220 mμ (log ϵ 3.89) at 1.5×10^{-5} mole/l., 225 mμ (log ϵ 3.93) at 1.2×10^{-4} mole/l. One more recrystallization gave an analytical sample, m.p. 220–220.5°.

(10) W. G. Dauben, G. A. Boswell, and W. H. Templeton, *J. Am. Chem. Soc.* **83** 5006 (1961), reported a similar situation for the Δ^1-enol acetate of A-norcholestane-2-one, and stated the dihedral angle of about 90° needed for a zero coupling constant between a 3-vinyl proton and a 5α-proton did not appear reasonable from examination of models.

(11) We are indebted to Dr. Harry Agahigian of the Olin Mathieson Chemical Corp. for the determination and interpretation of the n.m.r. spectrum.

(12) Melting points are corrected and were determined with a Hershberg apparatus. The analytical samples were recrystallized to constant melting point. Analyses by Dr. S. M. Nagy and associates, Microchemical Laboratory, Massachusetts Institute of Technology.

Anal. Calcd. for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.87; H, 11.12.

Dehydration with Phosphorus Pentoxide.—A mixture of 148 mg. of the hydroxy acid, 0.70 g. of phosphorus pentoxide, and 35 ml. of anhydrous decalin was boiled under reflux for 1.5 hr. The liquid was then decanted from solid material, concentrated to a small volume under reduced pressure, and diluted with moist ether. The ether solution was extracted with four 25-ml. portions of 0.2 *N* potassium hydroxide, concentrated to 50 ml., and extracted twice more with 10-ml. portions of the potassium hydroxide solution. The alkaline extracts and the flocculent material from the interface were combined, acidified with dilute hydrochloric acid, and the resulting mixture was extracted with 70 ml. of ether. The ether extract was dried and evaporated to give 91 mg. of a semisolid residue, which was dissolved in a benzene–petroleum ether mixture (1 part to 2 parts). This solution was then chromatographed on a column of 5 g. of silica gel and 5 g. of Supercel. Elution with benzene gave 25 mg. of an oil. Elution with more polar solvents (finally 0.3% acetic acid in methanol) gave 62 mg. (68%) of crystalline unsaturated acid, m.p. 197–207°. Three recrystallizations from ether–petroleum ether gave needles, m.p. 217–218.5°, m.m.p. with the material obtained by pyrolysis, 218–219°.

The methyl ester was prepared by treatment of the acid with diazomethane in ether as described above, and had, after three recrystallizations from methanol, m.p. 85.5–87°, $[\alpha]D$ +49° (1.1% in $CHCl_3$), λ_{max}^{KBr} 5.84, 6.24 μ, λ_{max}^{MeOH} 227 mμ (log ϵ 4.01).

Anal. Calcd. for $C_{28}H_{46}O_2$: C, 81.10; H, 11.18. Found: C, 80.87; H, 11.05.

A solution of 25 mg. of the methyl ester and 1 g. of sodium hydroxide in 50 ml. of methanol was allowed to stand at room temperature for 40 hr., and then was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was dried, the ether was evaporated and the residue was triturated with petroleum ether to give 9 mg., m.p. 215.5–217°. One recrystallization from ether–petroleum ether gave 6 mg., m.p. 217–218°, m.m.p. with the unsaturated acid described above, 218–219°.

A-Norcholestan-2-one (V).—A solution of 34 mg. (0.081 mmole) of A-norcholestan-2-ol-2-carboxylic acid (m.p. 257–257.5°) and 102 mg. of lead tetraacetate in 17 ml. of acetic acid was allowed to stand at room temperature in a sealed tube for 40 hr. The contents of the tube were added to 20 ml. of water and the mixture was extracted with one 20-ml. and two 15-ml. portions of ether. The ether extract was washed once with 10 ml. of water, four times with 15-ml. portions of half-saturated potassium bicarbonate solution, and once with water, and then was dried over anhydrous sodium sulfate. The ether was evaporated to give 29 mg. (97%) of A-norcholestan-2-one, m.p. 97–98°, $[\alpha]D$ +135° (0.8% in $CHCl_3$). One half of the product was recrystallized from alcohol and water to give 11 mg., m.p. 102–102.5°, m.m.p. with an authentic sample (m.p. 99–99.5°) 102–102.5°.

The second half was converted to the oxime, 15 mg., m.p. 194–196°, after recrystallization from alcohol and water 9 mg., m.p. 203.5–205°, m.m.p. with an authentic sample (m.p. 201–202°) 203.5–205.5°.

Attempted Decarboxylation of Δ^1- or Δ^2-Cholesten-2-carboxylic Acid. (a) With Cupric Oxide.—A mixture of 70 mg. of the unsaturated acid, 40 mg. of cupric oxide (wire), and 10 ml. of quinoline was heated at 230° for 3 hr. under a nitrogen atmosphere. The liquid was decanted from the cupric oxide and 50 ml. of ether was added. This solution was washed well with dilute hydrochloric acid and with water, the ether solution was then dried, and evaporated to give 50 mg. of a brown oil. The oil was dissolved in benzene–petroleum ether and chromatographed on 3 g. of alumina. None of the seven fractions could be obtained crystalline and the largest fraction had $\lambda_{max}^{CHCl_3}$ 2.90, 5.81, and 6.32 μ.

(b) By Distillation of the Barium Salt.—A solution of 300 mg. of the unsaturated acid in 2 ml. of ether was mixed with a solution of 130 mg. of barium hydroxide in 2 ml. of water. The ether was evaporated, the water was decanted from the precipitate, and the solid was washed with 1 ml. of water and with 1 ml. of ether, and dried. It did not melt below 340°. The salt was then heated in a small distillation flask at 340–360° (16 mm.) and 75 mg. of oily material distilled, which could not be obtained crystalline and had $\lambda_{max}^{CHCl_3}$ 2.80, 5.75, 5.88 (sh.), and 6.16 μ.

Unsaturated Amines. XVII. Preparation of Enamines by a Reductive Process[1-3]

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Hydrolytically stable enamines can be isolated from the lithium-*n*-propylamine reduction of aromatic amines. The synthesis is illustrated in the preparation of Δ^6-tetrahydrojulolidine (II) from julolidine (I) and 1-methyl-Δ^8-(V) and 1-methyl-Δ^9-octahydroquinoline (IV) from 1-methyltetrahydroquinoline (III). These enamines—*i.e.*, II and IV—undergo N- rather than C-methylation, and physical and chemical proof is provided for the structures of the corresponding methiodides and methoperchlorates (X and IX).

The reductive route to enamines from compounds of the tetrahydroquinoline type offers the possible advantage of avoiding the attendant hydroxylation in the oxidative route from decahydroquinoline types.[4-6] We therefore turned to the lithium–primary amine reducing system, which has been found capable of producing enamine *intermediates* during reduction of aromatic amines.[7,8] Enamine

(1) For article XVI in this series, see N. J. Leonard and W. K. Musker, *J. Am. Chem. Soc.*, **82**, 5148 (1960).

(2) This investigation was supported by a research grant (USPHS-RG5829) from the National Institutes of Health, U. S. Public Health Service.

(3) Presented at the Seventeenth National Organic Chemistry Symposium of the American Chemical Society, June, 1961, Bloomington, Indiana.

(4) N. J. Leonard, L. A. Miller, and P. D. Thomas, *J. Am. Chem. Soc.*, **78**, 3463 (1956).

(5) P. D. Thomas, Ph.D. thesis, University of Illinois, 1954.

(6) F. Bohlmann and C. Arndt, *Ber.*, **91**, 2167 (1958).

(7) R. A. Benkeser, R. F. Lambert, P. W. Ryan, and D. G. Stoffey, *J. Am. Chem. Soc.*, **80**, 6573 (1958).

(8) R. A. Benkeser, J. J. Hazdra, R. F. Lambert, and P. W. Ryan, *J. Org. Chem.*, **24**, 854 (1959).