3-(2-Veratroyloxy-4,5-dimethoxyphenyl)-pentanone-2.[17] **(XVI).**—A solution of 8 g. of IX sulfate in 50 cc. of water was treated with 8 cc. of 30% hydrogen peroxide and warmed for one hour on the steam-bath. The mixture was cooled and the aqueous layer decanted from the oil, which was then crystallized from ethanol, to give 3.9 g. of fine, colorless needles, m. p. 125–126.5°. Recrystallization from ethanol afforded material of m. p. 128.5–129° (reported m. p. 129–130°).

Anal. Calcd. for $C_{22}H_{26}O_7$: C, 65.66; H, 6.51; OCH_3, 30.85. Found: C, 65.96, 66.05; H, 6.56, 6.65; OCH_3, 30.54.

The **phenylhydrazone**[17] was obtained as hard, glittering needles, m. p. 203–207° with decomposition (reported 208–210°).

A mixture of 2.65 g. of XVI and 55 cc. of 15% aqueous sodium hydroxide was refluxed for two hours, cooled, acidified and extracted with chloroform. The chloroform solution was extracted with 10% sodium carbonate and the extract acidified and extracted with chloroform. Evaporation of the extract gave 1.15 g. (97%) of white needles, m. p. 172–177°. Recrystallization from ethyl acetate gave material of m. p. 180–181° alone or mixed with an authentic specimen of veratric acid.

Treatment of a solution of 100 mg. of XVI in 5 cc. of methanol with 1 cc. of 10% sodium hydroxide and excess iodine-potassium iodide solution gave 30 mg. of a canary-yellow precipitate, m. p. 118–119° alone or mixed with an authentic sample of iodoform. A blank test on the solvent was negative.

Summary

A firm experimental basis for assigning the structure 1-(3,4-dimethoxyphenyl)-2-methyl-3-ethyl-5,6-dimethoxyindane to diisohomogenol (III) has been provided by showing that crucial oxidation products, erroneously formulated as hydroxyketodiisohomogenol and 2-methyl-3-hydroxy-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindanone by Müller, have the structures, 3-(2-veratroyl-4,5-dimethoxyphenyl)-pentanone-2 and 6-veratroyl-3,4-dimethoxypropiophenone, respectively. Other products and reactions have been reformulated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. III. Ring Expansion of Tropinone to R-Homotropinone and its Degradation to 1,3,5-Cycloöctatriene[1]

BY ARTHUR C. COPE, HAROLD R. NACE AND LELAND L. ESTES, JR.

The difficulty with which pseudopelletierine is obtained has led us to investigate the synthesis of eight-membered cyclic polyolefins from tropinone, which is more readily available. This paper describes the preparation of R-homotropinone (IV), an isomer of pseudopelletierine, from tropinone (I) by application of the Tiffeneau method of ring expansion.[2] R-Homotropinone has been degraded to 1,3,5-cycloöctatriene (X) by a series of reactions analogous to the sequence used by Willstätter in the synthesis of 1,3,5-cycloöctatriene (and cycloöctatetraene) from pseudopelletierine.[3,4]

The hydrogenation of tropinone cyanohydrin (II) to 3-aminomethyl-3-tropanol (III) gave satisfactory, reproducible yields only when II was reduced immediately after purification. Recrystallization of II from ethyl acetate required large volumes of solvent and resulted in excessive losses, and it was preferable to wash the crude cyanohydrin with water, alcohol and ether, dry it briefly under reduced pressure, and then hydrogenate it at once in the presence of Adams platinum catalyst in glacial acetic acid at 40°. Initially, III was isolated as the free base by treating its hydrochloride with a strongly basic ion exchange resin in aqueous solution. Subsequently it proved to be unnecessary to isolate III, for addition of hydrochloric acid to the acetic acid solution obtained by hydrogenation of II, followed by concentration and treatment with sodium nitrite in aqueous acetic acid, gave R-homotropinone (IV) in 57% yield (43% over-all from tropinone). R-Homotropinone was isolated as a colorless, hygroscopic liquid, which darkened on exposure to air. It was characterized by preparation of the 2,4-dinitrophenylhydrazone. Catalytic hydrogenation of IV in the presence of W-7 Raney nickel[5] gave R-homotropanol (V) in 70% yield as a stable, viscous liquid.

Dehydration of V by treatment with sulfuric acid in glacial acetic acid yielded 64% of R-homo-2(or 3)-tropidine (VIa or VIb). It was expected that dehydration would yield a mixture of the two isomers, but the liquid product crystallized readily, m. p. 17.2–18°, and consequently was probably a single isomer. No evidence was obtained concerning the location of the double bond. A sample of VI was hydrogenated quantitatively to R-homotropane (XI), which was characterized as the picrate and perchlorate.

Reaction of R-homo-2(or 3)-tropidine with methyl iodide gave the methiodide (VII) in 99% yield, which was converted to the quaternary base with silver hydroxide. Distillation gave a dimethylaminocycloöctadiene (VIII) in 77% yield. The product had a constant boiling point and refractive index, and appeared to be a single compound rather than a mixture of isomers. It gave a picrate and a methiodide which did not depress the m. p. of the corresponding derivatives

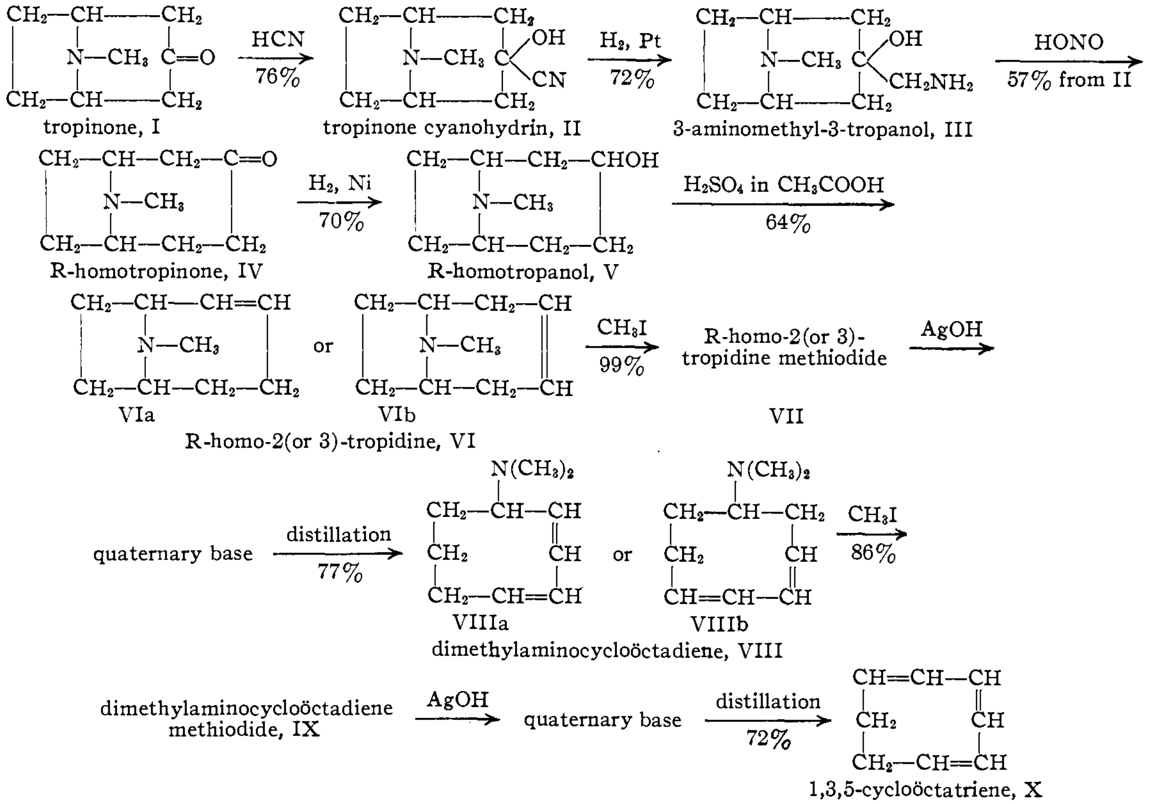
[1] Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

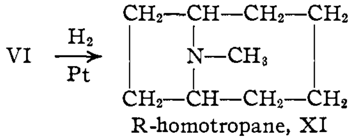
[2] Tiffeneau, Weill and Tchoubar, *Compt. rend.*, **205**, 54 (1937).

[3] Willstätter and Waser, *Ber.*, **44**, 3423 (1911); Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

[4] Cope and Overberger, THIS JOURNAL, **70**, 1433 (1948).

[5] Adkins and Billica, *ibid.*, **70**, 695 (1948).





of α-des-dimethylgranatenine (obtained by the degradation of pseudopelletierine[3,5]) and accordingly is presumed to have the same structure (previously designated as VIIIa, 1-dimethylamino-2,4-cycloöctadiene[3,4]). The isomeric structure VIIIb (1-dimethylamino-3,5-cycloöctadiene) cannot be excluded, however, for either structure would be consistent with the ultraviolet absorption spectrum,[4] which indicates that the double bonds are conjugated. The ultraviolet absorption spectrum of VIII prepared from VII in the present work (Fig. 1) differs considerably from the ultraviolet absorption spectrum of α-des-dimethylgranatenine derived from pseudopelletierine,[4] presumably because impurities were present in one or both of the samples, possibly formed by oxidation and polymerization which cause the amine to darken on exposure to air.

The dimethylaminocycloöctadiene (VIII) gave a methiodide (IX) in 86% yield, which was converted to the quaternary base. After decomposition of the base by distillation, 1,3,5-cycloöctatriene (X) was isolated in 71% yield. X prepared by this route differed slightly in refractive index and density from X prepared from pseudopelletierine, but the samples from the two sources had virtually identical ultraviolet and infrared absorption spectra. Further evidence for the structure of X prepared from R-homotropinone was obtained by its hydrogenation to cyclooctane, and by its reaction with maleic anhydride, which gave a crystalline adduct, m. p. 144–144.8°, that was identical (m. p. and mixed m. p.) with the adduct prepared from X derived from pseudopelletierine.

Experimental[6]

R-Homotropinone (IV).—A solution of 50 g. of tropinone in 75 ml. of water was neutralized by adding concentrated hydrochloric acid until the solution gave an acid reaction to congo red. (Tropinone obtained from Merck and Co. was purified by distillation under reduced pressure. One sample required additional purification by treatment with Raney nickel before distillation, or purification of the hydrochloride by recrystallization from absolute alcohol or treatment with Norite, to remove impurities which interfered with catalytic hydrogenation of the cyanohydrin.) The solution was cooled to 5–10° and 23.4 g. of potassium cyanide in 75 ml. of water was added in a period of fifteen minutes, with stirring. The white slurry which was formed was stirred for thirty minutes, filtered, and the solid product was washed successively with 150 ml. of cold water, 100 ml. of cold ethanol and two 100-ml. portions of dry ether. The cyanohydrin (II) was dried in a vacuum desiccator at 30 mm. over phosphorus pentoxide for one hour, and was obtained as a fluffy white powder (47 g., 78%) which was hydrogenated immediately.

Tropinone cyanohydrin (34.7 g.) was dissolved in 350 ml. of glacial acetic acid. The solution was filtered through glass wool to remove traces of undissolved mate-

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[6] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and Mrs. Louise W. Spencer for analyses.

rial and hydrogenated at 30–15 p. s. i. at 40° in the presence of 1.0 g. of prereduced Adams platinum oxide catalyst. After four hours 96% of two molar equivalents of hydrogen had been absorbed. The catalyst was removed by filtration, the filtrate was made acid to congo red with concentrated hydrochloric acid, and concentrated to a sirup under reduced pressure. The sirup was dissolved in 800 ml. of water and 110 ml. of glacial acetic acid, the solution was cooled to 0–5°, and kept at that temperature while 21.6 g. of sodium nitrite in 80 ml. of water was added in a period of fifty minutes, with stirring. The solution was stirred at 0–5° for one hour and overnight at room temperature. The colorless solution was concentrated under reduced pressure until sodium chloride began to precipitate, made basic by addition of 60 g. of sodium hydroxide in 60 ml. of water with cooling, and extracted with seven 50-ml. portions of methylene chloride. The combined extracts were filtered through anhydrous sodium sulfate and concentrated under reduced pressure. Distillation from a modified Claisen flask gave 18.2 g. (57%) of IV as a colorless liquid, b. p. 78–81° (1.5 mm.), and left 5.6 g. of an orange resinous residue. The product was hygroscopic and darkened on standing exposed to air. A sample of IV from a similar preparation was distilled through a semimicro fractionating column[7] with some loss through decomposition; b. p. 68–70° (1 mm.); $n^{25}\text{D}$ 1.4993; $d^{25}{}_4$ 1.0487.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.54; H, 9.87. Found: C, 70.39; H, 10.39.

The 2,4-dinitrophenylhydrazone of IV was prepared by treating 0.2 g. with a solution of 0.2 g. of 2,4-dinitrophenylhydrazine in 1 ml. of concentrated sulfuric acid, 1.5 ml. of water and 5 ml. of 95% ethanol overnight at room temperature. The derivative (0.25 g.) was precipitated by making the solution basic with sodium hydroxide, and was crystallized twice from ethanol to a constant m. p. of 138.5–139°.

Anal. Calcd. for $C_{15}H_{19}N_5O_4$: C, 54.04; H, 5.75; N, 21.01. Found: C, 54.15; H, 6.04; N, 20.95.

3-Aminomethyl-3-tropanol (III).—In several preparations III was isolated by the following procedure. Tropinone hydrochloride (12.6 g.) was converted to the cyanohydrin (9.37 g., 78%), which was hydrogenated by the procedure described above. The acetic acid solution of the product was made acid to congo red with concentrated hydrochloric acid, concentrated to dryness under reduced pressure, and further dried by adding two 50-ml. portions of benzene and one 50-ml. portion of ethanol and removing them under reduced pressure. The white crystalline residue (14.7 g.) of III dihydrochloride was dissolved in 200 ml. of water and passed through a 60 × 2.5 cm. column containing 200 g. of IRA-400 anion exchange resin (Resinous Products and Chemical Co.) at a rate of 25 ml. per minute. The column was washed with 200 ml. of water and the combined eluates were concentrated and distilled under reduced pressure. III was obtained in a yield of 6.9 g. (72% based on II), b. p. 115–123° (4 mm.), as a colorless, viscous, hygroscopic oil, which was characterized as the dihydrochloride and dipicrate.

The dihydrochloride of III was prepared by adding hydrogen chloride in ethanol to III in ethanol until the solution was acid to congo red. The white crystals which separated were recrystallized twice from a mixture of methanol and ether to a constant m. p. of 259–259.5° (dec.).

Anal. Calcd. for $C_9H_{18}N_2O \cdot 2HCl$: C, 44.45; H, 8.29; N, 11.52; Cl, 29.16. Found: C, 44.69; H, 8.29; N, 11.37; Cl, 28.95.

The dipicrate of III was prepared in ethanol, recrystallized from a mixture of acetone and water (1:3) and dried by suspending it in benzene and removing the benzene under reduced pressure, followed by heating at 80° and 0.5 mm. to constant weight over phosphorus pentoxide; m. p. 235–235.5° (dec.).

Anal. Calcd. for $C_{21}H_{24}N_8O_{15}$: C, 40.13; H, 3.85; N, 17.83. Found: C, 40.25; H, 4.00; N, 18.00.

R-Homotropanol (V).—A solution of 18.2 g. of IV in 100 ml. of absolute ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of 9 g. of W-7 Raney nickel,[5] added in two portions. Hydrogen absorption amounted to 96.5% of one molar equivalent and stopped after seven hours. The catalyst was separated by filtration and the filtrate was concentrated and distilled from a modified Claisen flask under reduced pressure. V distilled as a viscous, colorless oil, b. p. 93–98° (2 mm.); yield 12.9 g. (70%). This material was used for the preparation of VI without further purification. An analytical sample which was distilled through a semi-micro fractionating column[7] had b. p. 97.5–98° (2 mm.); $n^{25}\text{D}$ 1.5059; $d^{25}{}_4$ 1.0579.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.53; H, 10.77; N, 9.27.

The dipicrate of V was prepared in alcohol and crystallized from the same solvent. After drying at 78° and 1 mm. for four hours over phosphorus pentoxide it sintered at 275–280°.

Anal. Calcd. for $C_{15}H_{20}N_4O_8$: C, 46.87; H, 5.25; N, 14.58. Found: C, 46.83; H, 5.42; N, 14.66.

In each preparation of V a small amount of a lower boiling, mobile liquid was separated from the viscous product as a forerun, which probably contained the geometric isomer of V. Appreciable quantities of IV were not present as an impurity in this fraction, according to its infrared absorption spectrum in the region of carbonyl absorption, and its failure to react with 2,4-dinitrophenylhydrazine reagent. The lower boiling fraction gave an analytically pure dipicrate, presumably a mixture of the stereoisomers.

R-Homo-2(or 3)-tropidine (VI).—Glacial acetic acid (7.9 g.) was added with cooling to 17.9 g. of V, and 31.8 g. of concentrated sulfuric acid was added slowly with cooling to the resulting sirup. The solution was heated under reflux in a bath at 160° for eight and one-half hours. The mixture was cooled, 100 ml. of water was added, and the solution was made basic by the addition with cooling of 150 ml. of 20% sodium hydroxide solution. The mixture was extracted with five 100-ml. portions of ether, and the combined extracts were dried over magnesium sulfate, filtered and concentrated under reduced pressure. Distillation of the residue from a modified Claisen flask yielded 10.2 g. (64%) of VI, b. p. 86–89° (27 mm.), m. p. 16.3–17.9°. The average yield of four preparations was 64%. An analytical sample which was fractionated through a semi-micro column[7] had b. p. 88–89° (28 mm.); m. p. 17.2–18°; $n^{25}\text{D}$ 1.4988; $d^{25}{}_4$ 0.9568.

Anal. Calcd. for $C_9H_{15}N$: C, 78.77; H, 11.02; N, 10.21. Found: C, 78.66; H, 10.99; N, 10.12.

A sample of VI in absolute methanol was exactly neutralized to congo red with 70% perchloric acid. The solvent was removed and the perchlorate recrystallized from ethyl acetate containing a small amount of ethanol; m. p. 111.4–112.2°.

Anal. Calcd. for $C_9H_{16}ClNO_4$: C, 45.47; H, 6.79; N, 5.89. Found: C, 45.52; H, 6.80; N, 6.02.

R-Homotropane (XI).—Hydrogenation of 1.35 g. of VI in 25 ml. of glacial acetic acid in the presence of 0.08 g. of prereduced Adams platinum oxide catalyst was complete in thirty minutes and required 99% of one molar equivalent of hydrogen. The catalyst was separated by filtration, the filtrate was made basic with 100 ml. of 20% sodium hydroxide, and extracted with five 40-ml. portions of ether. The combined extracts were dried over potassium hydroxide, concentrated, and the residue was distilled, yielding 1.04 g. (77%) of XI, b. p. 80–83° (30 mm.). An analytical sample which was refractionated through a semi-micro column[7] had b. p. 80–82° (30 mm.); $n^{25}\text{D}$ 1.4810.

Anal. Calcd. for $C_9H_{17}N$: C, 77.63; H, 12.30; N, 10.06. Found: C, 77.75; H, 12.56; N, 9.89.

The picrate of XI, prepared in 95% ethanol and re-

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(7) Gould, Holzman and Niemann, *Anal. Chem.*, **20**, 361 (1948).

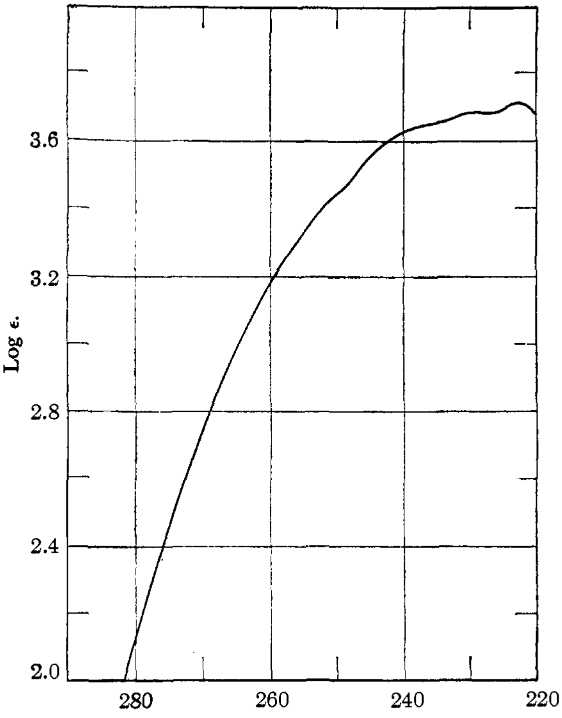

Fig. 1.—Ultraviolet absorption spectrum of dimethylaminocycloöctadiene (VIII) prepared from R-homo-2 (or 3)-tropidine methiodide (VII).

crystallized from a mixture of ethanol and acetone, had m. p. 272.4-273.2° (dec.).

Anal. Calcd. for $C_{15}H_{20}N_4O_7$: C, 48.91; H, 5.47; N, 15.21. Found: C, 48.99; H, 5.40; N, 15.03.

The perchlorate of XI was prepared in methanol and recrystallized from ethyl acetate containing a small amount of methanol; m. p. 236-237° (dec.).

Anal. Calcd. for $C_9H_{18}ClNO_4$: C, 45.09; H, 7.57; N, 5.84. Found: C, 44.96; H, 7.53; N, 6.14.

R-Homo-2(or 3)-tropidine Methiodide (VII).—A solution of 9.63 g. of VI and 20 g. of freshly distilled methyl iodide in 150 ml. of cyclohexane was heated under reflux at 80° for thirty minutes. Filtration separated 16.4 g. of VII, and the filtrate was heated with an additional 5 g. of methyl iodide for four hours, which yielded an additional 3.0 g. (total yield 99%). After washing with two 50-ml. portions of cyclohexane VII had m. p. 304-306° (dec.). The average yield of four preparations was 98.6%. An analytical sample of VII purified by recrystallization from ethanol had m. p. 306.4-306.6° (dec.).[8]

Anal. Calcd. for $C_{10}H_{18}IN$: C, 43.02; H, 6.50; N, 5.02. Found: C, 42.94; H, 6.34; N, 5.00.

Dimethylaminocycloöctadiene (VIII).—A solution of 28.9 g. of VII in 200 ml. of water was stirred for fifty minutes at room temperature with the freshly precipitated, alkali-free silver oxide prepared from 35.3 g. of silver nitrate. At the end of this period the solution gave a negative test for iodide ion. The mixture was filtered, and the filter cake was stirred with 75 ml. of water. After filtration the combined filtrates were concentrated under reduced pressure at a bath temperature of 45°. The concentrate was distilled nearly to dryness at 15-20 mm. in a 125-ml. Claisen flask heated in a bath at 100-110°, and the distillate was collected in a cooled receiver. The upper parts of the flask were rinsed with 5 ml. of water to dissolve any remaining quaternary base, and the solution was distilled to dryness. The colorless oil in the distillate was extracted with two 50-ml. portions of ether. The extracts were dried over magnesium sulfate, filtered, concentrated under reduced pressure, and the residue was distilled from a modified Claisen flask. The yield of VIII was 12.1 g. (77%), b. p. 75-76° (7 mm.). An analytical sample fractionated through a semi-micro column[7] had b. p. 78° (8 mm.), $n^{25}D$ 1.5004, d^{25}_4 0.9079.

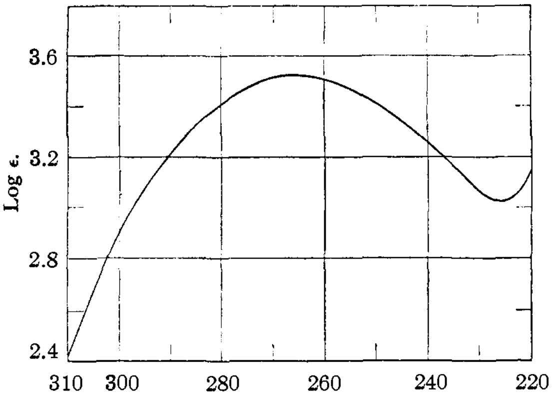

Fig. 2.—Ultraviolet absorption spectrum of 1,3,5-cyclo-octatriene (X) prepared from R-homotropinone.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.40; H, 11.33; N, 9.26. Found: C, 79.49; H, 11.37; N, 9.27.

The picrate of VIII was prepared in 95% ethanol and recrystallized from absolute ethanol; m. p. 180.2-181° (slight darkening), which was not depressed in a mixed m. p. with a sample of α-des-dimethylgranatenine picrate[9] (derived from pseudopelletierine[4]).

Anal. Calcd. for $C_{16}H_{20}N_4O_7$: C, 50.52; H, 5.30; N, 14.73. Found: C, 50.92; H, 5.28; N, 14.49.

Hydrogenation of a 0.198-g. sample of VIII in glacial acetic acid in the presence of prereduced Adams platinum catalyst required 100.5% of two molar equivalents of hydrogen. The product was separated in the same manner as XI and (without purification by distillation) converted to the picrate in ethanol. Recrystallization from 7:3 ethanol-acetone to constant m. p. gave dimethylaminocycloöctane picrate, m. p. 197.2-197.8°; mixed m. p. with an authentic sample[10] with m. p. 197.4-198.2° was 197.2-198°.

The product from a similar quantitative hydrogenation was treated with methyl iodide in ether solution and yielded dimethylaminocycloöctane methiodide; m. p. after recrystallization from a mixture of acetone and cyclohexane 275-275.4° (dec.)[8] (ref. 4 reports m. p. 274-275° dec.).

Dimethylaminocycloöctadiene Methiodide (IX).—Methyl iodide (20.9 g.) was added to 11.13 g. of VIII in 100 ml. of cyclohexane. The mixture was boiled under reflux for one hour, cooled and filtered to separate 13.8 g. of IX, m. p. 182-183° (dec.). An additional 10 g. of methyl iodide was added to the filtrate, which was boiled under reflux for one hour and allowed to stand for forty-eight hours. Filtration separated an additional 4.9 g. of IX, making the total yield 86%. An analytical sample which was recrystallized from a mixture of ethyl acetate and ethanol had m. p. 183.4-184° (dec.).[8]

Anal. Calcd. for $C_{11}H_{20}IN$: C, 45.05; H, 6.88; N, 4.77. Found: C, 45.11; H, 6.80; N, 4.87.

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(8) The sample was introduced into the melting point bath 10° below the m. p. and the temperature was increased at a rate of 2° per minute.

(9) We are indebted to Mr. Alfred A. D'Addieco for the preparation of this compound.

(10) Cope and Estes, THIS JOURNAL, **72**, 1128 (1950).

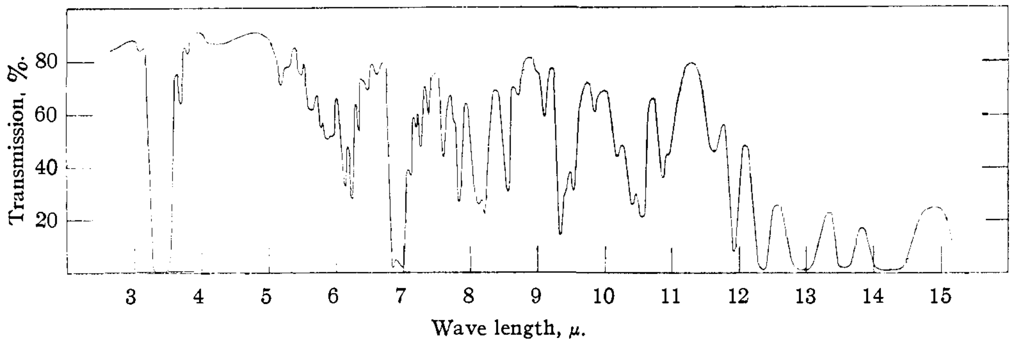

Fig. 3.—Infrared absorption spectrum of 1,3,5-cycloöctatriene (X) prepared from R-homotropinone.

A mixed m. p. of IX with α-des-dimethylgranatenine methiodide (m. p. 183-183.5° dec., derived from pseudopelletierine[4]) was not depressed, but this fact is not valid evidence that the samples were identical because they melted with decomposition.

1,3,5-Cycloöctatriene (X).—The freshly precipitated alkali-free silver oxide prepared from 15.9 g. of silver nitrate was added to a solution of 13.7 g. of IX in 100 ml. of water. Conditions similar to those described for the conversion of VII to VIII were used for the conversion of IX to X. The colorless liquid which separated in the receiver (cooled with Dry Ice) on distillation of the quaternary base was extracted with 25 ml. of ether, and the aqueous layer was extracted with two 25-ml. portions of ether. The extracts were dried over magnesium sulfate and concentrated by distillation of the ether under reduced pressure through a Widmer column. Distillation of the residue yielded 3.54 g. (71%) of X, b. p. 79-80° (90 mm.). Redistillation through a semi-micro column[7] gave X with b. p. 81° (90 mm.), $n^{25}\mathrm{D}$ 1.5217, d^{25}_4 0.8978.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.62; H, 9.49.

Quantitative hydrogenation of a 0.116-g. sample of X in the presence of prereduced Adams platinum oxide catalyst in absolute ethanol required 93% of three molar equivalents of hydrogen. The catalyst was separated, and the filtrate was diluted with 25 ml. of water and extracted with three 25-ml. portions of ether. The extracts were dried over magnesium sulfate, and the ether was distilled through a glass helix-packed column. The residue was distilled through a micro column[11] and then passed through a column containing 325-mesh activated silica gel to remove the last traces of ether. This procedure yielded cycloöctane, m. p. 8-10°.

1,3,5-Cycloöctatriene-Maleic Anhydride Adduct.—A solution of 0.425 g. of X (prepared from IX) and 0.454 g. of freshly distilled maleic anhydride in 4.5 ml. of dry benzene was boiled under reflux for two hours and allowed to stand at room temperature for forty-eight hours. The solution was concentrated to a volume of 1-2 ml. and the crystalline product was separated by centrifugation in a Craig tube. The yield of the adduct was 0.521 g. (64%), which on recrystallization from cyclohexane containing a little acetone separated as long, thin needles, m. p. 144-144.8°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.90.

A sample of X prepared from pseudopelletierine[9] gave a maleic anhydride adduct with m. p. 143.3-144.3° which did not depress the m. p. of the adduct described above.

Absorption Spectra.—The ultraviolet absorption spectra of VIII and X were determined in purified cyclohexane as a solvent with a Beckman Model DU quartz ultraviolet spectrophotometer, and are shown in Figs. 1 and 2, in which the logarithms of the molar extinction coefficients are plotted against the wave length in millimicrons.

We are indebted to Dr. R. C. Lord, Mr. R. S. McDonald and Miss B. J. Fax for determining the infrared spectrum of X (Fig. 3).

Summary

Tropinone has been converted to an eight-membered cyclic homolog, R-homotropinone (IV), by the Tiffeneau method of ring expansion. R-Homotropinone has been degraded to 1,3,5-cycloöctatriene (X) by a sequence of reactions similar to the one used by Willstätter for the preparation of 1,3,5-cycloöctatriene from pseudopelletierine.

CAMBRIDGE, MASSACHUSETTS

RECEIVED SEPTEMBER 30, 1949

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[11] Gettler, Niederl and Benedetti-Pichler, *Microchem.*, 11, 74 (1932).