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40 ml. of water on the steam-bath overnight. Acidification of the cooled solution yielded 2.3 g. of 2-hydroxycinchoninic acid. Treatment of the remaining solution with concd. ferric chloride solution yielded 1.29 g. (47%) of solid which was redissolved in ammonium hydroxide. The ferric hydroxide was removed by filtration and the solution was acidified with hydrochloric acid to yield after thirty-six hours 0.52 g. (40%) of benzenesulfinic acid, m. p. 83-85° (reported.<sup>11</sup> 83-84°).

Treatment of Esters with Sodamide.—To the cooled reaction mixture from refluxing of 0.050 mole of ethyl 2-phenylthiocinchoninate with 0.100 mole of sodamide in benzene for twenty-four hours was added water and ether and the phases were separated. Acidification of the aqueous layer gave 11.6 g. (82%) of 2-phenylthiocinchoninic acid after precipitation from bicarbonate solution.

The 2-phenylthiocinchoninamide was recovered unchanged on treatment with sodium hydroxide, ammonium hydroxide, benzene and water under conditions comparable to those used in working up the above reaction mixture.

Another cooled reaction mixture from treatment of 0.050 mole of ethyl 2-phenylthiocinchoninate with 0.100 mole of sodamide was poured into ice and aqueous acetic acid. Ether was added and the mixture was separated into an ether extract, 4.6 g. (ca. 34%) of a solid obtained by filtration, and an aqueous layer which did not yield any material on acidification to congo red.

any material on acidification to congo red. The solid, m. p.  $224-233^{\circ}$  after precipitation from dioxane by addition of water, showed a melting point lowering on mixing with either amide or acid. Boiling of the solid for five minutes with 3 N sodium hydroxide yielded ca.~90% of 2-phenylthiocinchoninamide, m. p. 229.5- $232.5^{\circ}$  after recrystallization from dioxane and ca.~80%of 2-phenylthiocinchoninic acid.

Evaporation of the ether layer yielded 8.6 g. of a gummy mixture from which the only pure material isolated was 1.28 g. of 2-phenylthiocinchoninic acid.

Treatment of ethyl 2-aminocinchoninate with 1.50 moles of sodamide in benzene for twenty-four hours, followed by addition of water to the cooled reaction mixture, gave a 32% recovery of ester and a 66% yield of acid. The much less soluble methyl ester gave a 74% recovery of

(18) Otto, J. prakt. Chem., [2] 30, 177 (1884).

ester and an 11% yield of acid. The butyl ester with 2 moles of sodamide gave no recovery of ester, no appreciable amount of butene or butylamine but a 92% yield of acid and a 76% yield of butyl alcohol.

The butyl ester was shaken with 3 M sodium hydroxide for five minutes and let stand thirty minutes, no acid being obtained, only a 95% recovery of ester being made. Treatment of 2-aminocinchoninamide with sodamide as for the esters gave a 93% recovery of unchanged amide.

esters gave a 93% recovery of unchanged amide. When the treatment of the butyl ester with sodamide was repeated and the cooled reaction mixture poured into dilute acetic acid, there was obtained *ca*. 93% of a solid, m. p. 213-221°. Precipitation of the material from dioxane by addition of water gave a product, m. p. 258-268° (dec.). Boiling of 4.86 g. of this material for five minutes with 30 ml. of 2 N sodium hydroxide gave after two precipitations from basic solution 3.91 g. of 2-aminocinchoninic acid. Heating the material with base in a modified Kjeldahl analysis gave 0.82 and 0.78% N (as —CONH<sub>2</sub>), 0.815 being the theoretical for a polymeric amide of ten units. The same type analysis (forty-five minutes) on 2-aminocinchoninamide gave 7.51% N (as —CONH<sub>2</sub>), the theoretical being 7.48.

## Summary

New cinchoninic acids and derivatives have been prepared which contain the 2-substituents: piperidino, morpholino, dibutylamino, novalamino, phenoxy, phenylthio and benzenesulfonyl.

As possible antimalarials,  $\alpha$ -(2-piperidyl)-4quinolinemethanols have been synthesized with the 2-position of the quinoline nucleus substituted by piperidino, morpholino, dibutylamino and hydroxy.

Observations have been reported on the stability to cleavage by acid or base of the various 2-substituents and on the behavior of certain of the cinchoninic esters toward sodamide in benzene.

Los Angeles 24, Calif.

RECEIVED APRIL 5, 1946

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology No. 1048]

# Potential Antimalarials. Additional (2-Phenylquinolyl-4)- $\alpha$ -piperidylcarbinols<sup>1</sup>

By E. R. BUCHMAN AND D. R. HOWTON

The present paper reports the syntheses of three additional<sup>2</sup> (2-phenylquinolyl-4)- $\alpha$ -piperidylcarbinols (V) by conventional methods. The cinchoninic esters (I) were prepared via the Doebner reaction.<sup>3</sup>

RCOOC	2H₅	5	steps $\rightarrow$ RCHOH- $\alpha$ -piperidyl
I			V
Series a.	$\mathbb{R}^4$	=	6-Methyl-2-phenylquinolyl-4
ь.	R	=	8-Methyl-2-phenylquinolyl-4
с.	R	=	2,8-Diphenylquinolyl-4

(1) The work described in this paper was done under a contract recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the California Institute of Technology.

(2) For other substituted (2-phenylquinolyl-4)- $\alpha$ -piperidylcarbinols see: (a) Koepfli, et al., THIS JOURNAL, **68**, 2697 (1946); (b) Brown, Jacobs, Winstein, et al., ibid., **68**, 2705 (1946); (c) Buchman, et al., ibid., **68**, 2710 (1946).

(3) Cf. Doebner and Gieseke, Ann., 242, 296, 298 (1887).

(4) Vb and Vc analogs of the type RCHOHCH<sub>2</sub>NR'<sub>2</sub> have been prepared by Lutz and co-workers, THIS JOURNAL, **68**, 1813 (1946).

# Experimental<sup>5</sup>

## 2-Phenylcinchoninic Esters

Ethyl 6-Methyl-2-phenylcinchoninate (Ia).<sup>6</sup>—The acid corresponding to Ia was prepared essentially as described in the literature<sup>8</sup> (glacial acetic acid in place of ethanol was less satisfactory) except that a technical (ca. 50%aqueous solution) pyruvic acid<sup>7</sup> was used. An equivalent of aqueous sodium hydroxide was added before removing the ethanol from the reaction mixture. The residue was extracted with *i*-propyl ether; acidification of the aqueous phase gave an oil which soon crystallized. This was dried and esterified with ethanolic sulfuric acid; after removal of solvent, the residue was basified with 15 N ammonium hydroxide and the oily Ia taken up in ether and recrystallized from ethanol at 0°; light yellow needles, m. p. 74.8-75.5° in agreement with the lit.<sup>6</sup>; yield 35.5% from ptoluidine.

(5) All melting points are corrected; microanalyses by Dr. G. Oppenheimer and staff of this Institute and by the Huffman Microanalytical Laboratories, Denver 2, Colorado.

(6) "Beilstein," 4th ed., Suppl. Vol. XXII, p. 520.

(7) Supplied by the Calco Chemical Division of the American Cyanamid Company.

Ethyl 8-Methyl-2-phenylcinchoninate (Ib).<sup>8</sup>—The above method applied to o-toluidine (2 moles), gave 339 g. of crude acid corresponding to Ib which was recrystallized (unrecrystallized material gave poorer yields of Ib) from ethanol-benzene (11:1); yield 104.5 g. of pale yellow needles (19.9%), m. p. 250° (lit.<sup>3,8</sup> m. p. 245°). The acid was esterified (see under Ia) and the product taken up in benzene and crystallized from *i*-propyl ether; yield 99.1 g. (17.1% from *o*-toluidine). A sample was recrystallized from ligroin and again from ethanol; transparent, tan, irregular clusters, m. p. 71.3-71.8° (lit.<sup>8</sup> m. p. 70°). Ib was also obtained from recrystallized acid on treatment first with thionyl chloride and then with ethanol.

Ethyl 2,8-Diphenylcinchoninate (Ic).—Crude 2,8-diphenylcinchoninic acid was similarly prepared from 169 g. (1 mole) of technical o-aminobiphenyl.<sup>9</sup> A small portion was washed with ethanol and methanol until free from oil and recrystallized from ethanol, sparse clusters of fine yellow needles, m. p. 243.0–243.6°.

Anal. Calcd. for  $C_{22}H_{15}NO_2$ : C, 81.21; H, 4.65; N, 4.31. Found: C, 81.16; H, 4.73; N, 4.68.

The bulk of the crude acid was esterified, giving 93.6 g. of crystalline Ic which was recrystallized from ethanol; yield 79.7 g. (22.6% from *o*-aminobiphenyl), compact clusters of fine white needles from ethanol-benzene, m. p. 104.6-105.2°.

Anal. Calcd. for  $C_{24}H_{19}\mathrm{NO}_2\colon$  C, 81.56; H, 5.42; N, 3.96. Found: C, 81.77; H, 5.40; N, 3.97.

#### Piperidylcarbinols

 $\epsilon$ -(6-Methyl-2-phenylcinchoninyl)-*n*-amylamine Dihydrobromide (IIIa).—The sodamide condensation<sup>2</sup><sup>o</sup> was carried out starting with 11.4 g. (0.496 mole) of sodium, 105.8 g. (0.402 mole) of ethyl benzamidocaproate (II),<sup>10</sup> 116.8 g. (0.402 mole) of Ia, and 240 ml. of benzene, heating for twenty-four hours. After hydrolysis by refluxing for fifty-four hours with 300 ml. of water and 210 ml. of concentrated sulfuric acid, the reaction mixture was made basic and the product extracted with chloroform. Solvent was removed (steam-bath, *in vacuo*) and the residue was cautiously added to 150.5 g. of  $48C_0$  hydrobromic acid; cooling and scratching gave a yellow solid which was filtered off and washed with *i*-propanol, yield 77.3 g.; 19.0 g. more was obtained from the filtrate by concentration and cooling; total yield 48.3% (*ca.* 100%, taking into account the recovered cinchoninic acid). A sample was recrystallized from cthanol-water, yellow bars, m. p.  $244-245^{\circ}$  dec.

*Anal.* Caled. for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O·2HBr: C, 53.45; H, 5.30; N, 5.67. Found: C, 53.21; H, 5.62; N, 5.42.

 $\epsilon$ -Bromo- $\epsilon$ -(6-methyl-2-phenylcinchoninyl)-*n*-amylamine Dihydrobromide (IVa).—IIIa (77.3 g. = 0.156 mole) was dissolved in hot 18% hydrobromic acid and treated rapidly with a solution of 24.9 g. (0.156 mole) of bromine in an equal volume of 48% hydrobromic acid. The crude product was filtered off, dispersed in 400 ml. of boiling ethanol, and water (57 ml.) added until a clear solution resulted; cooling gave 54.5 g. of light-yellow needle clusters; yield (including 9.8 g. from the mother liquors) 67.7%, m. p. 187.7–188.1°.

Anal. Calcd for  $C_{22}H_{23}BrN_2O\cdot 2HBr\cdot 2H_2O$ : C, 43.47; H, 4.80; N, 4.60. Found: C, 43.32; H, 4.90; N, 4.63.

 $(6-Methyl-2-phenylquinolyl-4)-\alpha$ -piperidylcarbinol (Va) (SN9875).<sup>11</sup>—IVa (60.8 g. = 0.106 mole) was cyclized (one hour) and hydrogenated (0.75 g. of catalyst, two hours) as described previously.<sup>20</sup> The reduction mixture was filtered and the filter cake washed with ethanol and

(8) John and Schmit, J. prakt. Chem., [2] 132, 15 (1931).

(9) Supplied by the Monsanto Chemical Company.

(10) Supplied by Dr. R. C. Elderfield (Columbia University) and Dr. C. C. Price (University of Illinois).

(11) The Survey Number, designated SN, identifies a drug in the records of the Survey of Antimalarial Drugs. The antimalarial activities of those compounds to which the Survey Numbers have been assigned will be tabulated in a forthcoming monograph.

with boiling chloroform. Evaporation of the light yellow filtrate left a crystal slurry which was treated with 100 ml. of water and 200 ml. of warm chloroform. An insoluble white fibrous solid (1.5 g.) was filtered off, m. p. 246° dec., which left a residue on ignition; treating this solid with 6 N hydrochloric acid gave a solution from which a Va hydrochloride melting at 208° separated (converted to Va, m. p. 182.5°). The brown chloroform phase, after filtering off this fibrous solid, was freed of solvent, leaving a brown crystalline slurry which was taken up in 200 ml. of warm ethanol and saturated with anhydrous hydrogen chloride. The crystalline salt was filtered off and washed with isopropanol; yield 27.0 g. of light tan powder, m. p. 233-235° dec.; concentration and cooling of the filtrate gave an additional 2.28 g., total yield 65.4%; the over-all yield from Ia was 21.4% (44.4% taking into account re-covered cinchoninic acid). Va dihydrochloride, on recrystallization from ethanol-water, formed a monohydrate, sparse clusters of small, colorless needles, m. p. 233.6° dec., analysis for  $C_{22}H_{24}N_2O.2HCl\cdot H_2O$ . Under various conditions, salts of other melting points were obtained, probably different hydrates<sup>20</sup> (salt melting at 208° see above); recrystallizing the  $233.6^{\circ}$  salt from 6 N hydrochloric acid-ethanol gave tiny colorless needles m. p. ca. 244° dec. Va formed clusters of colorless hexagonal plates from acetonitrile, m. p. 182.5-182.9°.

Anal. Caled. for  $C_{22}H_{21}N_2O$ : C, 79.48; H, 7.28; N, 8.43. Found: C, 79.33; H, 7.15; N, 8.31.

Va tends to form stable solvates<sup>2a,o</sup>; when recrystallized from acetonitrile containing ethanol, large, colorless, latticed crystals were obtained, m. p. 109–114° dec., resolidifying and melting again *ca*. 182°.

 $\epsilon$ -(8-Methyl-2-phenylcinchoninyl)-*n*-amylamine Hydrobromide (IIIb).—The condensation of 116.8 g. (0.402 mole) of Ib with II (twenty hours) was carried out as in series a. After hydrolysis (forty-three hours) and the usual working-up procedure, evaporation of the chloroform extracts left 98 g. of dark-brown, viscous oil, which was treated with 40.0 g. of 48% hydrobromic acid, then diluted with about 100 ml. of acetone. On standing overnight, a 14.7-g. erop of light yellow flakes crystallized out, m. p. 132–137°; after two recrystallizations from glacial acetic acid, this substance formed dense clusters of light yellow, thin rectangular blades with bluntly pointed terminations, m. p. 136–137° (prior sintering).

Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O·2HBr·2H<sub>3</sub>O: C, 49.82; H, 5.70; N, 5.28. Found: C, 50.17; H, 5.73; N, 5.57.

Dilution of the mother liquors from this first crop with ether to incipient oil formation and cooling overnight in a refrigerator gave 42.7 g. of a tan powder melting at about 157°; further cooling of the mother liquors and acetone-ether washings gave an additional 7.2 g. of the same material; this salt crystallized from glacial acetic acid in clusters of light tan needles, m. p.  $178-179^{\circ}$ .

Anal. Calcd. for  $C_{22}H_{24}N_2O \cdot HBr$ : C, 63.92; H, 6.10; N, 6.78. Found: C, 64.07; H, 5.94; N, 6.88.

 $\epsilon$ -Bromo- $\epsilon$ -(8-methyl-2-phenylcinchoninyl)-*n*-amylamine Hydrobromide (IVb).—In 93 ml. of hot 48% hydrobromic acid, 38.4 g. of IIIb (monohydrobromide) was dissolved and treated with a solution of 14.9 g. of bromine in about 15 ml. of the same solvent; an orange oil was formed which quickly redissolved. After filtering from a little tar, the warm solution was diluted with 200 ml. of *i*-propanol and cooled; clusters of tiny pale-yellow needles formed which were filtered off and washed with *i*propanol, yield 51.5 g. of crude IVb (possibly a dihydrobromide), m. p. 156–162°. (A small sample (4.13 g.) of IIb dihydrobromide, on bromination, gave 3.44 g. of IVb.) After two recrystallizations from *i*-propanolwater, sparse clusters of long, shiny, yellow needles were obtained, m. p. 175.8–176.0° dec.

Anal. Calcd. for  $C_{22}H_{23}BrN_2O$  HBr: C, 51.78; H, 5.14; N, 5.49. Found: C, 52.23; H, 5.18; N, 5.88.

 $(8-Methyl-2-phenylquinolyl-4)-\alpha-piperidylcarbinol (Vb) (SN12238).<sup>11</sup>—Crude (IVb) (56.1 g.) was cyclized (eighty minutes) and reduced (0.75 g. of catalyst, three$ 

hours). The resulting slurry was heated to boiling and insoluble inorganic solids were filtered off and washed well with benzene. On evaporation, the clear yellow filtrate left a light tan, crystalline residue which was washed well with water, yield 26.6 g. Three recrystallizations of a sample from acetonitrile-pyridine gave clusters of brilliant, colorless needles, m. p. 187.8–188.3° (prior sintering).

Anal. Calcd. for  $C_{22}H_{24}N_2O$ : C, 79.48; H, 7.28; N, 8.43. Found: C, 79.40; H, 7.15; N, 8.45.

Crude Vb (26.2 g.) was dissolved in 400 ml. of boiling ethanol and treated with 13.9 ml. of 6 N hydrochloric acid; the mass of tiny white needles which formed was filtered off and washed with ethanol, yield 25.7 g. (24.7% over-all from Ib; 44.1% taking into account the recovered cinchoninic acid). Vb hydrochloride crystallized from ethanol-water in sparse clusters of colorless bars, m. p. 247° dec., analysis for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O·HCl.  $\epsilon$ -(2,8-Diphenylcinchoninyl)-n-amylamine Hydrobro-

mide (IIIc).—Ic (145.7 g. = 0.413 mole) was condensed with II (forty hours) and the product hydrolyzed (seventeen hours). After basifying the hydrolyzate in the presence of chloroform, the resulting emulsion was centrifuged and the solid at the interface was extracted further with benzene and chloroform and filtered off with the aid of Celite. The combined chloroform-benzene extracts were evaporated (solid which separated was filtered off) on the steam-bath, finally at 2 mm., leaving 143.4 g. of viscous brown oil. This was treated with 62 g. of 48% hydrobromic acid and 100 ml. of hot *i*-propanol, freed of the solvent, and the residual oil dissolved in 250 ml. of acetone and cooled. The resulting crystals weighed  $38.5~{\rm g}$ ; concentration and dilution of the mother liquors with acetone yielded two additional crops (43.5 g. and 16.7 g.); total yield of crude IIIc, m. p. 223–226°, about 43%. A sample was dissolved in a little boiling glacial acetic acid and, on cooling, a small quantity of tiny tan needle-clus-ters emerged which were recrystallized from the same solvent to give sparse clusters of glistening, colorless needles, m. p. 270.6-271.1°; the analysis (Found: C, 69.92; H, 5.68; N, 6.04) indicates the presence of IIIc monohydrobromide. Acetone-dilution of the mother liquors from this higher-melting compound gave a considerably larger quantity of golden-yellow, jagged clusters which were crystallized again from warm glacial acetic acid by diluting with acetone, m. p.  $224-226^{\circ}$  (prior sintering).

Anal. Calcd. for  $C_{27}H_{26}N_2O$ ·2HBr: C, 58.29; H, 5.07; N, 5.04. Found: C, 58.08; H, 5.30; N, 4.62.

(Quinolyl-8)- $\alpha$ -piperidylcarbinol<sup>1</sup>

# BY E. R. BUCHMAN AND H. SARGENT

In studies dealing with hydroquinine isomers, Rubtsov<sup>2</sup> has sought to determine the effect on the antimalarial potency in this series caused by a transfer of the quinuclidyl grouping from the 4position to other positions on the quinoline ring. As a further contribution to this general problem, we have synthesized (quinolyl-8)- $\alpha$ -piperidylcarbinol (III) (SN10277)<sup>3</sup> by application of methods

(1) The work described in this paper was done under a contract recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the California Institute of Technology.

(2) Rubtsov, J. Gen. Chem. (U. S. S. R.), 9, 1493 (1939); 13, 593 (1943) [C. A., 34, 2850 (1940); 39, 705 (1945)]; see also Campbell, Helbing and Kerwin, THIS JOURNAL, 68, 1840 (1946), and ref. 7b.

(3) The Survey Number, designated SN, identifies a drug in the records of the Survey of Antimalarial Drugs. The antimalarial activities of those compounds to which the Survey Numbers have been assigned will be tabulated in a forthcoming monograph. ε-Bromo-ε-(2,8-diphenylcinchoninyl)-*n*-amylamine Hydrobromide (IVc).—Crude IIIc (81.4 g.) was dissolved in 172 ml. of hot 48% hydrobromic acid and treated with a solution of 27.4 g. of bromine in 27 ml. of the same solvent, causing precipitation of a yellow oil which redissolved readily on warming. After removal of a small amount of tar, the solution was diluted with about 250 ml. of hot ethanol and cooled, giving clusters of fine, bright yellow needles which were filtered off and washed with acetone; concentration of the filtrates followed by dilution with ethanol gave altogether four crops (m. p.'s in the range 147-168°), total yield 84.7 g. (may contain dihydrobromide). Several recrystallizations from glacial acetic acid with the aid of Norite gave a product, m. p. 177.1-177.4° dec.

Anal. Calcd. for C<sub>27</sub>H <sub>5</sub>BrN O·HBr·1.5H O: C, 55.78; H, 5.03; N, 4.82. Found: C, 55.67; H, 5.11; N, 4.96.

(2,8-Diphenylquinolyl-4)- $\alpha$ -piperidylcarbinol (Vc) (SN12239).<sup>11</sup>—Crude IVc (63.7 g.) was cyclized (ninety minutes) and reduced (1.5 g. of catalyst, thirty hours). Inorganic solids were filtered off and washed with hot ethanol; the filtrate was evaporated and the solid residue taken up in hot benzene. After again freeing from solvent, the base was dissolved in 6 N hydrochloric acid, liberated to benzene and finally crystallized from benzene-ethanol; yield 16.9 g. of light tan needles, m. p. 195–197°; the mother liquors yielded an additional 3.3 g. (total yield of Vc, 20.0% from Ic) and a solid by-product (17.8 g.). Recrystallization of Vc from ethanol-benzene gave clusters of fine white needles, m. p. 195.8–196.2°.

Anal. Caled. for C<sub>77</sub>H<sub>\*6</sub>N<sub>2</sub>O: C, 82.20; H, 6.64; N, 7.10. Found: C, 81.95; H, 6.62; N, 7.10.

A solution of 20.1 g. of Vc in 100 ml. of hot 6 N hydrochloric acid was diluted with 650 ml. of acetone followed by 100 ml. of water; on cooling 12.7 g. of colorless bars slowly emerged, m. p. 242°. The salt was recrystallized from ethanol-6 N hydrochloric acid, m. p. 242–243° dec., analysis for  $C_{27}H_{26}N_2O$ ·HCl.

## Summary

(6-Methyl-2-phenylquinolyl-4)- $\alpha$ -piperidylcarbinol, (8-methyl-2-phenylquinolyl-4)- $\alpha$ -piperidylcarbinol and (2,8-diphenylquinolyl-4)- $\alpha$ -piperidylcarbinol have been prepared.

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previously used<sup>4</sup> for preparation of the quinolyl-4 isomer.

In avian tests, SN10277<sup>3</sup> was devoid of activity; this finding strengthens the conclusion which may be drawn from Rubtsov's work<sup>2</sup> that quinolyl-8 carbinols are not of interest as antimalarials.

#### Experimental<sup>5</sup>

(Quinolyl-8)- $\alpha$ -piperidylcarbinol (III).<sup>6</sup>—Ethyl quinoline-8-carboxylate<sup>7</sup> (54.0 g. = 0.269 mole) was condensed with ethyl  $\epsilon$ -benzamidocaproate (twenty hours) and the product was hydrolyzed by refluxing for twenty-four hours with 200 ml. of 12 N hydrochloric acid and 100 ml.

(4) Ainley and King, Proc. Roy. Soc. (London), **125B**, 60 (1938); see also Senear, Sargent, Mead and Koepfli, THIS JOURNAL, **68**, 2695 (1946).

(5) All melting points are corrected; microanalyses by Dr. G. Oppenheimer and her staff of this Institute.

(6) Cf. preparation (6-methoxyquinolyl-4)- $\alpha$ -piperidylcarbinol, Sargent, THIS JOURNAL, **68**, 2688 (1946).

(7) (a) Cook, Heilbron and Steger, J. Chem. Soc., 413 (1943);
(b) Campbell, Kerwin, LaForge and Campbell, This JOURNAL, 68, 1844 (1946). This material was supplied by Dr. F. W. Bergstrom (Stanford University).