crystallized from toluene in shiny brown leaflets, m.p. 309°.

Anal. Calcd. for $C_{28}H_{28}Cl_2N_2O_2$: C, 67.9; H, 5.6. Found: C, 67.5; H, 5.7.

N-(p-Cyclopentylphenyl)tetrachlorophthalimide. To a boiling solution of 1 g. of tetrachlorophthalic anhydride in 15 ml. of acetic acid, 0.6 g. of *p*-cyclopentylaniline was added dropwise, and the mixture refluxed for a few minutes. The solid formed after cooling was recrystallized from acetic acid, giving shiny colorless needles, m.p. 242°.

Anal. Calcd. for $C_{19}H_{13}Cl_4NO_2$: C, 53.2; H, 3.0. Found: C, 53.4; H, 2.9.

N-(p-Cyclopentylphenyl)glycine (IV). A mixture of 3.2 g. of *p*-cyclopentylaniline, 2 g. of chloroacetic acid, and 6 g. of sodium acetate in aqueous solution was heated on a water bath for 1 hr. After cooling, and dilution with water, the precipitate formed was collected, redissolved in 10% aqueous ammonium carbonate, and the filtrate acidified with acetic acid; the precipitate, obtained in 50% yield, crystallized from water in shiny colorless prisms, m.p. 199°.

Anal. Calcd. for $C_{13}H_{17}NO_2$: C, 71.2; H, 7.8. Found: C, 71.1; H, 7.8.

The corresponding *ethyl ester* was prepared by heating for 3 hr. on a water bath a mixture of 6.4 g. of *p*-cyclopentylaniline, 8 g. of ethyl bromoacetate, and 15 g. of sodium acetate. 50 ml. of water was then added, the reaction product taken up in chloroform, the chloroform solution washed with water and dried over sodium sulfate, the solvent removed, and the residue fractionated to yield 77% of an ester, b.p. 219–221°/15 mm., crystallizing from petroleum ether in colorless prisms, m.p. 42°.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.9; H, 8.5. Found: C, 72.7; H, 8.4.

The corresponding *hydrazide* was prepared by refluxing for 2 hr. a solution of 2.5 g. of the foregoing ester and 1.5 g. of 98% hydrazine hydrate in 20 ml. of ethanol; the precipitate obtained in 98% yield after cooling, was recrystallized from ethanol, giving shiny colorless prisms, m.p. 153°.

Anal. Calcd. for $C_{13}H_{19}N_3O$: C, 66.9; H, 8.1. Found: C, 66.8; H, 8.0.

Preparation of thiocarbanilides derived from I. Equimolar amounts of *p*-cyclopentylaniline and the appropriate aryl isothiocyanate were heated at 50–60° for 30 min. in ethanol medium; the precipitate formed on cooling was recrystallized from ethanol, giving in every instance shiny colorless prisms, with a bitter taste.

Preparation of N,N'-diarylureas derived from I. *p*-Cyclopentylaniline was allowed to react with an equimolar quantity of the appropriate aryl isocyanate in benzene medium in the cold; the urea obtained was recrystallized from ethanol or an ethanol-benzene mixture.

2-(p-Cyclopentylphenyl)indole (VII). A mixture of 3 g. of *p*-cyclopentylacetophenone and 2 g. of phenylhydrazine was heated for a few minutes at 140–150° with removal of water; to this crude phenylhydrazone, 7 g. of finely powdered, fused zinc chloride was added, and the mixture heated for 15 min. at 185–195°. After cooling, aqueous acetic acid was added, the reaction product taken up in benzene, and the benzene solution washed with water and dried over sodium sulfate. The residue from evaporation of the solvent was vacuum distilled, and the fraction, b.p. 270–272°/13 mm., recrystallized from a benzene-ethanol mixture. Yield: 70% of shiny colorless prisms, m.p. 236°, giving a deep violet picrate.

Anal. Calcd. for $C_{19}H_{19}N$: C, 87.3; H, 7.3. Found: C, 87.0; H, 7.4.

Pfitzinger reactions with 4-acylcyclopentylbenzenes. A mixture of 1 mole of isatin and 1 mole of the appropriate ketone with a 20% ethanol solution of 3 moles of potassium hydroxide was gently refluxed on a water bath for 72 hr.; after dilution with water and ether-extraction of the neutral impurities, the aqueous layer was acidified with acetic acid, and the precipitated *cinchoninic acid* was washed with water, dried, and recrystallized from ethanol, giving yellowish needles in every instance. The yields ranged from 30% for *p*-cyclopentylbutyrylphenone, to 80–85% of *p*-cyclopentylacetophenone. For the preparation of the corresponding quinolines, the appropriate cinchoninic acid was heated above its melting point, and the decarboxylation product was vacuum-distilled and recrystallized from ethanol, to give shiny colorless prisms.

Acknowledgment. Our thanks are due to Dr. Thomas D. Waugh, of Arapahoe Chemicals, Inc., Boulder, Colo., for kindly supplying the chlorocyclopentane and cyclopentanol used in this work.

PARIS V^e^, FRANCE

[CONTRIBUTION FROM THE RADIUM INSTITUTE OF THE UNIVERSITY OF PARIS]

α,α-Dimethyl-β-arylethylamines, and Their Behavior in the Bischler-Napieralski Reaction

N. P. BUU-HOÏ, C. T. LONG, AND N. D. XUONG

Received July 29, 1957

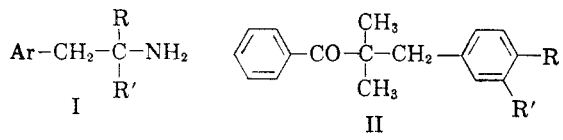
Several new *p*-substituted α,α-dimethyl-β-phenethylamines have been synthesized for biological testing as potential sympathomimetic amines, and their amides found to resist the Bischler-Napieralski cyclization to dihydroisoquinolines. This failure is accounted for on the grounds of steric hindrance.

α,α-Dialkyl-β-arylethylamines (I), investigated first by Mentzer,[1] and then by Mentzer, Buu-Hoï, and Cagniant,[2] possess interesting sympathomimetic activity, and recently one of the compounds of this group, *N*-methyl-α,α-dimethyl-β-phenethylamine, has found therapeutic application[3] under the name of "Mephentermine," as a vasoconstrictor with no cerebral-stimulating effects. It was of interest to examine the biological properties of a number of hitherto unknown *p*-substituted α,α-dimethyl-β-phenethylamines, and the synthesis of several of these new compounds is now described.

(1) C. Mentzer, *Compt. rend.*, **213**, 581 (1941).

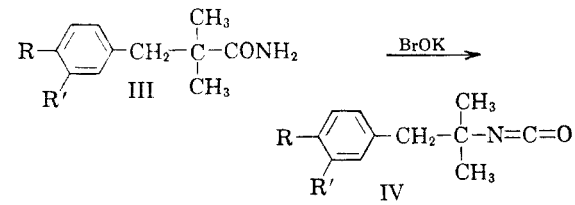
(2) C. Mentzer, N. P. Buu-Hoï, and P. Cagniant, *Bull. soc. chim., France*, 9 [5], 813 (1942).

(3) *cf.* A. Burger, *Medicinal Chemistry*, Interscience Publishers Inc., New York, 1951, p. 311.



I II

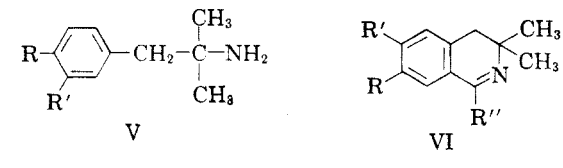
The starting point for these syntheses was *p*-substituted benzyl chlorides, which were condensed with isobutyrophenone in the presence of sodium amide to α,α-dimethyl-β-arylpropionylbenzenes of general formula II; these ketones, treated with sodium amide, underwent a Haller cleavage reaction[4] to give α,α-dimethyl-β-arylpropionamides (III) and benzene, and this reaction was also successful with halogenated ketones such as the condensation product (II; R = Cl, R′ = H) of *p*-chlorobenzyl chloride with isobutyrophenone. Hofmann degradation of the amides (III) by means of potassium hypobromite led to stable iso-cyanates[5] (IV), which underwent hydrolysis with hydrochloric acid to furnish the amines. α,α-Dimethyl-β-(4-ethylphenyl)- (V; R = C_2H_5, R′ = H), α,α-dimethyl-β-(4-isopropylphenyl)- (V; R = *i*-C_3H_7, R′ = H), and α,α-dimethyl-β-(3,4-dimethylphenyl)-



III IV

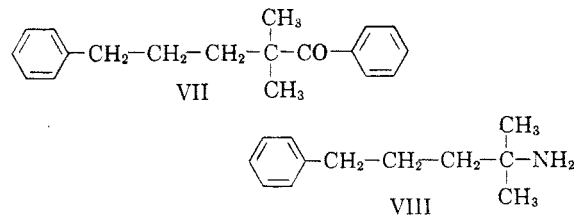
ethylamine (V; R = R′ = CH_3) were obtained in this way, starting from the chloromethyl derivatives of ethylbenzene, cumene, and *o*-xylene, respectively.

In view of the outstanding antispasmodic activity of numerous compounds bearing the isoquinoline ring system,[6] cyclization of the amides of the aforementioned phenethylamines to 1-substituted 3,3-dimethyl-3,4-dihydroisoquinolines of type (VI) was attempted by means of the Bischler-Napieralski reaction.[7] In the case of the *N*-acetyl and *N*-



V VI

benzoyl derivatives of α,α-dimethyl-β-(4-ethylphenyl)ethylamine, no cyclization product was obtained, even under drastic experimental conditions. With the *N*-benzoyl derivative of α,α-dimethyl-β-(3,4-dimethylphenyl)ethylamine, whose cyclization would be expected to be easier in view of the favorable influence of the methyl group in the position *para* to the prospective site of ring formation, only traces of cyclization product could be detected. These failures are consistent with the observations of Dey and Ramanathan[8] concerning the resistance of the *N*-benzoyl derivative of α,β-diphenylethylamine to cyclization; they also tally with the sharp drop recorded by Whaley and Hartung[9] in the cyclization yields of the benzamides of α-alkylated β-hydroxy-β-phenethylamines when the length of the alkyl chain is increased. The postulated role of steric hindrance in these negative results is further confirmed by the failure encountered in an attempted Knorr-Paal condensation[10] between acetonylacetone and α,α-dimethyl-β-arylethylamines.



VII VIII

In the course of this work, α,α-dimethyl-δ-phenylbutylamine (VIII) was prepared by the same sequence of reactions as for the amines (V), *via* ketone VII, which was obtained by condensation of δ-phenylbutyl bromide and isobutyrophenone.

Results of the biological tests will be reported elsewhere.

EXPERIMENTAL

α,α-Dimethyl-β-(4-ethylphenyl)propionylbenzene (II; R = C_2H_5, R′ = H). A solution of 42 g. of isobutyrophenone in 700 ml. of dry toluene was refluxed with 17 g. of sodium amide for 7 hr.; after cooling, 44 g. of *p*-ethylbenzyl chloride was added, along with 1 g. of anhydrous sodium iodide (used as a catalyst), and the refluxing continued for 14 hr. The reaction mixture was then decomposed with ice and a few drops of acetic acid, the organic layer washed with water and dried over sodium sulfate, the solvent distilled off at reduced pressure, and the residue vacuum-fractionated. Yield: 47 g. (62%) of a pale yellow oil, b.p. 210–211°/13 mm.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.4; H, 8.1.

α,α-Dimethyl-β-(4-ethylphenyl)propionamide (III; R = C_2H_5, R′ = H). A solution of 46 g. of the foregoing ketone in 400 ml. of dry toluene was refluxed with 11 g. of sodium amide for 20 hr.; after cooling, the reaction mixture was treated with ice and a few drops of acetic acid, the toluene solution washed with water and dried over sodium sulfate, the solvent distilled off at reduced pressure, and the residue vacuum-fractionated. Yield: 31 g. (86%) of an *amide*, b.p. 196–197°/14 mm., crystallizing from petroleum ether in lustrous colorless leaflets, m.p. 51°

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.1; H, 9.3. Found: C, 76.0; H, 9.5.

(4) A. Haller, *Bull. soc. chim. France*, **31** [4], 1073 (1902).

(5) M. Montagne and M. Casteran, *Compt. rend.*, **191**, 139 (1930).

(6) See excellent monograph in A. Burger, *Medicinal Chemistry*, Interscience Publishers Inc., New York, 1951, p. 403.

(7) A. Bischler and B. Napieralski, *Ber.*, **26**, 1903 (1893).

(8) B. B. Dey and V. S. Ramanathan, *Proc. Natl. Inst. Sci. India*, **9**, 193 (1943).

(9) W. Whaley and W. Hartung, *J. Org. Chem.*, **14**, 650 (1949).

(10) L. Knorr, *Ber.*, **18**, 2254 (1885); N. P. Buu-Hoï, *J. Chem. Soc.*, 2882 (1949).

α,α-Dimethyl-β-(4-ethylphenyl)ethyl isocyanate (IV; R = C_2H_5, R′ = H). To an ice-cooled solution of 48 g. of bromine in 280 ml. of 20% aqueous potassium hydroxide, a solution of 51 g. of the foregoing amide in 100 ml. of dioxane was added portionwise with stirring, and the mixture then shaken for 30 min. The reaction product was taken up in ether, the ethereal solution washed with water and dried over sodium sulfate, the solvent distilled off, and the residue vacuum-fractionated. Yield: 26 g. (51%) of a colorless oil with an aromatic odor, b.p. 134–135°/13 mm., n_D^{22} 1.5096.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.5; H, 8.5.

α,α-Dimethyl-β-(4-ethylphenyl)ethylamine (V; R = C_2H_5, R′ = H). Hydrolysis of 30 g. of the foregoing isocyanate was effected by stirring with 200 ml. of warm hydrochloric acid; after the vigorous reaction had subsided, the mixture was refluxed for 30 min. After cooling, and removal of the neutral impurities by ether-extraction, the aqueous layer was basified with 30% aqueous sodium hydroxide, and the amine taken up in ether; the ethereal solution was dried over sodium sulfate, the solvent removed, and the residue vacuum-distilled. Yield: 23 g. (88%) of a colorless liquid, b.p. 116°/12 mm., n_D^{20} 1.5122.

Anal. Calcd. for $C_{12}H_{19}N$: N, 7.9. Found: N, 7.6.

The corresponding *hydrochloride* was obtained with hydrogen chloride in ether, as colorless, sublimable needles, m.p. 199°.

Anal. Calcd. for $C_{12}H_{20}ClN$: Cl, 16.6. Found: Cl, 16.5.

The *picrate* crystallized from toluene in shiny yellow needles, m.p. 155°. The *N-benzoyl derivative*, prepared by shaking vigorously for 15 min. a mixture of 3 g. of the amine, 3 g. of dry pyridine, and 3 g. of benzoyl chloride, crystallized from aqueous ethanol in shiny colorless prisms, m.p. 96°, b.p. 222–223°/12 mm.

Anal. Calcd. for $C_{19}H_{23}NO$: N, 5.0. Found: N, 4.7.

The *N-acetyl derivative*, prepared in the same way, crystallized from aqueous ethanol in colorless prisms, m.p. 98°.

Attempted Bischler-Napieralski reactions. The attempted cyclizations of the two foregoing amides were performed with: (1) phosphorus oxychloride; (2) phosphorus pentoxide in boiling tetralin for 17 hr.; (3) fused zinc chloride. In no instance did the working up of the reaction mixture furnish any trace of a base, other than partly recovered starting amine (characterization was done through the picrate). In an attempted Knorr-Paal reaction, a mixture of 1.5 g. of α,α-dimethyl-β-(4-ethylphenyl)ethylamine and 3 g. of acetonylacetone was refluxed for 5 hr., but vacuum distillation yielded only the starting material.

α,α-Dimethyl-β-(4-isopropylphenyl)propionylbenzene (II; R = *i*-C_3H_7, R′ = H). Prepared as for the lower homolog, and with the same yield, from 62 g. of *p*-isopropylbenzyl chloride, 60 g. of isobutyrophenone, and 25 g. of sodium amide, this *ketone* was a pale yellow oil, b.p. 212–213°/12 mm., n_D^{20} 1.5502.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.7; H, 8.6. Found: C, 85.4; H, 8.5.

Cleavage of 30 g. of this ketone by means of 11 g. of sodium amide in 600 ml. of toluene (15 hours' refluxing) furnished 22 g. (94%) of *α,α-dimethyl-β-(4-isopropylphenyl)propionamide* (III; R = *i*-C_3H_7, R′ = H), b.p. 203°/12 mm., crystallizing from cyclohexane in shiny colorless leaflets, m.p. 105°.

Anal. Calcd. for $C_{14}H_{21}NO$: N, 6.4. Found: N, 6.5.

Hofmann degradation of 22 g. of this amide yielded 11 g. (51%) of *α,α-dimethyl-β-(4-isopropylphenyl)ethyl isocyanate* (IV; R = *i*-C_3H_7, R′ = H), a colorless oil, b.p. 160°/22 mm., n_D^{24} 1.5095.

Anal. Calcd. for $C_{14}H_{19}NO$: N, 6.5. Found: N, 6.2.

α,α-Dimethyl-β-(4-isopropylphenyl)ethylamine (V; R = *i*-C_3H_7, R′ = H). Hydrolysis of 11 g. of the foregoing isocyanate with 120 ml. of hydrochloric acid yielded 7 g. (72%) of this *amine* as a colorless oil, b.p. 129°/13 mm., n_D^{20} 1.5090.

Anal. Calcd. for $C_{13}H_{21}N$: N, 7.3. Found: N, 7.4.

The corresponding *hydrochloride* crystallized from ethanol-benzene in colorless, sublimable needles, m.p. 207° (decomp.). The *picrate* crystallized from benzene in short yellow needles, m.p. 168°.

α,α-Dimethyl-β-(3,4-dimethylphenyl)propionylbenzene (II; R = R′ = CH_3). Prepared from 74 g. of 3,4-dimethylbenzyl chloride, 70 g. of isobutyrophenone, and 28 g. of sodium amide, this ketone was a pale yellow viscous oil, b.p. 210–211°/12 mm., n_D^{19} 1.5633; yield: 70 g. (55%).

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 86.0; H, 8.3.

α,α-Dimethyl-β-(3,4-dimethylphenyl)propionamide (III; R = R′ = CH_3), b.p. 198–199°/11 mm., obtained by cleavage of 70 g. of the foregoing ketone with 18 g. of sodium amide, crystallized from petroleum ether in colorless needles, m.p. 82°; yield: 46.5 g. (86%).

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.1; H, 9.3. Found: C, 75.8; H, 9.1.

α,α-Dimethyl-β-(3,4-dimethylphenyl)ethyl isocyanate (IV; R = R′ = CH_3), prepared in 51% yield (23 g.) from 46 g. of the foregoing amide, was a colorless liquid, b.p. 147–148°/13 mm., n_D^{21} 1.5200.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.6; H, 8.6.

α,α-Dimethyl-β-(3,4-dimethylphenyl)ethylamine (V; R = R′ = CH_3). Obtained in 95% yield from the foregoing isocyanate, this *amine* was a colorless oil, b.p. 130°/14 mm., n_D^{21} 1.5240. Its *hydrochloride* crystallized from ethanol-benzene in colorless, sublimable needles, m.p. 223° (decomp.).

Anal. Calcd. for $C_{12}H_{20}ClN$: N, 6.6. Found: N, 6.5.

The *picrate* crystallized from xylene in shiny, bright yellow needles, m.p. 187° (decomp. above 175°).

The *N-benzoyl derivative*, b.p. 223–224°/12 mm., crystallized from cyclohexane in shiny colorless prisms, m.p. 140°.

Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.1; H, 8.2. Found: C, 80.9; H, 8.1.

The Bischler-Napieralski reaction was performed by refluxing for 12 hr. a solution of 7 g. of this amide and 35 ml of phosphorus oxychloride in 70 ml. of dry xylene; after cooling, the supernatant liquid was decanted, the dark residue basified with aqueous sodium hydroxide, and the reaction product taken up in ether. The residue from evaporation of the solvent was treated with picric acid in benzene, and the very small quantity of picrate obtained crystallized from the same solvent in yellow prisms, decomposing above 230°, but no further identification was possible, for want of material.

α,α-Dimethyl-β-(4-chlorophenyl)propionylbenzene (II; R = Cl, R′ = H). This ketone was prepared from 72 g. of *p*-chlorobenzyl chloride, 70 g. of isobutyrophenone, and 28 g. of sodium amide in toluene, the time of heating being extended to 48 hr. Yield: 40 g. (31%) of a product boiling at 218–219°/13 mm., and crystallizing from ethanol in colorless prisms, m.p. 75°.

Anal. Calcd. for $C_{17}H_{17}ClO$: C, 74.8; H, 6.2. Found: C, 75.0; H, 6.3.

This ketone gave an *oxime*, m.p. 165° (sintering at 161°). Cleavage of 40 g. of the ketone by means of 12 g. of sodium amide (10 hours' refluxing in toluene) afforded 17 g. (55% yield) of *α,α-dimethyl-β-(4-chlorophenyl)propionamide* (III; R = Cl, R′ = H), b.p. 218°/13 mm., crystallizing from cyclohexane in colorless prisms, m.p. 100°.

Anal. Calcd. for $C_{11}H_{14}ClNO$: C, 62.4; H, 6.6. Found: C, 62.1; H, 6.5.

α,α-Dimethyl-δ-phenylvalerophenone (VII). Prepared by refluxing for 8 hr. a solution of 199 g. of δ-phenylbutyl bromide in 750 ml. of toluene with the sodio-derivative from 148 g. of isobutyrophenone, this ketone was a pale yellow oil, b.p. 226°/21 mm., n_D^{22} 1.5556. The excellent yield obtained (220 g., 83%), in contrast with the relatively low yield of the ketones derived from benzyl chloride, is probably due to the absence of steric hindrance.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.7; H, 8.5.

Cleavage of this ketone (220 g.) by means of sodium amide (50 g.) was also effected in considerably higher yield 135 g. (79%) of *α,α-dimethyl-δ-phenylvaleramide* being obtained after only 6 hours' refluxing. The product crystallized from cyclohexane in colorless needles, m.p. 92°.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.1; H, 9.3. Found: C, 76.0; H, 9.3.

On the other hand, the Hofmann degradation of this amide (80 g.) gave a considerably lower yield (34%, 27 g.) of *α,α-dimethyl-δ-phenylbutyl isocyanate*, as a colorless oil, b.p. 154°/18 mm., n_D^{22} 1.5236.

Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.8; H, 8.4. Found: C, 76.5; H, 8.5.

Hydrolysis of 27 g. of this isocyanate gave only 3 g. of *α,α-dimethyl-δ-phenylbutylamine* (VIII), as a colorless liquid, b.p. 148°/21 mm., n_D^{25} 1.5348. The corresponding *hydrochloride* was obtained in ether medium as colorless, sublimable needles, m.p. 189° (decomp.).

Anal. Calcd. for $C_{12}H_{20}ClN$: Cl, 16.6. Found: Cl, 16.3.

PARIS V^e, FRANCE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF PHARMACY, UNIVERSITY OF ILLINOIS]

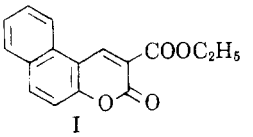
Catalytic Hydrogenation of Ethyl 5,6-Benzocoumarin-3-carboxylate[1]

JAMES E. GEARIEN AND KENNETH J. LISKA

Received July 2, 1957

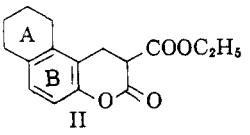
The stepwise hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I), using W-1 Raney nickel as the catalyst, yielded ethyl 2,3,7,8,9,10-hexahydro-3-keto-1*H*-naphtho[2,1-*b*]pyran-2-carboxylate (II), 2-(2-hydroxy-5,6,7,8-tetrahydro-1-naphthylmethyl)propane-1,3-diol (III), and 1-isobutyl-2-decalol (IV), the last identified tentatively. At low pressure, with platinum oxide as the catalyst, and in the presence of hydrochloric acid, I yielded diethyl (2-hydroxy-1-naphthylmethyl)-malonate (V). Characterization of I and of its hydrogenated derivatives was accomplished by conversion to the amides.

In the course of an investigation leading to the preparation of several compounds with possible medicinal activity, it became necessary to study the stepwise hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I).



I

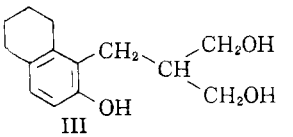
Saturation of the 3,4 double bond in I was reported by Smith and Horner[2] who obtained ethyl 3,4-dihydro-5,6-benzocoumarin-3-carboxylate by the low pressure hydrogenation of I at room temperature and in the presence of small amounts of Raney nickel catalyst. It was found that the time of this reaction could be greatly decreased if a higher ratio of catalyst to unsaturated compound was employed. When hydrogenations using large amounts of Raney nickel were allowed to proceed for over 24 hours a previously unreported compound was isolated in high yield. This new compound was prepared more conveniently by hydrogenating I at room temperature and at pressures up to 1900 pounds per square inch. Ultraviolet and infrared analyses showed this compound to be ethyl 2,3,-7,8,9,10 - hexahydro - 3 - keto - 1*H* - naphtho - [2,-1-*b*]pyran-2-carboxylate (II). The ultraviolet spectrum of II in cyclohexanol exhibited maxima at 274 and 283 millimicrons, indicating the oxygenated tetralin structure.[3] The infrared spectrum, in liquid petrolatum, showed carbonyl absorption both at 1729 and 1760 cm.$^{-1}$, attributable to a saturated ester group and a vinyl type lactone, respectively. This carbonyl absorption was identical with that of the simple dihydrobenzocoumarin. A 1,2,3,4-tetrasubstituted benzene structure[4] in II was confirmed by an infrared absorption band at 816 cm.$^{-1}$ A vinyl type lactone function in II and a 1,2,3,4-tetrasubstituted benzene ring can exist only if ring B is aromatic.



II

The formation of II in the W-1 Raney nickel catalyzed hydrogenation of I confirms Stork's postulation[5] that almost any type of substitution on one benzene ring of naphthalene will stabilize that ring toward reduction.

At 90°, and under a hydrogen pressure of 1520 pounds per square inch, hydrogenation of I yielded a mixture of products. Only one compound, 2-(2 - hydroxy - 5,6,7,8 - tetrahydro - 1 - naphthylmethyl)propane-1,3-diol (III) was isolated from the



III

mixture. The ultraviolet absorption curve of III in 95% ethanol, exhibited a single, somewhat broad

(1) Abstracted from a thesis submitted by Kenneth J. Liska to the faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1956.

(2) L. Smith and L. Horner, Jr., *J. Am. Chem. Soc.*, **60**, 678 (1938).

(3) R. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley, New York, N. Y., 1951, Spectrum No. 52.

(4) P. Launer and D. McCauley, *Anal. Chem.*, **23**, 1975 (1951).

(5) G. Stork, *J. Am. Chem. Soc.*, **69**, 576 (1947).