The residual oil was dissolved in ether and treated with ether saturated with hydrogen chloride. The resulting mixture was concentrated to dryness in a stream of nitrogen and the residue upon trituration with ether yielded 60 mg. of crystalline VI ($R = CH_3$) hydrochloride, m.p. 190–192°. A mixed melting point with authentic amitriptyline hydrochloride showed no depression, m.p. 190.5–193°. This material had an infrared spectrum in chloroform identical with that of amitriptyline hydrochloride; $\lambda_{\max}^{\text{MeOH}}$ 240 mμ (13,800).

Anal. Calcd. for $C_{20}H_{24}NCl$: C, 76.53; H, 7.71; N, 4.46. Found: C, 76.24; H, 7.63; N, 4.58.

5-(γ-Methylaminopropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (VI. R = H) Hydrochloride.—In the same manner as described for the preparation of VI ($R = CH_3$) a 100-mg. sample (0.372 mmole) of 5-(γ-chloropropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (III. X = Cl) was converted to VI (R = H). The latter was converted to its hydrochloride in ether solution, (50 mg.), m.p. 200–210°, which after recrystallization from ether–ethanol, melted at 213–215°. A mixed melting point with authentic material showed no depression; $\lambda_{\max}^{\text{MeOH}}$ 240 mμ (13,900).

Anal. Calcd. for $C_{19}H_{22}NCl$: C, 76.10; H, 7.39; N, 4.67. Found: C, 75.61; H, 7.05; N, 4.38.

5-(γ-Aminopropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (V) Hydrochloride.—(a) A solution of 1.0 g. (3.19 mmoles) of 5-(γ-bromopropylidene) 5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (III. X = Br) in 25 ml. of absolute ethanol in a Carius tube was saturated with anhydrous ammonia at 0°. The tube was sealed, allowed to stand at 100° for 18 hr., then cooled and opened. The clear, light tan ethanol solution was taken to dryness *in vacuo*, the residue treated with charcoal in ethanol, filtered, and again taken to dryness *in vacuo*. Trituration of the residue with benzene yielded 900 mg. of crystalline material. A 500-mg. sample of this material was dissolved in 50 ml. of hot water and the resulting cloudy solution filtered, the filtrate cooled and treated with 5% potassium bicarbonate solution to a pH of 9. The aqueous mixture was extracted with three 20-ml. portions of ethyl acetate and the combined extracts were dried over magnesium sulfate and taken to dryness *in vacuo*. The residual oil was dissolved in 18 ml. of ether and treated with 8 ml. of ether saturated with hydrogen chloride to precipitate V as its hydrochloride (230 mg.), m.p. 245–255°. Recrystallization from ethanol yielded material, m.p. 258–263°; $\lambda_{\max}^{\text{MeOH}}$ 239 mμ (13,700).

Anal. Calcd. for $C_{18}H_{20}NCl$: C, 75.65; H, 7.05; Cl, 12.40. Found: C, 75.35; H, 7.33; Cl, 12.19.

(b) A solution of 1.30 g. (7 mmoles) of potassium phthalimide in 15 ml. of dimethylformamide and 2 ml. of water was added to 1.78 g. (6.6 mmoles) of 5-(γ-chloropropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (III. X = Cl) in 10 ml. of dimethylformamide, and the resulting clear solution heated on a steam bath for 16 hr. The reaction mixture was then cooled to room temperature and diluted with 25 ml. of chloroform and 150 ml. of water. The aqueous layer was extracted with two 15-ml. portions of chloroform, and the combined chloroform extracts washed successively with 15 ml. of water, 15 ml. of 0.2 *N* sodium hydroxide, 15 ml. of water, and 20 ml. of saturated salt solution. The chloroform solution was dried over magnesium sulfate and taken to dryness *in vacuo*. The solid white residue after trituration with 50% ether–petroleum ether and filtration yielded 1.18 g. (3.1 mmoles) of 5-(γ-phthalimidopropylidene)-5H-dibenzo-[*a,d*]-10,11-dihydrocycloheptene which had m.p. 140–146° and $\lambda_{\max}^{\text{CHCl}_3}$ 5.7 and 5.9 μ. This material without further purification was refluxed for 2 hr. with 185 mg. (3.1 mmoles) of hydrazine hydrate in 10 ml. of 95% ethanol. The mixture was cooled to room temperature and acidified with concentrated hydrochloric acid until acid to Congo Red paper, filtered, and the precipitate washed with 95% ethanol. The precipitate was dissolved in 35 ml. of hot water, filtered through Celite, and taken to dryness *in vacuo*. The residue was recrystallized by dissolving in ethanol, concentration to 10–15 ml. followed by dilution with 20 ml. of ether to yield 400 mg. of 5-(γ-aminopropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (V) hydrochloride, m.p. 256–262°. An additional 240 mg. was obtained from the aqueous ethanolic mother liquors.

Rate Study Procedures.—(a) The acid hydrolysis of the 5-hydroxy-5-cyclopropyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (II) was followed by measuring the increase of absorption with time at 240 mμ on a Bausch & Lomb 505 recording spectrometer. A 2-ml. sample of a stock solution of 15 mg. of the carbinol in 500 ml. of spectro grade dioxane (12.0×10^{-5} moles/l.) were mixed with 2 ml. of the appropriate molarity stock solution of aqueous perchloric acid (*e.g.*, 0.2 *M* stock solution for a 0.1 *M* final reaction mixture) directly in the cell. Measurements made at 25°.

(b) The rearrangement of the *i*-steroid (VIII) was followed by measuring the decrease in rotation at 365 mμ on a Zeiss photoelectric precision polarimeter. A 2-ml. sample of a stock solution of 10 mg. of the steroid in 10 ml. of spectro grade dioxane (3.46×10^{-3} moles/l.) were mixed with 2 ml. of the appropriate molarity stock solution of aqueous perchloric acid and placed in a 1-dm. cell. Measurements made at 24°.

The *K*'s were calculated from the equation $Kt = \ln (a/a - x)$, where t = time (sec.), a = initial concentration of reactant (moles/l.), and x = concentration of product (moles/l.) at time t.

A New Interpretation of the Lithium Aluminum Hydride Reduction of Arylaminomethylenemalonate Esters

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Received August 20, 1962

The lithium aluminum hydride reduction of diethyl 2-naphthylaminomethylenemalonate (*4*) is shown unequivocally to yield 2-(2-naphthylaminomethyl)-2-propen-1-ol (*5*). This result proves that the previous interpretation[2] of the reduction is in error. A mechanism for this conversion is presented.

During the course of some synthetic studies, we reduced diethyl 2-pyridylaminomethylenemalonate (*1*) with lithium aluminum hydride. A single product, isolated in 78% yield, was assigned the 2-(2-pyridylaminomethyl)-2-propen-1-ol structure (*2*) on the basis of analysis of the fumarate salt, and infrared and nuclear magnetic resonance (n.m.r.) spectra. Catalytic hydrogenation of compound *2* gave a dihydro amino alcohol for which the

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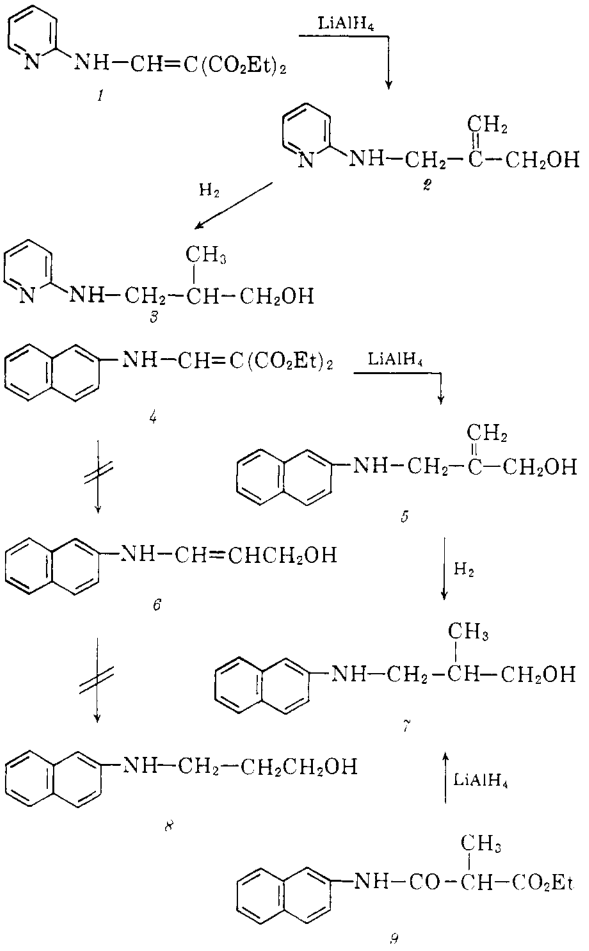
[2] R. L. Shivalkar and S. V. Sunthankar, *J. Am. Chem. Soc.*, **82**, 718 (1960).

anticipated structure *3* was fully supported by analysis and spectra.

Subsequently an article appeared by Shivalkar and Sunthankar[2] which described the lithium aluminum hydride reduction of several arylaminomethylenemalonate esters. In the case of the reduction of compound *1*, these workers reported a cleavage product, 2-aminopyridine. Further, the reduction of diethyl 2-naphthylaminomethylenemalonate (*4*) was said to yield 3-(2-naphthylamino)-allyl alcohol (*6*) "as the result of partial hydrogenolysis." Because their result was completely different from ours in the former case and their interpretation of reductions involving hydrogenolysis was at variance with our view of the reaction, we investigated the lithium aluminum hydride reduction of diethyl 2-naphthylaminomethylenemalonate (*4*) in order to be able to compare directly with the previous results. Compound *4* was treated with four moles of lithium aluminum hydride in ether at room temperature. A crystalline product was obtained in theoretical yield; however, this material was found to darken upon standing, and after recrystallization, only a 50% yield of pure product was obtained. Our product appears to be the same as that reported,[2] the only available criterion being melting point. However, the correct structure for this compound is 2-(2-naphthylaminomethyl)-2-propen-1-ol (*5*). Supporting evidence for this structural assignment includes infrared and n.m.r. spectra and analysis. Catalytic hydrogenation of compound *5* gave 2-methyl-3-(2-naphthylamino)propanol (*7*) which also agrees in melting point with the compound incorrectly identified[2] as *8*. Infrared spectrum and analysis of the dihydro compound are compatible with structure *7*.

Final proof for the correctness of assignment of the hydride reduction product as *5* rests on the unambiguous synthesis of the dihydro compound *7*. 2-Naphthylamine was condensed with diethyl methylmalonate to give the amido ester (*9*) in 45% yield. This compound was reduced with lithium aluminum hydride to give a 75% yield of 2-methyl-3-(2-naphthylamino)propanol (*7*), identical by mixed melting point and comparison of the infrared and ultraviolet spectra with the sample obtained by hydrogenation of *5*. From these results it would seem reasonable to conclude that the products from other arylaminomethylenemalonate ester reductions involving hydrogenolysis also have incorrect structural assignments.[2] We are still at a loss to explain the course of the reactions reported to cause cleavages.[3]

The path of the reaction is easily explainable in the light of other hydride reduction mechanisms.



The first step involves the abstraction by hydride of the proton on the nitrogen to give compound *10;* this anion would exist as a resonance hybrid with the form *11*. Hydride replacement of the ethoxy group leads to *12*. A second attack of hydride ion at the carbon atom bearing the metaloxy group gives *13*, which, by a retrograde shift of electrons, can then lose the metaloxy function leaving compound *14*. Excess hydride would then complete the sequence from *14* to the final product *15*, since *14* contains simply an ester group and a Schiff's base, the reductions of which are well documented.[4] The Schiff's base, being formed essentially in the first step, could of course be reduced in one of the early steps before the canonical form *14* is reached. However, the order of reducible groups does not affect the over-all course of the reaction.

Analogy for this mechanism is drawn from the work of Dreiding and Hartman[5] who described the lithium aluminum hydride reduction of 1,3-dicarbonyl compounds. In their reduction of 2-carbethoxycyclohexanone (*16*), an intermediate of structure *17* is reached. Here attack of hydride at

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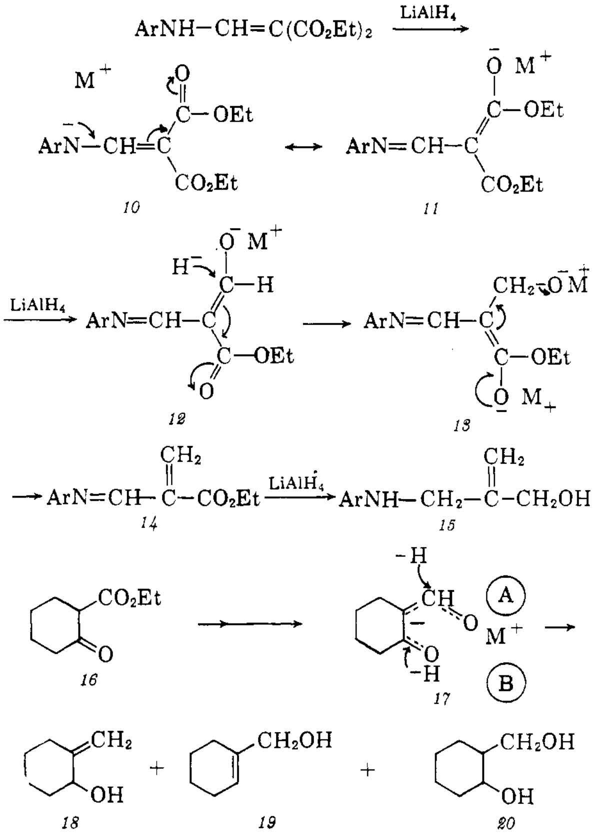
(3) Since the previous article[2] fails to specify exact experimental procedures for some of the compounds, we are uncertain as to the conditions used for the reduction of compound *1*. Therefore we subjected the pyridyl compound (*1*) to the most severe conditions previously mentioned and were able to isolate only methylene alcohol (*3*).

(4) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 391 and 796.

(5) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).



A and B leads to the formation of different products [2-methylenecyclohexanol (*18*) and 1-cyclohexenemethanol (*19*), respectively]. However, in our case attack of hydride at either site of the 1,3-dicarbonyl system will necessarily give the same product because of the symmetry of the malonate function. The unsaturated alcohols in the former case[5] arise from hydride reduction of the enolate form, while a small yield of the expected diol (*20*) is formed in the normal fashion from the non-enolized portion. Our examples, on the other hand, possess a very acidic proton and would be expected to be found almost completely in the enolate form in the presence of excess hydride. It is not surprising then that we were unable to detect any of the unsaturated diol.

Experimental[6]

Diethyl 2-pyridylaminomethylenemalonate (*1*) was prepared according to the method of Lappin,[7] m.p. 67.5–68° (T-H) (lit.[7] m.p. 65–66°), after recrystallization from ethanol. The product shows infrared absorption[8] at 3270 cm.$^{-1}$ (N-H), 1695 and 1678 cm.$^{-1}$ (ester carbonyl), 1601 cm.$^{-1}$ (C=C) and 1247 and 1228 cm.$^{-1}$ (C—O of ester). The ultraviolet spectrum shows maxima at 274 and 322 mμ (ϵ 10,005; 30,010).

Anal. Calcd. for $C_{13}H_{16}N_2O_4$: N, 10.60. Found: N, 10.73.

2-(2-Pyridylaminomethyl)-2-propen-1-ol (*2*).—A. A solution of 39.6 g. (0.15 mole) of diethyl 2-pyridylaminomethylenemalonate in 600 ml. of anhydrous ether was added during 5 hr. to a well stirred mixture of 14.0 g. (0.35 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether at such a rate as to maintain gentle refluxing. After the addition, the mixture was refluxed for 4 hr., then stirred at room temperature for 15 hr. The mixture was decomposed with wet ether (U.S.P.) and then quenched in a mixture of ice and 330 ml. of 3 *N* hydrochloric acid. The organic layer was extracted with dilute aqueous acid solution. The combined aqueous acid solution was made basic and extracted with ether. The ether portions were combined, dried with anhydrous magnesium sulfate, and concentrated. The residual oil was fractionally distilled to give 19.2 g. (78%) of a golden oil, b.p. 128–134° (0.1 mm). The product shows infrared absorption[9] at 3470–3185 cm.$^{-1}$ (N—H, O—H), 1605 cm.$^{-1}$ (C=C), 1504 cm.$^{-1}$ (N—H bending), and 908 cm.$^{-1}$ (>C=CH$_2$) with ultraviolet maxima at 243 and 305 mμ (ϵ 14,900; 4130).

The hydrogen fumarate of this compound was prepared in 2-propanol solution and recrystallized from a 2-propanol–ether mixture, m.p. 110–111.5° (K). The solid exhibits infrared absorption[8] at 3350 cm.$^{-1}$ (N—H), 2610 cm.$^{-1}$ (broad, N—H of salt), 1705 and 1680 cm.$^{-1}$ (acid carbonyl), and 907 cm.$^{-1}$ (>C=CH$_2$) with ultraviolet absorption at 242 and 305 mμ (ϵ 16,000; 4230).

Anal. Calcd. for $C_{13}H_{16}N_2O_5$: C, 55.71; H, 5.75; N, 10.00. Found: C, 55.55; H, 6.08; N, 10.16.

B. To a slurry of 3.0 g. (0.08 mole) of lithium aluminum hydride in 100 ml. of purified tetrahydrofuran[10] was added a solution containing 5.0 g. (0.02 mole) of diethyl 2-pyridylaminomethylenemalonate in 50 ml. of tetrahydrofuran[10] in 5 min. The addition caused refluxing which was continued with external heating for 1.5 hr. The mixture was decomposed by the careful addition of 15 ml. of water. Ether was added, and the mixture was then stirred for 1 hr. and filtered. The filter cake was washed with ether and the combined organic portions concentrated giving 3.1 g. (100%) of a clear oil whose infrared spectrum was the same as that of the product described above. This oil was distilled to give 2.25 g. (73%), b.p. 105° (0.05 mm.), n^{23}D 1.5713. A sample was converted to the acid fumarate, m.p. 111–113° (K), which was identical to the salt described in A by infrared spectrum and mixed melting point.

The n.m.r. spectrum of the free base exhibits a signal at 4.07 p.p.m. (methylene protons adjacent to nitrogen), a partially resolved peak at 4.12 p.p.m. (methylene protons adjacent to oxygen) a multiplet at 5.09 p.p.m. (terminal vinyl protons) and complex signals at 6.55, 6.68, 7.48, and 8.09 p.p.m. ($\beta,\beta,\gamma,\alpha$ protons of pyridyl ring). The areas of these signals are in the ratio of 2:2:2:1:1:1:1.

2-Methyl-3-(2-pyridylamino)propanol (*3*).—2-(2-Pyridylaminomethyl)-2-propen-1-ol (4.11 g., 0.03 mole) in 75 ml. of absolute ethanol was hydrogenated at room temperature and atmospheric pressure using 0.1 g. of prereduced platinum oxide catalyst. After 95% of the theoretical amount of hydrogen had been taken up, the mixture was filtered and concentrated. The residue was fractionally distilled giving 3.6 g. (87%) of a viscous clear oil, b.p. 92–95° (0.1 mm.), n^{27}D 1.5562. The product exhibits infrared absorption[11] at 3400 cm.$^{-1}$ (O—H) 3190 cm.$^{-1}$ (N—H), 1600 cm.$^{-1}$ (pyridine) and 1440 and 1380 cm.$^{-1}$ (C—CH$_3$) with ultraviolet absorption at 244 and 308 mμ (ϵ 14,500; 3700).

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(6) Melting points were taken on a Kofler block (K) and a Thomas-Hoover capillary apparatus (T-H) and are corrected. Infrared spectra were measured with a Model 21 Perkin-Elmer infrared spectrophotometer, and the ultraviolet spectra, in methanol, with a Model 14 Cary spectrophotometer. Analyses were performed by the Scandinavian Microanalytical Laboratory. Nuclear magnetic resonance spectra were measured at 60 Mc. on a Varian Model A-60 spectrometer in deuterioacetone solution with added hydrochloric acid vapor using tetramethylsilane as internal standard.

(7) G. R. Lappin, *J. Am. Chem. Soc.*, **70**, 3348 (1948).

(8) Determined as a Nujol mull.

(9) Determined in carbon tetrachloride solution.

(10) Dried over potassium hydroxide pellets, then distilled from lithium aluminum hydride.

(11) Determined in chloroform solution.

Anal. Calcd. for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.85. Found: C, 64.86; H, 8.56; N, 16.63.

Diethyl 2-Naphthylaminomethylenemalonate (*4*).—A mixture of 14.3 g. (0.1 mole) of 2-naphthylamine, 21.6 g. (0.1 mole) of diethyl ethoxymethylenemalonate, and 200 ml. of benzene was refluxed for 2 hr., then concentrated. The residue solidified and after two recrystallizations from methanol gave 27.0 g. (87%) of solid, m.p. 78–80° (T-H).[12] The product shows infrared absorption[13] at 3150 cm.$^{-1}$ (N—H), 1682 cm.$^{-1}$ (ester carbonyl), 1605 cm.$^{-1}$ (C═C), and 1235 cm.$^{-1}$ (broad, C—O of ester) with ultraviolet absorption at 277, 287, and 328 mμ (ϵ 15,300; 22,200; and 32,600).

2-(2-Naphthylaminomethyl)-2-propen-1-ol (*5*).—To a suspension of 19.5 g. (0.52 mole) of lithium aluminum hydride in 350 ml. of anhydrous ether was added a slurry of 40 g. (0.13 mole) of diethyl 2-naphthylaminomethylenemalonate in 500 ml. of anhydrous ether. The mixture was stirred at room temperature for 15 hr. and then decomposed by the careful addition of 97.5 ml. of water. The mixture was stirred for 2 hr. and filtered. The filter cake was washed with ether. The filtrate and wash were combined, dried with anhydrous magnesium sulfate, and concentrated. The residual solid, which darkened on standing, was washed with ether, recrystallized once from benzene, and washed with ether to give 13.5 g. (50%) of a white solid, m.p. 103.5–105.5° (T-H). An analytical sample (three recrystallizations from benzene) melted at 111–112.2° (K).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.57; H, 7.18; N, 6.68.

The product exhibits infrared absorption[13] at 3280 cm.$^{-1}$ (O—H), 3175 cm.$^{-1}$ (N—H), 1035 cm.$^{-1}$ (C—O), and 898 cm.$^{-1}$ ($>C{=}CH_2$) with ultraviolet absorption at 244, 273, 283, and 293 mμ (ϵ 51,600; 7160; 9600; 8430).

The n.m.r. spectrum exhibits single peaks at 4.05 and 4.30 p.p.m. (methylene protons adjacent to nitrogen and oxygen, respectively), a partially resolved multiplet at 5.29 p.p.m. (terminal vinyl protons) and a complex pattern between 7.14 and 7.90 p.p.m. (naphthyl protons). The areas of these signals are in the ratio of 2:2:2:7.

2-Methyl-3-(2-naphthylamino)propanol (*7*).—2-(2-Naphthylaminomethyl)-2-propen-1-ol (10 g., 0.05 mole) in 150 ml. of ethyl acetate was hydrogenated at room temperature using 0.5 g. of platinum oxide catalyst. Theoretical uptake of hydrogen was complete in 5 min. The mixture was filtered and concentrated leaving a dark oil which was crystallized from an ether–petroleum ether mixture to yield 8.36 g. (83%) of solid, m.p. 61–67° (T-H). An analytical sample (two recrystallizations from a benzene–hexane mixture) melted at 75.5–76° (K).

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 77.94; H, 8.03; N, 6.49.

The product shows infrared absorption[13] at 3245 cm.$^{-1}$ (N—H, shoulder at 3380 cm.$^{-1}$, O—H), 1042 cm.$^{-1}$ (C—O) with ultraviolet absorption at 245, 273 (s), 284 and 293 mμ (ϵ 50,700; 6740; 9780; 8930).

Ethyl 2-(2-Naphthylcarbamoyl)propionate (*9*).—A mixture of 7.2 g. (0.05 mole) of 2-naphthylamine and 43.5 g. (0.25 mole) of diethyl methylmalonate was refluxed for 16 hr. Then the excess diester was removed by distillation under vacuum. The residue was triturated with methylene chloride; a glistening purple solid (0.9 g.) m.p. 223–225° (T-H) was removed by filtration. The filtrate was extracted with dilute aqueous acid solution, dried, and concentrated. The residual oil solidified on standing, and upon trituration with ether yielded 9.5 g. of white solid, m.p. 107–118° (T-H), and 0.65 g. of solid, m.p. 75–97°. This latter crop was washed with ether and combined with the first crop. The combined material was recrystallized once from benzene and once from ethyl acetate to give 6.0 g. (45%), m.p. 121.5–123° (T-H). An analytical sample (two recrystallizations from ethyl acetate and a benzene–hexane mixture) melted at 122–123° (K).

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.63; H, 6.32; N, 5.17.

The product exhibits infrared absorption[13] at 3300 cm.$^{-1}$ (N—H), 1741 cm.$^{-1}$ (ester carbonyl), and 1654 cm.$^{-1}$ (amide carbonyl) with ultraviolet absorption at 243, 250 (s), 273, 284, and 295 mμ (ϵ 51,200; 41,000; 7940; 9050; 6320).

2-Methyl-3-(2-naphthylamino)propanol (*7*) **from Hydride Reduction of Ethyl 2-(2-Naphthylcarbamoyl)propionate** (*9*).—To a suspension of 4.0 g. (0.11 mole) of lithium aluminum hydride in 100 ml. of purified tetrahydrofuran[10] was added a solution containing 4.95 g. (0.018 mole) of ethyl 2-(2-naphthylcarbamoyl)propionate in 150 ml. of tetrahydrofuran.[10] The resulting mixture was refluxed for 6 hr., cooled, and decomposed by the careful addition of 21 ml. of water. Ether was added, and the mixture stirred for 1 hr. and then filtered. The filter cake was washed with ether; the combined filtrate and wash was concentrated. The residual oil was taken up in ether, treated with Darco and Norit, filtered, and brought to the cloud point with petroleum ether. The solution deposited 2.9 g. of solid, m.p. 72–74° (K), and then 0.2 g., m.p. 67.5–72° (K) (total yield 80%). An analytical sample (three recrystallizations from benzene) melted at 77–77.5° (K).

Anal. Calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.12; H, 7.99; N, 6.49.

The product shows infrared absorption[13] at 3245 cm.$^{-1}$ (N—H, shoulder at 3380 cm.$^{-1}$, O—H), 1042 cm.$^{-1}$ (C—O) with ultraviolet absorption at 245, 273, 284, and 293 mμ (ϵ 52,200; 6870; 9940; 9040).

The infrared spectra of this sample and that prepared from *5* as described above were identical. The melting point of the two samples upon admixture was 75–75.5° (K).

Acknowledgment.—The authors wish to thank Dr. G. I. Poos for his helpful suggestions during the course of this work and also Dr. H. R. Almond, Jr., for measuring, and help with the interpretation of, the n.m.r. spectra.

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[12] R. E. Foster, R. D. Lipscomb, T. J. Thompson, and C. S. Hamilton, *J. Am. Chem. Soc.*, **68**, 1327 (1946), reported m.p. 78–78.5°.

[13] Determined in a potassium bromide pellet.