dissociation constant of the acid or base, and (b) the partition ratio between an organic solvent and a neutral aqueous phase. Determinations of the pK_A, and partition ratio were therefore carried out with 2-(*p*-hydroxyphenoxy)ethylhydrazine, and some related compounds which had shown activity *in vivo*.

The results (Table IV) show that the pK_A values for all the compounds examined are of similar magnitude and that under physiological conditions the compounds will be approximately 25% ionized. The partition data, however, show that 2-(*p*-hydroxyphenoxy)-ethylhydrazine (40) has a very much lower chloroform/water partition ratio than the other compounds examined and thus might be expected to penetrate cell membranes only with difficulty, hence its relative inactivity as an *in vivo* inhibitor of monoamine oxidase. The structurally related phenolic bases norepinephrine, dopamine, and 5-hydroxytryptamine are known to penetrate the blood-brain barrier at a very slow rate.

The results of *in vitro* and *in vivo* tests for monoamine oxidase inhibition have shown 2-phenylthioethylhydrazine and (1-methyl-2-phenoxyethyl)hydrazine to be the most active of the series of compounds studied. (1-Methyl-2-phenoxy)ethylhydrazine (2) seemed to be a compound of particular interest in that it combines activity approximately equal to that of phenethylhydrazine and α-methylphenethylhydrazine, with an acute toxicity considerably lower than either of these two substances. Accordingly (1-methyl-2-phenoxy)-ethylhydrazine has been submitted to a more detailed pharmacological and toxicological investigation,[24] and subsequently to clinical evaluation. This product is now known in Great Britain by the B.P. Commission approved name phenoxypropazine.[25]

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(24) Ruth A. Davis, M. Horlington, R. Lazare, G. A. Poulter, Hazel Thorpe and Alicia Urbanska—unpublished results.

(25) Drazine®, phenoxypropazine hydrogen maleate.

The Synthesis of Cycloheptatriene Homologs of Some Physiologically Active Compounds[1,2]

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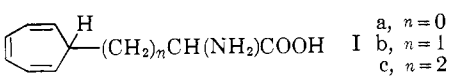
Three tropyl amino acids have been prepared and found lacking in activity against phenylalanine in *Lactobacillus*. Three tropylethylamines, however, showed analeptic activity. The preparation of ditropylindanedione is also reported.

Tropilidene (1,3,5-cycloheptatriene) bears a striking structural resemblance to benzene (6π electrons, similar molecular dimensions, and approximate planarity) and has even been called "pseudoaromatic."[4] A well-recognized device in the search for new substances of biological activity is to substitute for groups in compounds of established physiological activity new groups of similar structure to those replaced.[5] Our experience[6] in the synthesis of substituted alkyl tropilidenes led us to the synthesis and testing of a number of substances in which the tropyl group is substituted for the phenyl group of compounds of known activity.

We chose first to investigate various tropyl α-amino acids (I). Tropylglycine (Ia) is an isomer of phenyl-



I a, $n=0$; b, $n=1$; c, $n=2$

alanine; tropylalanine (Ib) is the analog (and a homolog) of phenylalanine; α-amino-γ-tropylbutyric acid (Ic) is a homolog of the analog.

These substances were prepared by the application of standard methods. Acetamido-(or phthalimido)-malonic ester was alkylated with tropylium perchlorate to give tropylacetamido-(or phthalimido)-malonic ester which was hydrolyzed to Ia in two stages. Tropylethyl bromide[6] was used to alkylate acetamidomalonic ester in the preparation of Ic. The Strecker synthesis was used starting from tropylacetaldehyde[7] for the preparation of Ib. The tendency of functionally substituted tropylalkyl compounds to undergo fragmentation reactions in acid media necessitated the use of basic hydrolysis in these preparations in place of the usual acid hydrolyses. The yields of the amino acids were 18% (three stages using ethyl acetamidomalonate; 3% using ethyl phthalimidomalonate), 29% (two stages from the aldehyde) and 24% (three stages from the bromide) for $n = 0$, 1, and 2, respectively.

A second group of substances chosen were the analogs of certain phenethylamines which are useful as sympathomimetic drugs. Along this line we have prepared β-tropylethylamine (IIa),[6] β-tropylisopropylamine (IIb) and its N-methyl derivative (IIc).

(1) Abstracted in part from a thesis submitted by D. N. Naik to the University of California in partial satisfaction of the requirements for the degree of Master of Science, 1961.

(2) Grateful acknowledgment is made to the National Science Foundation for support under G-13121.

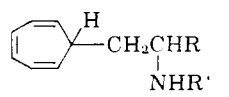
(3) Kansas State University.

(4) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956); see, however, K. Conrow, *J. Am. Chem. Soc.*, **83**, 2958 (1961).

(5) D. W. Wooley, "A Study of Antimetabolites," John Wiley & Sons, Inc., New York, N. Y., 1952, p. 212.

(6) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

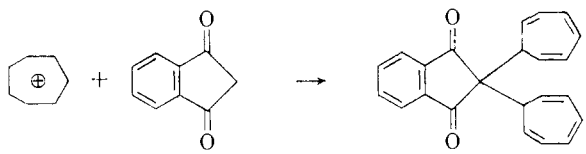
(7) M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, *Zhur. Obshchei Khim.*, **30**, 159 (1960); *C. A.*, **54**, 22535i (1960).



II a, R = R' = H
b, R = CH_3, R' = H
c, R = R' = CH_3,

β-Tropylisopropylamine (51% yield in two stages) was prepared by lithium aluminum hydride reduction of the oxime of tropylacetone,[6] for which an improved preparation is given. The primary amine was converted to its formamide which was reduced to the N-methyl derivative (25% yield in two stages) by lithium aluminum hydride.

We also did some experiments toward the preparation of an analog of phenindione but were successful only in obtaining a disubstituted derivative (66% yield). Other workers have reported independently their experiences with this preparation,[8] and since we have no results of physiological testing, we merely report our preparation of the di-adduct.



Physiological Testing.—The amino acids were tested microbiologically as antagonists and/or substitutes for L-phenylalanine at half-maximum concentration for the growth of various *Lactobacillus* species. There was no significant effect in any case; apparently the tropyl amino acids are neither substitutes for nor effective antagonists against L-phenylalanine.[9]

The tropylethylamines proved to be quite active analeptics. In jiggle cage screening tests, IIb and IIc showed about half the stimulation caused by equivalent doses of *d,l*-amphetamine. In pentobarbitalized dogs IIa showed short-lived pressor action (+3) at doses of 1.0 to 8.0 mg./kg., IIb showed prolonged pressor action (+2) at doses of 0.5 to 1.0 mg./kg. and short lived depressor action (+2) at doses of 8.0 mg./kg. In the rat, IIb produced 50% inhibition of food intake in a one hour feeding test at 8.2 mg./kg. and produced central nervous system stimulation at these doses. The LD_{50} of IIa is of the order of 100 mg./kg.[10]

Experimental

Microanalyses were performed by Miss Heather King. Ultraviolet spectra were determined in 95% ethanol. Infrared spectra were determined on neat liquid samples or in potassium bromide discs. The spectral work was done by Miss Donna Karasek. Melting points are corrected, and were taken in capillaries; boiling points are uncorrected. Tropylium perchlorate was prepared as indicated earlier.[11] Tropylium fluoroborate is preferable; the perchlorate is violently explosive.[11a]

Diethyl Tropylacetamidomalonate.—To a solution of 6.52 g. (30 mmoles) of diethyl acetamidomalonate in 15 ml. of pyridine, was added 5.80 g. (30 mmoles) of tropylium perchlorate and the mixture was stirred magnetically for 4 hr. It then was poured over crushed ice, acidified with 15 ml. of concd. hydrochloric acid and extracted with 4 portions of ether. The ether extracts were dried over anhydrous magnesium sulfate, concentrated and distilled to give 7.27 g. (78%) of a very viscous oil, b.p. 160–165° (0.3 mm.). It was taken up in a minimum amount of cold ethanol and water was added until slight turbidity appeared. On standing in the icebox for 24 hr., it yielded white micro-needles, m.p. 55.5–56.5°.

Anal. Calcd. for $C_{16}H_{21}NO_5$: C, 62.52; H, 6.88; N, 4.56. Found: C, 62.51; H, 6.95; N, 4.65.

The infrared spectrum showed strong absorption at 3210 cm.$^{-1}$ (N–H), 2940 cm.$^{-1}$ (C–H stretch), 1730 cm.$^{-1}$ (ester C=O) and 1640 cm.$^{-1}$ (amide C=O), among others.

N-Acetyl Tropylglycine.—A solution of 6.14 g. (20 mmoles) of diethyl tropylacetamidomalonate in 5 ml. of ethanol was added to a solution of 4.5 g. (80 mmoles) of potassium hydroxide in 45 ml. of water and the mixture was refluxed on steam bath for 1.5 hr. It then was chilled in ice and 10 ml. of concd. hydrochloric acid was run in slowly. The solution was warmed on the steam bath to complete decarboxylation and allowed to stand in the ice-box overnight. It yielded 2.75 g. (66%) of a crystalline product which on recrystallization from water–ethanol gave colorless platelets, m.p. 202° dec.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.92; H, 6.34; N, 7.00.

The infrared spectrum showed strong, sharp bands, among others, at 3300 cm.$^{-1}$ and 1545 cm.$^{-1}$ (N–H deformation) and a broad absorption region between 2480 cm.$^{-1}$ and 2880 cm.$^{-1}$ (O–H stretch).

Tropylglycine.—To a solution of 0.70 g. (17.5 mmoles) of sodium hydroxide in 7 ml. of water was added 0.92 g. (4.4 mmoles) of N-acetyltropylglycine and the mixture was refluxed for 23 hr. It was decolorized with charcoal, neutralized with 1 ml. (*ca.* 17.5 mmoles) of glacial acetic acid and allowed to stand in the ice-box overnight, whereupon a white, crystalline deposit was obtained. It contained a considerable amount of an infusible substance (produced by attack of alkali on glass) which was separated by re-solution of the amino acid; the latter on crystallization from water yielded 0.25 g. (34.5%) of white crystals, m.p. 227.5–229.5° dec., λ_{max} 257 mμ (log ε 3.45), λ_{min} 225 mμ (log ε 2.88).

Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71. Found: C, 65.64; H, 6.47.

The infrared spectrum showed a broad region of strong absorption between 2500 and 3100 cm.$^{-1}$ with maxima at 3040, 2980, 2900 and 2540 cm.$^{-1}$; strong bands at 1585 cm.$^{-1}$ (COO^-, antisymmetrical) with a shoulder at 1610 cm.$^{-1}$ (NH_3^+), 1510 cm.$^{-1}$ (NH_3^+) and 1355 cm.$^{-1}$ (COO^-, sym.); and a sharp band of medium intensity at 2530 cm.$^{-1}$ (NH_3^+).

Diethyl Tropylphthalimidomalonate.—To a solution of 3.05 g. (10 mmoles) of diethyl phthalimidomalonate[12] in 15 ml. of pyridine was added 1.90 g. (10 mmoles) of tropylium perchlorate and the mixture was stirred at room temperature for 2 hr. before it was poured over crushed ice and acidified with 20 ml. of concd. hydrochloric acid. It was then extracted with three 25 ml. portions of ether, the ether extracts were dried with anhydrous magnesium sulfate and finally the solvent was removed on the steam bath. The residual oil, on trituration with water, solidified to give 3.70 g. (94%) of a white product, m.p. 92–95°. Two crystallizations from absolute ethanol yielded white crystals, m.p. 96–97°.

Anal. Calcd. for $C_{22}H_{21}NO_6$: C, 66.82; H, 5.35; N, 3.54. Found: C, 66.64; H, 5.50; N, 3.70.

The infrared spectrum showed a broad band of strong intensity in the region 1675–1775 cm.$^{-1}$ (carbonyl absorption) with peaks at 1745 cm.$^{-1}$ and 1710 cm.$^{-1}$ and shoulders at 1765 cm.$^{-1}$ and 1625 cm.$^{-1}$ (amide C=O).

Tropylglycine from Diethyl Tropylphthalimidomalonate.—A solution of 4 g. (10.1 mmoles) of diethyl tropylphthalimidomalonate in 5 ml. of ethanol was added to a solution of 2.52 g. (45 mmoles) of potassium hydroxide in 10 ml. of water and the mixture was refluxed on the steam bath for 3 hr. It was then cooled in ice, acidified with 25 ml. of 6 *N* hydrochloric acid and kept in

(8) N. W. Jordon and I. W. Elliott, *J. Org. Chem.*, **27**, 1445 (1962).

(9) The authors are indebted to Miss Audre Fowler, University of California at Los Angeles, for conducting the microbiological assays. The growth medium and procedure were essentially those of S. Eiduson, M. N. Camien and M. S. Dunn, *Arch. Biochem.*, **29**, 302 (1950). An L-phenylalanine concentration of 8 λ/tube was used for *L. citrovorum* and *L. mesenteroides* P-60 and 17 λ/tube for *L. brevis* and *L. gayonii*. Tropylamino acid concentrations were varied from 0 to 1000 λ/tube.

(10) The authors are indebted to Dr. Fred P. Hauck, Jr., of Parke, Davis and Company, through whose good offices the testing of these amines was accomplished.

(11) K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961); G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5847 (1960).

(11a) P. G. Ferrini and A. Marxer, *Angew. Chem., internat. ed.*, **1**, 405 (1962).

(12) A. E. Osterberg, "Org. Synth.," Coll. Vol. I, 2nd Ed., H. Gilman and A. H. Blatt, eds., John Wiley & Sons, Inc., New York, N. Y., 1941.

the ice-box overnight. On filtration, it yielded 0.70 g. of an amorphous product, m.p. 171.5–174.5°. This was suspended in 10 ml. of water, 4 ml. of concd. hydrochloric acid was added to it and the mixture was heated on steam bath for 3 hr. The dark brown reaction mixture then was decolorized with activated charcoal and kept in the ice-box overnight whereupon it deposited a crystalline product, m.p. 204–206° (phthalic acid), which was removed by filtration and washed with cold water. The washings and filtrate were combined and evaporated under reduced pressure. The white residue was dissolved in the minimum amount of water and the solution made just basic to litmus with concd. aqueous ammonia. The precipitated amino acid was collected by filtration and crystallized from water to give 50 mg. (3%) of white needles, m.p. 228–229.5° dec. The product thus obtained is identical (superimposable infrared spectra) with tropylglycine synthesized *via* the acetamidomalonic ester.

β-Tropylethyl Bromide.—The β-tropylethanol required was prepared as described earlier.[6] The preparation follows that given for β-tropylisopropyl bromide.[6]

A mixture of 1.2 ml. (3.36 g., 12.4 mmoles) of phosphorus tribromide, 0.75 ml. of pyridine and 2 ml. of benzene was prepared and cooled in ice. 2-Tropylethanol (4.7 g., 34.5 mmoles) was added dropwise and the reaction mixture was allowed to warm up to room temperature with continuous stirring overnight. Benzene then was distilled off at 60 mm. up to a bath temperature of 90°. The pressure was reduced and the distillate collected at 65–66° (0.6–0.7 mm.) while the bath temperature was raised gradually to a maximum of 150°. The product, a colorless oil turning brown on standing, amounted to 5.32 g. (77.5%). No analysis was obtained in view of the instability of the material.

The infrared spectrum showed a set of three bands at 2995, 2900 and 2840 cm.$^{-1}$ (C–H stretch). The strong band of 2-tropylethanol at 3240–3360 cm.$^{-1}$ had disappeared.

Diethyl β-Tropylethylacetamidomalonate.—To a solution of 0.615 g. (26.5 mg.-atoms) of sodium in 20 ml. of absolute ethanol was added 5.94 g. (27.3 mmoles) of diethyl acetamidomalonate followed by 5.32 g. (26.7 mmoles) of freshly distilled β-tropylethyl bromide and the mixture was refluxed on the steam bath overnight. It then was diluted with 100 ml. of water and extracted with five 50-ml. portions of ether. The ether extracts were dried with anhydrous magnesium sulfate, concentrated and distilled at 0.3–0.5 mm. to remove unreacted bromide and alcohol, if present. The residual liquid solidified on cooling and on crystallization from water–ethanol gave an analytical sample, m.p. 77.5–78.5°, λ_{max} 258 mμ (log ε 3.54), λ_{min} 225 mμ (log ε 3.14).

Anal. Calcd. for $C_{18}H_{15}NO_5$: C, 64.46; H, 7.51. Found: C, 64.56; H, 7.69.

The infrared spectrum showed a band of medium intensity at 3200 cm.$^{-1}$ (N–H) and a set of three strong bands between 2900 and 3000 cm.$^{-1}$ along with a weaker one at 3090 cm.$^{-1}$; strong bands at 1750 cm.$^{-1}$ (ester C=O) and 1630 cm.$^{-1}$ (amide C=O).

α-Acetamido-γ-tropylbutyric Acid.—A solution of 2.0 g. (5.98 mmoles) of diethyl β-tropylethylacetamidomalonate in 7 ml. of 95% ethanol was added to a solution of 1.5 g. of potassium hydroxide in 8 ml. of water and the mixture was refluxed on the steam bath for 4 hr. before it was poured over crushed ice; 1.5 ml. of concd. hydrochloric acid was added and it was finally extracted with four 25-ml. portions of ether. The ether extracts were dried with anhydrous magnesium sulfate before the solvent was removed on the steam bath. The solid residue was taken up in 10 ml. of water, the solution was refluxed for 2.5 hr. and then allowed to stand in the ice-box overnight. The white deposit which was collected by filtration gave, after one crystallization from ethyl acetate–petroleum ether, 1.23 g. (88%) of shiny platelets, m.p. 152.5–154.5°. Two further crystallizations from the same solvent gave the analytical sample, m.p. 154–155°.

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.17; H, 7.07; N, 5.82.

The infrared spectrum showed strong bands at 3300 cm.$^{-1}$ (N–H), 1705 cm.$^{-1}$ (C=O) with a shoulder at 1670 cm.$^{-1}$ (amide C=O), 1610 cm.$^{-1}$ and 1560 cm.$^{-1}$ (N–H deformation) besides a broad absorption region between 2480 and 2700 cm.$^{-1}$ (O–H stretch). It also showed a set of three bands of strong absorption with peaks at 3000, 2910 and 2820 cm.$^{-1}$ (C–H stretch) along with one of medium intensity at 3090 cm.$^{-1}$.

α-Amino-γ-tropylbutyric Acid.—A sample (0.66 g., 2.81 mmoles) of α-acetamido-γ-tropylbutyric acid was added to a solution of 0.54 g. (13.5 mmoles) of sodium hydroxide in 5 ml. of water and the mixture was refluxed on the steam bath for 24 hr. It then was diluted with 5 ml. of water, neutralized with 0.81 g. (13.5 mmoles) of glacial acetic acid and chilled in ice. The resulting precipitate was collected by filtration and an infusible, glassy material was removed. The rest of the product was crystallized from water–ethanol to give 0.22 g. (40%) of grayish crystals which on recrystallization from 50% ethanol gave micro-needles, m.p. 292.5–294.5° dec., λ_{max} 258 mμ (log ε 3.48), λ_{min} 223 mμ (log ε 2.85).

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82. Found: C, 68.24; H, 7.77.

The infrared spectrum showed all the characteristic absorption bands of an α-amino acid indicated in the spectrum of tropylglycine.

α-Amino-β-tropylpropionitrile.—A solution of 1.77 g. (33.0 mmoles) of ammonium chloride in 5 ml. of water and another of 1.67 g. (32.4 mmoles) of 95% sodium cyanide in 3 ml. of water were mixed in a flask and a solution of 4.35 g. (32.4 mmoles) of tropylacetaldehyde[7,13] in 4 ml. of 95% ethanol was added. After the reaction mixture had cooled down, 2 ml. of concd. aqueous ammonia was added, the flask was well stoppered and the mixture was stirred magnetically for 5 hr. before it was extracted with ether. The ether extracts were dried with anhydrous magnesium sulfate and all solvent was removed under reduced pressure. The oily residue was again taken up in dry ether, dry hydrogen chloride gas was passed through it and the aminonitrile was collected as its hydrochloride to give 3.70 g. (58%) of a shiny, light crystalline product. Two successive crystallizations from absolute ethanol–ethyl acetate gave the analytical sample, m.p. 184.5–186.5° dec.

Anal. Calcd. for $C_{10}H_{13}ClN_2$: C, 61.04; H, 6.66. Found: C, 61.13; H, 6.84.

The infrared spectrum of the free aminonitrile showed a pair of strong bands at 3340 and 3280 cm.$^{-1}$ (primary —NH_2); a triplet of bands at 2980, 2890 and 2820 cm.$^{-1}$ (C–H stretch); a band of moderate intensity at 2220 cm.$^{-1}$ (C≡N) and another at 1595 cm.$^{-1}$ (N–H deformation).

The **N-benzoyl derivative** was prepared by treating a pyridine solution of the free aminonitrile with benzoyl chloride. It was isolated by pouring the reaction mixture into water, collecting the precipitate and recrystallizing it from benzene-petroleum ether (b.p. 80–100°) with use of decolorizing charcoal. The fluffy micro-needles were colorless and melted at 115–117°.

Anal. Calcd. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.47; H, 6.29; N, 10.51.

β-Tropylalanine.—To a solution of 2.86 g. of sodium hydroxide in 20 ml. of 50% ethanol was added 3.45 g. (17.5 mmoles) of α-amino-β-tropylpropionitrile hydrochloride and the mixture was refluxed on the steam bath for 4 hr. By this time the evolution of ammonia, vigorous in the beginning, had essentially ceased. The reaction mixture was cooled, washed with two portions of ether, carefully neutralized with about 4 ml. of concd. hydrochloric acid (to pH 5) and allowed to stand overnight in the ice-box. The voluminous, jelly-like product was collected by filtration with suction and dried in vacuum to give 1.58 g. (50.5%) of a white, amorphous substance, m.p. 236–237° dec. Two crystallizations from water–acetone gave white needles, m.p. 236–238.5° dec., λ_{max} 258 mμ (log ε 3.46), λ_{min} 224 mμ (log ε 2.82).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31. Found: C, 67.22; H, 7.31.

The infrared spectrum showed all the characteristic absorption bands of an α-amino acid indicated in the spectrum of tropylglycine.

Tropylacetone, a Simplified Procedure (*cf.* ref. 6).—To a solution of 13.01 g. (0.10 mole) of ethyl acetoacetate in 50 ml. of pyridine was added slowly 19.06 g. (0.10 mole) of tropylium perchlorate while the mixture was cooled in a water bath. After 1 hr. of stirring at room temperature, it was poured over crushed ice, acidified with 50 ml. of concd. hydrochloric acid and extracted with 4 portions of ether. The ether extracts were concentrated on the steam bath, the residue together with 60 ml. of 95% ethanol was added to a solution of 10 g. of potassium hydroxide in 50 ml. of water and the mixture was refluxed on the steam bath for 1 hr. before it was steam-distilled. The steam distillate was

(13) We found tropylacetaldehyde to have rather a variable index of refraction (1.515–1.530, lit. 1.534) and to decompose quite rapidly on standing. The use of freshly prepared, once distilled material, gave satisfactory results. The *2,4-Dinitrophenylhydrazone* crystallized from 95% ethanol as golden yellow platelets, m.p. 153–154° (reported[7] without analysis, dec. above 190°). *Anal.* Calcd. for $C_{16}H_{14}N_4O_4$: C, 57.32; H, 4.49. Found: C, 57.50; H, 4.60.

extracted with several portions of ether, the ether extracts were dried with anhydrous magnesium sulfate, concentrated and finally distilled to give 11.50 g. (78%) of a mobile oil, b.p. 54–56° (0.1–0.3 mm.), or 71–73° (1.5 mm.), $n^{21}D$ 1.5215. The infrared spectrum showed maxima at 2980 cm.$^{-1}$ (C–H) and 1705 cm.$^{-1}$ (C=O) among several other bands.

Tropylacetoxime.—A solution of 11.14 g. (75.4 mmoles) of tropylacetone in 15 ml. of 95% ethanol was added to a solution of 6.95 g. (0.10 mole) of hydroxylamine hydrochloride in 35 ml. of water and the mixture was stirred while 5.30 g. (0.05 mole) of anhydrous sodium carbonate was cautiously added to it. The resulting mixture was refluxed on the steam bath for 2 hr. before it was poured over crushed ice, acidified with 3 ml. of concd. hydrochloric acid and extracted with 4 portions of ether. The ether extracts were dried with anhydrous magnesium sulfate, concentrated and finally distilled to give 11.51 g. (93.5%) of a light yellow, very viscous oil, b.p. 106–107° (0.5 mm.), or 123–124° (1.5 mm.), which later solidified.

After standing on a porous clay plate and crystallization from petroleum ether (60–80°) at −20°, the analytical sample, colorless platelets, melted at 54–56°.

Anal. Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found: C, 73.39; H, 8.03.

The infrared spectrum showed a broad band of strong intensity between 3400 and 2800 cm.$^{-1}$ with maxima at 3180, 2980 and 2860 cm.$^{-1}$; and a band of moderate intensity at 1655 cm.$^{-1}$ (C=N).

β-Tropylisopropylamine.—A solution of 5.35 g. (32.8 mmoles) of tropylacetoxime in 100 ml. of dry tetrahydrofuran was added slowly to a suspension of 2 g. of lithium aluminum hydride in 100 ml. of dry tetrahydrofuran and the mixture was refluxed on the steam bath for 16 hr. after which the excess of hydride was destroyed by careful addition of 4 ml. of water and 3 ml. of 10% sodium hydroxide solution. It was boiled again for 10 min., cooled, filtered and the solid cake was washed with several portions of ether. The filtrate and ether washings were combined and 100 ml. of 1 *N* hydrochloric acid was added. Tetrahydrofuran was removed from the resulting aqueous solution by extraction with several portions of ether before it was made basic with excess of 10% sodium hydroxide solution. The basic solution was extracted with 4 portions of ether, the ether extracts were dried with anhydrous magnesium sulfate, concentrated and distilled to give 2.68 g. (55%) of a colorless oil, b.p. 52–53° (0.1 mm.), 70–71° (1.0 mm.) (0.27 g. (5%) of the oxime was recovered).

The *hydrochloride* was prepared by passing dry hydrogen chloride gas through the solution of the amine in dry ether, and crystallized from absolute ethanol–chloroform as a white, fluffy mass of micro-crystals, m.p. 219.5–220.5° dec., λ_{max} 258 mμ (log ε 3.55), λ_{min} 223 mμ (log ε 2.93).

Anal. Calcd. for $C_{16}H_{16}ClN$: C, 64.67; H, 8.68; N, 7.54. Found: C, 64.89; H, 8.81; N, 7.72.

The infrared spectrum of the free amine showed a pair of bands of medium intensity at 3340 and 3260 cm.$^{-1}$ (primary $-NH_2$) among several others. A similar run using dry ether as solvent, after 48 hr. at reflux, gave the amine in 50% yield, about 15% of the starting material being recovered.

N-Formyl-β-tropylisopropylamine.—A mixture of 2.57 g. (17.2 mmoles) of β-tropylisopropylamine and 0.775 g. (17.2 mmoles) of formamide was heated on steam bath for 10 hours. It then was taken up in ether and washed with one 10-ml. portion of *N* hydrochloric acid, and another 10-ml. portion of water. The ethereal solution was dried with anhydrous magnesium sulfate, concentrated and distilled to give 1.14 g. (37.5%) of a thick, yellow oil. β-Tropylisopropylamine (6.24 mmoles, 36%) was recovered from the hydrochloric acid washings. The infrared spectrum showed strong absorption at 3250 cm.$^{-1}$ (N–H) and 1655 cm.$^{-1}$ (C=O); equally strong was a band at 2830–3020 cm.$^{-1}$ with a shoulder at 2740 cm.$^{-1}$ and peaks at 3020, 2980, 2940, 2880 and 2830 cm.$^{-1}$ (C–H stretch).

N-Methyl-β-tropylisopropylamine.—A solution of 1.29 g. (7.3 mmoles) of N-formyl-β-tropylisopropylamine in 50 ml. of dry ether was added to a slurry of 1 g. of lithium aluminum hydride in 100 ml. of dry ether and the mixture was refluxed on the steam bath for 3 hr. before the excess reagent was destroyed by careful addition of 2 ml. of water and 1.5 ml. of 10% sodium hydroxide solution. After standing overnight, the mixture was filtered and the solid cake was washed with ether. The ether washings and filtrate were dried over magnesium sulfate, dry hydrogen chloride gas was passed through the solution and the amine was collected as its hydrochloride by filtration. The white product was crystallized from absolute ethanol–petroleum ether to give 0.96 g. (66%) of a woolly mass of needles, m.p. 137.5–138.5°, λ_{max} 257 mμ (log ε 3.54) λ_{min} 223 mμ (log ε 2.90).

Anal. Calcd. for $C_{11}H_{18}ClN$: C, 66.13; H, 9.08. Found: C, 66.06; H, 9.00.

Attempted Synthesis of 2-Tropyl-1,3-diketohydrindene: 2,2-Ditropyl-1,3-diketohydrindene.—To a solution of 2.96 g. (20 mmoles) of 1,3-diketohydrindene in dry acetonitrile was added 0.93 g. (20 mmoles) of 51.7% sodium hydride dispersed in mineral oil and the mixture was stirred for 15 min. before 3.80 g. (20 mmoles) of powdered tropylium perchlorate was added slowly. The mixture turned deep purple immediately. It was stirred for 5 min. before it was diluted with water and extracted with ether. The ether extracts were worked up as usual to give 2.17 g. (66%) of product which was crystallized from absolute ethanol to give very light yellow prisms, m.p. 168.5–169°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.84; H, 5.56.