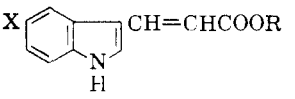
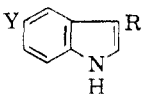
TABLE I



Compound	X	R	M.p., °C.	Formula	% Calcd. C	% Calcd. H	% Calcd. N	% Found C	% Found H	% Found N
I	$N(CH_2CH_2Cl)_2$	H								
II[a]	NH_2	Et	98–99	$C_{12}H_{14}N_2O_2$	67.8	6.13	12.2	67.3	6.18	12.1
III[b]	NO_2	H	202–204	$C_{11}H_{18}N_2O_6$	55.8	3.62	11.8	55.4	3.60	11.9
IV	NO_2	Me	192–195	$C_{12}H_{10}N_2O_4$	58.5	4.09	11.4	58.2	4.18	11.3
V[c]	$C_6H_5CH_2OCONH$	H	210.5–211.5	$C_{19}H_{16}N_2O_3$	67.9	4.80	8.33	68.2	5.24	8.20
VI[d]	$C_6H_5CH_2OCONH$	Et	189.5–191.5	$C_{21}H_{20}N_2O_3$	69.2	5.53	7.69	69.0	5.66	7.77

[a] Prepared by hydrogenation of 500 mg. of VI with 50 mg. of 5% palladium-on-carbon in absolute ethanol at 1 atm. for 4.25 hr. and recrystallization of the product from benzene; λ_{max}^{EtOH} 232 mμ (ε 21,900), 282 (10,700), 339 (13,000), in sharp contrast to methyl 5-aminoindole-3-propionate (see ref. 1a), which had λ_{max}^{EtOH} 280 mμ (ε 5400), 310 (3400). [b] Prepared by Doebner (see K. N. Shaw, A. McMillan, A. G. Gundmunson, and M. D. Armstrong, *J. Org. Chem.*, **23,** 1171 (1958); "Organic Reactions," Vol. I, Roger Adams, Ed., John Wiley and Son, New York, N. Y., 1942, p. 210) condensation of 5 g. of VII with 5 g. of malonic acid in 60 ml. of pyridine containing 0.5 ml. of piperidine at 90–100° for 15 hr. and recrystallization of the product from ethyl acetate; λ_{max}^{EtOH} 276 mμ (ε 19,200); analysis calculated for 0.25 H_2O of solvation. [c] Condensation at 45–55° for 27 hr. using the quantities of reagents described for preparation of III. The product was recrystallized from 90% aqueous acetone. [d] Prepared by mixed anhydride procedure using isobutyl chloroformate. The product was recrystallized from ethyl acetate (see B. R. Erlanger, W. V. Curran, and N. Kobowsky, *J. Am. Chem. Soc.*, **81,** 3051 (1959)).

TABLE II



Compound	Y	R	M.p., °C.	Formula	% Calcd. C	% Calcd. H	% Calcd. N	% Found C	% Found H	% Found N
VII[a]	NO_2	CHO	280–300 dec.	$C_9H_6N_2O_3$	56.8	3.18	14.7	56.7	3.41	15.1
VIII	$C_6H_5CH_2OCONH$	H	114–115	$C_{16}H_{14}N_2O_2$	72.2	5.30	10.5	72.4	5.29	10.3
IX[b]	$C_6H_5CH_2OCONH$	CHO	237.5–239.0	$C_{17}H_{14}N_2O_3$	69.4	4.80	9.52	69.2	5.10	9.67
X[c]	CH_3CONH	H	117–118	$C_{10}H_{10}N_2O$	69.0	5.79	16.1	69.3	5.96	16.2
XI[d]	CH_3CONH	CHO	231–234	$C_{11}H_{10}N_2O_2$	65.3	4.98	13.9	65.3	4.99	13.8

[a] Prepared by reaction of 5-nitroindole and N,N-dimethylformamide (DMF) in the presence of phosphoryl chloride (see G. F. Smith, *J. Chem. Soc.*, 3842 (1954)); previously prepared in low yield by the nitration of 3-formylindole (see G. Berti and A. DaSettimo, *Gazz. chim. ital.*, **91,** 728 (1961); W. E. Noland and R. D. Rieke, *J. Org. Chem.*, **27,** 2250 (1962)). [b] Prepared by reaction of VIII and DMF with phosphoryl chloride; an intermediate indolenine–enamine hydrochloride was the direct product on work-up and this had to be heated with 5% aqueous potassium carbonate to hydrolyze it to the aldehyde (IX) which was recrystallized from acetonitrile. [c] Prepared by reaction of 5-aminoindole and acetic anhydride in pyridine. [d] Prepared by reaction of X and DMF with phosphoryl chloride; the product was crystallized from ethanol; λ_{max}^{EtOH} 246 mμ (ε 23,600), 304 (11,500).

necessary intermediate, ethyl 5-aminoindole-3-acrylate (II) was prepared; however, the low yields encountered rendered impractical the preparation of I in quantities sufficient for biological evaluation.

Two approaches for the synthesis of II were investigated. The first, *via* 5-nitroindole-3-acrylic acid (III) failed when it was not found possible to reduce the nitro group of III or its methyl ester (IV) by various chemical or catalytic methods. The second, a successful approach, used 5-aminoindole as the starting material and utilized the selective hydrogenolysis of the carbobenzyloxy protecting group in the presence of the acrylate double bond. The properties of the new compounds isolated in the research are outlined in Tables I and II.

Synthesis of Nortriptyline and Related Compounds

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Received December 23, 1963

The recent publication[1] of methods for the synthesis of N-substituted 5-(3-aminopropylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptenes, of which a number are useful psychotherapeutic drugs, prompts us to report a new synthesis of one of these, nortriptyline (IX), using propargylic intermediates. The methods described have been used for the preparation of large quantities of nortriptyline hydrochloride as well as smaller amounts of various analogs and homologs.

Experimental

5-Hydroxy-5-(3-hydroxypropynyl)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (I).—To a stirred suspension of 156 g. (4 moles) of sodamide in 3 l. of liquid ammonia there was added over a period of 90 min. a solution of 166 g. (0.8 mole) of 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene-5-one,[1a] 112 g. (2 moles) of propargyl alcohol, and 800 ml. of dry toluene. A low temperature condenser (solid CO_2) was employed during the addition and for 30 min. thereafter. The ammonia was then allowed to evaporate. When room temperature was reached, 1 l. of toluene and 1 kg. of ice were added. The resulting suspension was filtered and the cake was washed with water and with ether until the aqueous filtrates were neutral. The crude product was then dried and dissolved in alcohol (*ca.* 25 ml./g.) containing about 0.25% acetic acid. The hot solution was decolorized, filtered, cooled, and then concentrated *in vacuo*. Crystallization gave 175 g. (83% yield), m.p. 187–195°. A sample was recrystallized from alcohol and acetone; m.p. 191–195°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.45; H, 6.14.

The dibenzoate prepared from benzoyl chloride in pyridine[2] and crystallized from carbon tetrachloride and benzene–hexane melted at 128–129°.

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 81.19; H, 5.32.

5-Hydroxy-5-(3-hydroxypropyl)-10,11-dihydro-5H-dibenzo[*a,d*]-cycloheptene (II).—A 7.04 g. sample of I (described above) dissolved in 70 ml. of absolute ethanol containing 0.22 g. of 5% palladium-on-alumina was shaken with hydrogen at 3.5 kg./cm.[2]

(1) (a) S. O. Winthrop, M. A. Davis, G. S. Meyers, J. G. Gavin, R. Thomas, and R. Barber, *J. Org. Chem.*, **27,** 230 (1962); (b) R. D. Hoffsommer, D. Taub, and N. L. Wendler, *ibid.*, **27,** 4134 (1962); (c) R. D. Hoffsommer, D. Taub, and N. L. Wendler, *ibid.*, **28,** 1751 (1963).

(2) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 164.

and 29° for 2 hr. The mixture was filtered and concentrated *in vacuo* to yield 7.2 g. of colorless sirup which crystallized by trituration with toluene. This material proved to be toluene solvated and was crystallized from toluene; m.p. 82–86.5°. After drying *in vacuo* at 120°, a sample lost 12% of its initial weight and would not crystallize on cooling. The oil was analyzed.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.58; H, 7.51. Found: C, 79.92; H, 7.72.

5-(3-Bromopropylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (IIIa).—A small sample (0.46 g.) of II was boiled for 6 hr. with 1.9 ml. of 48% hydrobromic acid and 4.5 ml. of glacial acetic acid. The mixture was diluted with 40 ml. of water and extracted twice with 20-ml. portions of ether. The combined ether extract was washed with dilute sodium hydroxide solution, dried over magnesium sulfate, and the ether evaporated; yield, 0.43 g. (80%). Molecular distillation provided a sample with m.p. 67–69.5°, not depressed by an authentic sample[3] (lit.[1a,b] m.p. 70–71° and 69–71°).

5-(3-Hydroxypropylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (IV).—A 23.6 g. portion (0.088 mole) of the saturated glycol (II) was dissolved in 180 ml. of xylene and treated at 95° with 0.34 g. of toluenesulfonic acid. The mixture was boiled for 2 hr. using a trap to collect 1.1 ml. of water from the condensate. The solution was cooled, washed with water, 6 *N* sodium hydroxide, again with water, and then concentrated *in vacuo* to yield 19.1 g. of sirup which was crystallized from 120 ml. of hexane–isopropyl ether (5:1); yield, 13.3 g. (69%); m.p. 87–90°. The analytical sample was recrystallized from isopropyl ether; m.p. 88–91° (lit.[1b] m.p. 89–90°).

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.10; H, 7.71.

The benzoate prepared from benzoyl chloride in pyridine[2] and crystallized from ethanol had m.p. 115–118°.

Anal. Calcd. for $C_{25}H_{22}O_2$: C, 84.71; H, 6.26; O, 9.02. Found: C, 84.69; H, 6.36; O, 9.41.

A 5-fold scale-up of the dehydration described above (except that the toluenesulfonic acid was added at 80°) gave only a 40% yield of the hydroxypropylidene derivative (IV). The mother liquors from crystallization provided a 24% yield of an isomeric dehydration product, presumably a cyclic ether (V), m.p. 65–69°. A sample was recrystallized from hexane and methanol; m.p. 69–71.5°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25; O, 6.38. Found: C, 86.51; H, 7.50; O, 6.50.

5-(3-Chloropropylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (IIIb). A. From IV.—A solution of 16.7 g. of IV (0.066 mole), 5.4 g. (0.068 mole) of pyridine, and 34 ml. of chloroform was treated with 8.8 g. (0.074 mole) of thionyl chloride while maintaining the temperature at −5 to 0°. The mixture was gradually warmed to the reflux temperature, so held for 1.5 hr., then cooled and washed with 80 ml. of water containing 16 ml. of 36% hydrochloric acid and finally with cold water. The chloroform solution was dried with magnesium sulfate and the solvent removed *in vacuo;* yield, 17.5 g. (98%), m.p. 78.5–82°. After crystallization from ethanol, the m.p. was 80–84° (lit.[1b] m.p. 83–84°).

B. From II.—A 133-g. portion of the toluene solvate of the glycol (II), 455 ml. of chloroform, and 70 g. of pyridine were mixed and treated with 118 g. of thionyl chloride while maintaining the temperature at 0 to 2°. The mixture was heated slowly with stirring to the reflux temperature (1 hr.) and reflux maintained for an additional 4.5 hr. After cooling, the solution was washed with two 500-ml. portions of water, dried over magnesium sulfate and decolorizing carbon, filtered, and the chloroform removed *in vacuo;* yield, 115 g. (98%), m.p. 76–81°, not depressed by mixture with material from A.

N-Methyl-β-Chloroallylamine.—To 2.7 kg. (84 moles) of anhydrous methylamine contained in an autoclave provided with stirrer was added 2.24 kg. (20.2 moles) of 2,3-dichloropropene[4] while maintaining the temperature below 50° by means of cooling water. After stirring for 6 hr. (temperature dropped, 50° to 20°), the autoclave was emptied and the reaction mixture was warmed slightly to expel excess methylamine. Pentane (45 l.) was then added, followed by 6 kg. of 50% sodium hydroxide solution. After brief boiling to expel methylamine, the pentane layer was decanted and the residual aqueous sludge was extracted twice with 10-l. portions of pentane. The combined pentane solution and extracts were dried with sodium hydroxide and distilled. Distillate fractions boiling at 109–114°, $n^{25}D$ 1.448–1.449, weighed 1.59 kg. (75% yield). The picrate had m.p. 113–116° (lit.[5] m.p. 110°); the hydrochloride melted at 157–159.5° (lit.[5] m.p. 156°).

N-Methylpropargylamine. A.—Propargyl chloride (40 g., 0.54 mole) was added to 120 ml. of anhydrous methylamine cooled with solid CO_2. The mixture was sealed in a pressure bottle and kept at room temperature overnight. The bottle was opened and the contents heated to 45° to expel excess methylamine. Dry ether (100 ml.) was then added and the methylamine hydrochloride was removed by filtration. Distillation of the filtrate gave 15 g. (41% yield), b.p. 82–84°.

B.—N-Methyl-β-chloroallylamine (21.1 g., 0.2 mole) was added dropwise (25 min.) to a stirred suspension of sodamide (0.6 mole) in 400 ml. of liquid ammonia. After stirring for an additional 6 hr. at reflux (solid CO_2 condenser), the ammonia was allowed to evaporate. The dry residue was treated with 50 ml. of xylene and 10 ml. of water, triturated, and filtered. The filtrate was dried with potassium hydroxide pellets and distilled. The fraction with b.p. 80–85° weighed 9.4 g. (68% yield). Redistillation gave 1.8 g., b.p. 82–85°, and 5.8 g., b.p. 85°.

The **hydrochloride,** precipitated from an ethereal solution with anhydrous hydrogen chloride and crystallized from absolute ethanol–acetone, had m.p. 105–107.5°.

Anal. Calcd. for C_4H_8ClN: C, 45.49; H, 7.64. Found: C, 45.91; H, 7.86.

5-Hydroxy-5-(3-methylaminopropynyl)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (VI).—To a stirred suspension of 0.4 mole of sodamide in 300 ml. of liquid ammonia there was added (10 min.) 21.2 g. (0.2 mole) of N-methyl-β-chloroallylamine. After 1 hr., 40 g. (0.19 mole) of 10,11-dihydro-5H-dibenzo[*a,d*]-cycloheptene-5-one[1a] dissolved in 120 ml. of dry xylene was added (20 min.). The mixture was stirred for 1 hr. at reflux (solid CO_2 condenser) and the ammonia evaporated while stirring. A solution of 2 ml. of water in 40 ml. of methanol was then added. The product precipitated on cooling with stirring. More water (200 ml.) was added and the mixture was filtered. The crude product was washed with water and ether and dried; yield 48 g. (91%). It was dissolved in 670 ml. of methanol, the solution decolorized with charcoal, filtered, and then concentrated to 170 ml. Cooling with ice gave 43.7 g., m.p. 163–165.5°.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.33; H, 7.01; N, 4.89.

5-Hydroxy-5-(3-methylaminopropyl)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (VII).—A 5.9 g. sample of VI suspended in 60 ml. of absolute ethanol along with 0.3 g. of 5% palladium-on-alumina was shaken at room temperature under hydrogen at 3.5 kg./cm.^{2} for 22 hr. Filtration and evaporation of the ethanol *in vacuo* gave 6.1 g. of product, m.p. 89–94°, after trituration with hexane. Dissolved in anhydrous ether and treated with anhydrous hydrogen chloride, this base gave 6.5 g. of the hydrochloride (VII·HCl), m.p.17 1–173° dec. (with evolution of H_2O). Recrystallization from alcohol raised the decomposition temperature to about 192°.

Anal. Calcd. for $C_{19}H_{24}ClNO$: C, 71.79; H, 7.61. Found: C, 71.91; H, 7.40.

5-Hydroxy-5-(3-methylaminopropenyl)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (VIII).—In one experiment, using 1 kg. of VI, 6 l. of isopropyl alcohol, and 15 g. of 5% palladium-on-alumina, in which hydrogenation was carried out at 50–60° and 3.5 kg./cm.^{2}, reaction ceased when the olefinic intermediate (VIII) precipitated and the catalyst appeared to be deactivated. Recovered by filtration and crystallized from isopropyl alcohol, the m.p. was 120–123.5°.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.57; N, 5.01. Found: C, 81.62; H, 7.71; N, 4.87.

Further hydrogenation followed by dehydration with HCl gave nortriptyline hydrochloride (IX·HCl), m.p. 216–219°, in confirmation of structure VIII.

5-(3-Methylaminopropylidene)-10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene Hydrochloride (Nortriptyline Hydrochloride, IX·HCl).—A 36.5-g. portion of VII in 216 ml. of isopropyl alcohol was acidified with 11.7 ml. of 36% hydrochloric acid and the suspension boiled until the solid dissolved and for 1 hr. thereafter. Crystallization then occurred by cooling the resulting solution;

(3) Provided by Dr. Jack Mills, The Lilly Research Laboratories, Indianapolis, Ind.

(4) Purchased from Roberts Chemical Co., Nitro, W. Va.

(5) J. von Braun, M. Kühn, and J. Weismantel, *Ann.*, **449**, 255 (1926).

yield, 30.6 g. (78%), m.p. 216–219°. A second crop, 3.1 g., was obtained by concentration of the filtrate. The product showed the same X-ray pattern and infrared and ultraviolet absorption spectra as did an authentic sample.[1c,g]

Synthesis of a Cyclopropyl Carbinol in the Amitriptyline Series

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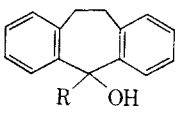
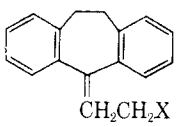
Received January 9, 1964

The cyclopropyl carbinol, 5-cyclopropyl-5-hydroxy-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (II),[1a] an intermediate in a synthesis of amitriptyline, can be prepared advantageously from the vinyl carbinol, 5-hydroxy-5-vinyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (I), with CH_2I_2 and zinc–copper couple.[2,3] The formation of accompanying amounts (7–8%) of 5-(γ-iodopropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (IV, X = $-CH_2I$) was also ascertained by conversion to 5-(γ-hydroxypropylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (IV, X = $-CH_2OH$) with potassium acetate and concluding saponification. Treatment of the iodo compound with alkali directly produced the diene, 5-allylidene-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene.[1b]

The vinyl carbinol (I) rearranges with great ease in the presence of dilute perchloric acid to give the primary system (III, X = OH). Similarly, hydrogen bromide or chloride in acetic acid affords III, X = Br and Cl, respectively (compare ref. 1a).





I, R = $-CH{=}CH_2$ III, X = OH, Br, Cl
II, R = IV, X = $-CH_2I$, $-CH_2OH$

Experimental

5-Hydroxy-5-vinyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (I).—A 100-ml. flask fitted with stirrer, Dry Ice–acetone condenser, nitrogen inlet, and addition funnel was charged with 1.17 g. (48 mmoles) of magnesium turnings. The magnesium metal was covered with 10 ml. of dry tetrahydrofuran (THF) and 2–3 ml. of a solution of 5.25 g. (49 mmoles) of vinyl bromide in 10 ml. of THF was added. The reaction mixture was warmed slightly until reaction started; the vinyl bromide solution was added dropwise, with stirring, at such a rate as to maintain a temperature of 50–60°. The addition was complete in 15 min. and stirring was continued under gentle reflux until all of the magnesium was consumed (2 hr.). A solution of 5.0 g. (24 mmoles) of 5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene-5-one in 25 ml. of THF was added, with stirring, to the warm reaction mixture at a rate sufficient to maintain a temperature of 40–50°. The addition was complete in 25 min., accompanied by considerable darkening of the reaction mixture. Stirring and heating (50°) were continued for 1 hr. At the end of this time a thin layer chromatographic probe (Al_2O_3 1:1 benzene–cyclohexane) indicated that the reaction was complete. The reaction mixture was chilled in an ice bath and treated, dropwise, with 25 ml. of saturated ammonium chloride. The aqueous layer was extracted with two 15-ml. portions of ether and the combined ether–THF solutions were washed with 15 ml. of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and taken to dryness *in vacuo* to yield 5.90 g. of the vinyl carbinol I as a yellow oil which exhibited the following properties: $\lambda_{max}^{CHCl_3}$ 2.7, 2.87, 6.18, 6.75, 6.9, 7.13, 7.62, 7.9, 8.63, 9.0, 9.48, 9.83, and 10.35 μ; $\lambda_{max}^{Me_2CO}$ 2730 Å. (sh.) (ε 470), 2700 (sh.) (557), 2660 (sh.) (645), and 2630 (690). This material was utilized in the next reaction without purification.

5-Hydroxy-5-cyclopropyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (II).—A 50-ml. flask fitted with a stirrer, condenser, and addition funnel was purged with dry nitrogen and charged with 1.53 g. of the copper–zinc couple,[4] 15 ml. of dry ethyl ether, and 2 crystals of iodine. Methylene iodide (4.90 g., 18.3 mmoles) was added and the reaction mixture was maintained at a gentle reflux for 30 min. The mixture was then cooled slightly and 2.00 g. (8.46 mmoles) of 5-hydroxy-5-vinyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (I) in 5 ml. of dry ethyl ether was added slowly, with stirring, over a period of 25 min. The reaction mixture was subsequently stirred and refluxed for 2.25 hr. Samples for thin layer chromatography (Al_2O_3 1:1 benzene–cyclohexane) were withdrawn after 30 min. and after 1 hr. and indicated the reaction to be complete after 30 min. with no further change after 1 hr. The reaction mixture was cooled to room temperature and treated with 15 ml. of saturated ammonium chloride solution. The aqueous layer was extracted with 2 portions of ether and the combined ether solution was washed with two 15-ml. portions of saturated potassium carbonate solution, 15 ml. of saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated *in vacuo* to 2.26 g. of a yellow oil. The crude oil was redissolved in ether, treated with charcoal, filtered through Celite, and the ether replaced with hexane while concentrating to small volume. Seeding the solution with a crystal of authentic 5-hydroxy-5-cyclopropyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (II),[1a] m.p. 69–71°, yielded 650 mg. of crystalline product with m.p. 68–69.5°. A mixture of the product crystals and authentic II did not depress the m.p., 68–71°. An additional 450 mg. of cyclopropyl carbinol II was obtained by alumina chromatography of the mother liquor to afford a total yield of 52% over the 2 steps.

An oily fraction from the chromatography (220 mg.) possessed essentially the same mobility and infrared spectrum as authentic γ-iodopropylidene derivative IV (X = $-CH_2I$).[1a] This oil was refluxed for 26 hr. with 200 mg. of potassium acetate in 6 ml. of acetone. The crude reaction product after work-up was saponified for 1 hr. with 50 mg. of potassium hydroxide in 4.5 ml. of aqueous methanol (1:9) and the product chromatographed on neutral alumina. Thereby was obtained crystalline IV (X = $-CH_2OH$),[1a] m.p. 86–88° not depressed on mixture with authentic material. The infrared spectra of this product was identical with that of authentic IV (X = $-CH_2OH$).

5-(β-Hydroxyethylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene III (X = OH).—A solution of 200 mg. (0.84 mmole) of 5-hydroxy-5-vinyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (I) in 10 ml. of dioxane was treated at room temperature with 4 ml. of 2 *M* aqueous perchloric acid. The reaction mixture was stirred for 1 hr., then quenched by the addition of solid anhydrous potassium carbonate, filtered over anhydrous magnesium sulfate, and concentrated to dryness *in vacuo*. The residual yellow oil crystallized spontaneously on standing to yield, after recrystallization from ether–hexane, 120 mg. of the ethylidene alcohol III (X = OH), m.p. 86–88°; λ_{max}^{MeOH} 2400 Å. (ε 13,942) and $\lambda_{max}^{CHCl_3}$ 2.66, 2.85, 6.73, 6.94, 8.93, and 9.9–10.0 μ.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.19; H, 7.00.

5-(β-Bromoethylidene)-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene III (X = Br).—A solution of 1.20 g. (5.07 mmoles) of crude 5-hydroxy-5-vinyl-5H-dibenzo[*a,d*]-10,11-dihydrocycloheptene (I) in 15 ml. of glacial acetic acid was chilled to 10° and 10 ml. of a 15% solution of anhydrous hydrogen bromide in glacial acetic acid added. The reaction mixture was stirred at 10–15° for 30 min., then taken to dryness *in vacuo*, flushed with xylene, and pumped down again to yield 1.44 g. of a dark oil which crystallized partially. Chromatography of the crude product afforded colorless crystalline bromide III (X = Br), m.p. 108–110°; λ_{max}^{MeOH} 2425 Å. (ε 13,285); and $\lambda_{max}^{CHCl_3}$ 6.15, 6.73, 6.94, 7.35, 8.37, and 9.1 μ.

Anal. Calcd. for $C_{17}H_{15}Br$: C, 68.23; H, 5.05; Br, 26.71. Found: C, 68.33; H, 4.86; Br, 26.11.

In a similar experiment employing hydrogen chloride in acetic

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