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

Cyclic Polyolefins. XVI. Phenylcycloheptatriene and Phenylcycloöctatriene[1]

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Pseudopelletierine (II) has been converted into phenylcycloöctatriene (XV) by a reaction sequence analogous to the one used by Willstätter to prepare 1,3,5-cycloöctatriene from II. In the first step of the synthesis pseudopelletierine was treated with phenyllithium to form 3-phenyl-N-methylgranatoline (IV). The reaction of IV with thionyl chloride followed by treatment with potassium hydroxide yielded 3-phenyl-N-methylgranatenine (VI), which was converted into phenylcycloöctatriene by two successive Hofmann exhaustive methylations. By a parallel series of reactions studied as models, phenylcycloheptatriene (XIV) was prepared from tropinone (I).

One possible route for the synthesis of substituted cycloöctatetraenes would follow the classical Willstätter synthesis,[2] modified by the introduction of a substituent through a reaction of the carbonyl group of pseudopelletierine. This paper reports the investigation of such a synthesis with a phenyl group as the substituent, and a parallel model study of the conversion of the more readily available alkaloid tropinone into phenylcycloheptatriene.

Tropinone (I) formed 3-phenyl-3-tropanol (III) in only 5% yield when it was treated with phenylmagnesium bromide, probably because an insoluble complex was formed, but with phenyllithium I yielded 74% of the tertiary alcohol III. A small amount (12%) of tropinone was recovered. Preliminary attempts to convert III into the corresponding olefin V by treatment with sulfuric acid in acetic acid at 165° or with iodine in refluxing benzene were unsuccessful. 3-Phenyltropidine (V) was obtained from III in 86% yield by reaction with thionyl chloride to form the tertiary chloride, which was not isolated, but treated directly with potassium hydroxide in aqueous ethanol. 3-Phenyltropidine methiodide (VII) was formed in 98% yield from V and methyl iodide. When the quaternary base prepared from VII and silver hydroxide was decomposed by heating at pressures below 1 mm. with a bath temperature which did not exceed 58°, and the product was isolated by a slow molecular distillation without heating above that temperature, 3-phenyl-α-des-methyltropidine (IX) was isolated as a light yellow liquid in 64% yield. The α-des base IX was characterized by a quantitative hydrogenation which required 104.2% of two molar equivalents of hydrogen, and by conversion into a crystalline methiodide (XII) in quantitative yield.

When the quaternary base prepared from VII was decomposed at slightly higher temperatures, and the product was distilled at 1 mm., an isomer of IX was formed by a molecular rearrangement. This compound was a vinyl-type amine, 3-phenyl-β-des-methyltropidine (XI), which was characterized by its ultraviolet absorption spectrum (Fig. 1), by a quantitative hydrogenation which required 107% of two molar equivalents of hydrogen, and by reaction with methyl iodide, which formed tetramethylammonium iodide rather than a methiodide. The rearrangement of IX to XI by heating parallels the rearrangement of α-des-methyltropidine to β-des-methyltropidine (structures analogous to IX and XI without the phenyl substituent).[2,3] The structure XI is based on analogy with the structure of β-des-methyltropidine; it is not certain that both double bonds of IX rearrange in forming XI, but one must migrate to form a vinyl-type amine in order to explain the reaction of the product with methyl iodide forming tetramethylammonium iodide. In one case in which IX was purified by molecular distillation, partial rearrangement to XI occurred, and the fractions contained IX plus amounts of XI which increased from the first to the last fraction (deter-

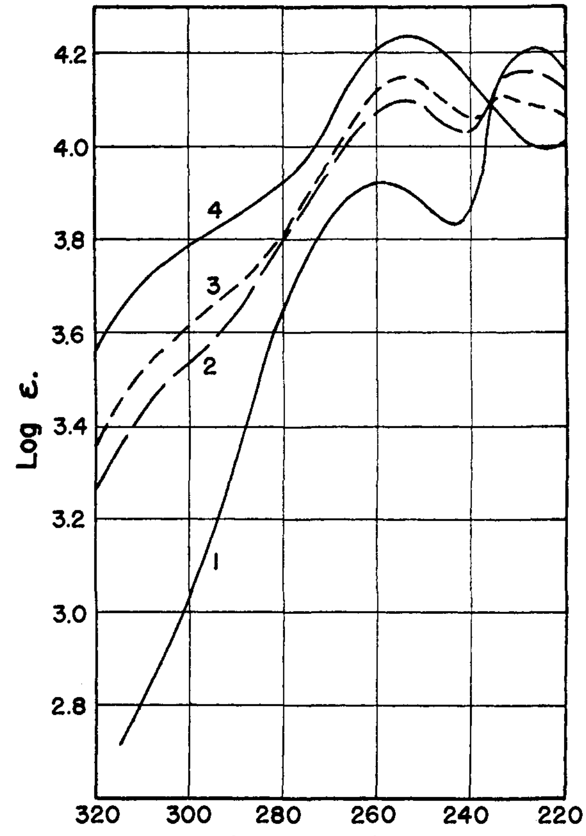

Fig. 1.—Ultraviolet absorption spectra: curves 1–3, mixtures of 3-phenyl-α-des-methyltropidine (IX) and 3-phenyl-β-des-methyltropidine (XI) with $n^{25}\mathrm{D}$ 1.5740, 1.5837 and 1.5881, respectively; curve 4, 3-phenyl-β-des-methyltropidine, $n^{25}\mathrm{D}$ 1.5958.

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

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

[3] G. Merling, *ibid.*, **24**, 3123, 3125 (1891); R. H. F. Manske and H. L. Holmes, "The Alkaloids," Vol. I, Academic Press, New York, N. Y., 1949, p. 285.

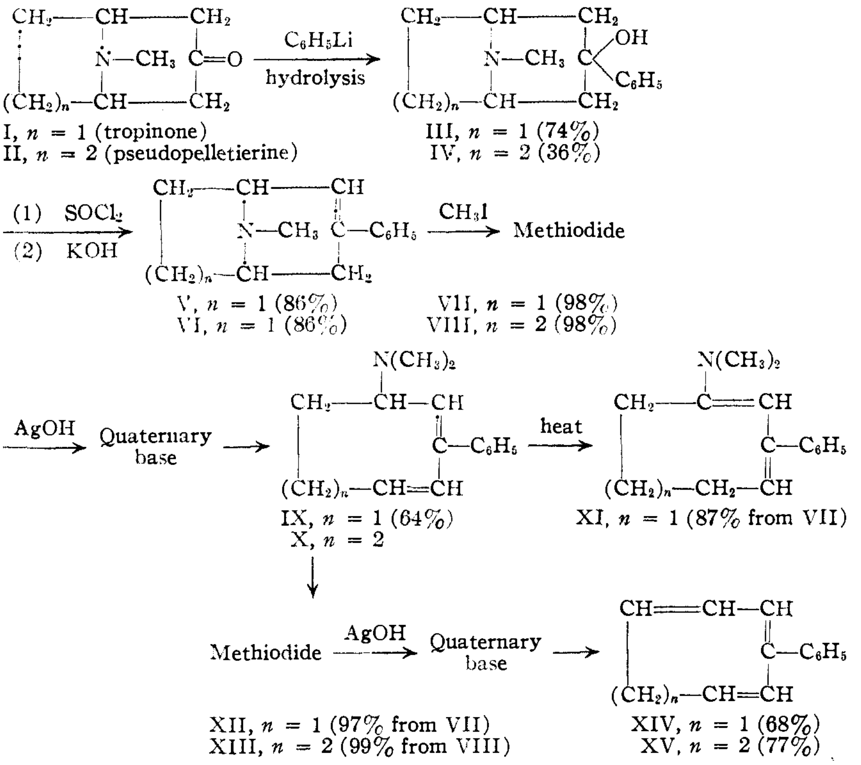

Fig. 2.—Synthesis of phenylcycloheptatriene (XIV) from tropinone (I), and synthesis of phenylcycloöctatriene (XV) from pseudopelletierine (II).

mined from their ultraviolet absorption spectra, Fig. 1).

In the reaction sequence leading to phenylcycloheptatriene (Fig. 2) it was possible to avoid loss through partial rearrangement of IX to XI by omitting the isolation of IX. The thermal decomposition of the quaternary base prepared from VII was conducted at a low temperature, and a solution of the crude product (not distilled) in benzene was washed with water to remove any remaining quaternary base and then treated with methyl iodide. In this manner 3-phenyl-α-desmethyltropidine methiodide (XII) was obtained in an over-all yield of 97% from 3-phenyltropidine methiodide (VII). In the final step of the synthesis the methiodide XII was converted into the quaternary base, which was decomposed at 45–60°. Distillation yielded phenylcycloheptatriene (XIV) (68%) as a colorless liquid, which was characterized by its ultraviolet absorption spectrum (Fig. 3). There are four possible structures (position isomers) for the product, assuming that cumulene structures can be excluded on steric grounds. The product may have any one of the four structures or be a mixture; formula XIV is written for convenience, and is the structure which would be formed if no rearrangement of double bonds occurred in the reaction sequence. A sample of phenylcycloheptatriene identical with the one formed by decomposition of the quaternary base was obtained by thermal decomposition of the methiodide XII at 136–157°, which yielded XIV and trimethylamine hydroiodide. Evidence for the structure of phenylcycloheptatriene (XIV) was obtained by quantitative hydrogenation in the presence of a palladium catalyst, which required 97.7% of three molar equivalents of hydrogen. The reduction product was identified as phenylcycloheptane by comparison of its physical properties with those reported by Pines, Edeleanu and Ipatieff[4] for phenylcycloheptane prepared from cycloheptanone. The 2,4-diacetamidophenylcycloheptane prepared as a derivative from phenylcycloheptane obtained from XIV had the melting point reported by these authors,[4] but another derivative, 4-sulfonamidophenylcycloheptane, had a higher melting point than the one previously reported.

The reaction sequence used to prepare phenylcycloöctatriene (Fig. 2) was exactly similar to the one used to prepare phenylcycloheptatriene from tropinone. In each step the reaction conditions used were those which resulted in optimum yields in the tropinone series. Synthetic pseudopelletierine[5] (II) reacted with phenyllithium to form 36% of 3-phenyl-N-methylgranatoline (IV) and 49% of recovered II. After this work was completed it was discovered that pseudopelletierine rapidly takes up water from the air forming a hemihy-

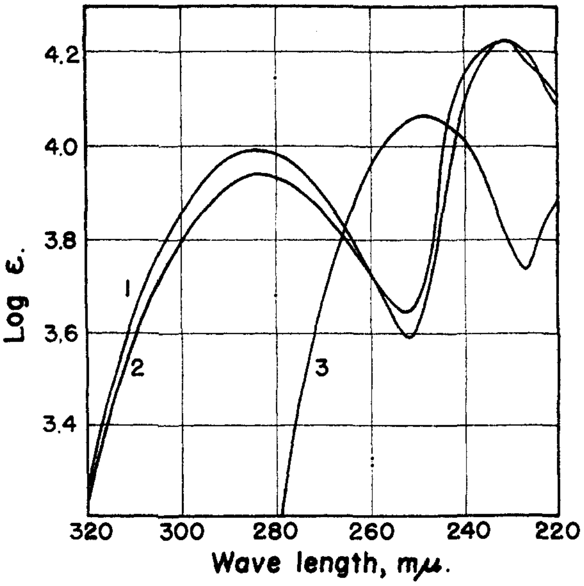

Fig. 3.—Curve 1, ultraviolet absorption spectrum of phenylcycloheptatriene (XIV); curve 2, phenylcyclooctatriene (XV); curve 3, 1-phenyl-1-cycloöctene (XVI).

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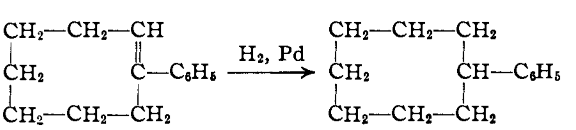
[4] H. Pines, A. Edeleanu and V. N. Ipatieff, THIS JOURNAL, 67, 2195 (1945).

[5] A. C. Cope, H. L. Dryden, Jr., C. G. Overberger and A. A. D'Addieco, *ibid.*, 73, 3416 (1951).

drate,[5] and partial hydrolysis of the phenyllithium reagent by water of hydration present in the pseudopelletierine may account for the low yield of IV and large recovery of II. In a preparation in which phenyllithium was added to pseudopelletierine (inverse addition) the yield of IV was reduced to 20%. The reaction of IV with thionyl chloride and subsequent reaction of the tertiary chloride (which was not isolated) with potassium hydroxide in aqueous ethanol formed 3-phenyl-N-methylgranatenine (VI) in 86% yield. Treatment of VI with methyl iodide yielded 3-phenyl-N-methylgranatenine methiodide (VIII) (98%). Because of the difficulty which arose in the tropinone series through rearrangement of the α-des base IX to the β-des base XI, the α-des base (X) was not isolated in the pseudopelletierine series. Instead the quaternary base prepared from VIII was decomposed at a low temperature, and a solution of the resulting α-des base (not distilled) in benzene was treated directly with methyl iodide to form 3-phenyl-α-des-dimethylgranatenine methiodide (XIII) (99% over-all from VIII). Decomposition at 45–50° of the quaternary base prepared from XIII yielded phenylcycloöctatriene (XV) (77%) as a colorless liquid. The double bonds in phenylcycloöctatriene prepared in this manner are conjugated, for its ultraviolet absorption spectrum is almost exactly identical with the spectrum of phenylcycloheptatriene (Fig. 3), in which the double bonds must be conjugated for stereochemical reasons. There are four possible position isomers of phenylcycloöctatriene in which the double bonds are conjugated; formula XV is written for the product for convenience, and is the structure which would be formed if no rearrangement of double bonds occurred in the series of reactions. Phenylcycloöctatriene prepared in this way appears to be contaminated by an isomer with a bridged structure containing two double bonds. Like 1,3,5-cycloöctatriene itself,[6] XV absorbed less than three molar equivalents of hydrogen (90.1%) in the presence of a palladium catalyst and formed somewhat impure phenylcycloöctane, m.p. −1.7 to +1.5°, contaminated with a compound of similar boiling point (probably a phenylbicycloöctane). The reduction product was identified as phenylcycloöctane by preparation of a known sample from cycloöctanone. Phenylmagnesium bromide and cycloöctanone yielded a mixture of 1-phenyl-1-cycloöctanol and 1-phenyl-1-cycloöctene, which was converted into pure 1-phenyl-1-cycloöctene (XVI) by treatment with iodine. Hydrogenation of XVI in the presence of a palladium catalyst yielded pure phenylcyclooctane (XVII), m.p. 7.3–8.5°. A mixture of pure XVII and the impure sample obtained by hydrogenation of XV melted at 2.0–7.3°.



XVI XVII

Experimental[7]

3-Phenyl-3-tropanol (III).—A dry 2-l. three-necked flask was fitted with a mechanical stirrer, a reflux condenser and a dropping funnel, and the condenser and funnel were protected with drying tubes attached to a source of nitrogen under a pressure of 1–2 cm. of mercury. The air in the system was displaced with nitrogen, and 120 ml. of dry ether and 6.76 g. of lithium wire (cut into short pieces) were added. A solution of 75.4 g. of bromobenzene in 160 ml. of dry ether was added with stirring during 1.5 hours at a rate that maintained reflux, and the mixture was heated under reflux for an additional period of 30 minutes. A solution of 55.6 g. of tropinone (obtained from Merck and Co., Inc., and redistilled) in 160 ml. of dry ether was added to the phenyllithium solution during 35 minutes. The heat of reaction maintained the reflux temperature during the addition, and the mixture was heated under reflux for an additional period of 30 minutes. The mixture was cooled in ice, and 200 ml. of ice-water was added, slowly at first. The white solid product was collected on a Büchner funnel, washed with cold water, sucked as dry as possible, and washed on the funnel with cold hexane to remove organic impurities. The crude product after drying melted at 161.5–162.5° and weighed 57.5 g. The aqueous layer in the filtrate was extracted with a 200-ml. and a 400-ml. portion of ether, and the combined organic layers were dried over sodium sulfate. A solid residue which was obtained by distillation of the solvent was purified by crystallization from hexane and yielded 6.3 g. of III, m.p. 161–162.5°, making the total yield 63.8 g. (74%). An analytical sample which was recrystallized from hexane melted at 161.5–162.5°.

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.54; H, 8.65; N, 6.35.

Extraction of the alkaline aqueous solution (from which III had been separated by ether extraction) with two 400-ml. portions of methylene chloride yielded 6.5 g. (12%) of recovered tropinone.

3-Phenyltropidine (V).—3-Phenyl-3-tropanol (69.9 g.) was added in small portions with mechanical stirring to a solution of 75 ml. of purified thionyl chloride in 150 ml. of dry ether with cooling in an ice-salt-bath. The resulting yellow solution was warmed in a bath at 45–50° for 30 minutes, and then the excess thionyl chloride and ether were removed by distillation under reduced pressure. The brown solid residue was dissolved in 50 ml. of ethanol (added slowly at first), and a solution of 40 g. of potassium hydroxide in 75 ml. of water and 150 ml. of ethanol was added slowly with cooling. A solution of 60 g. of potassium hydroxide in 250 ml. of water was then added to make the mixture strongly basic. The brown oil which formed was separated, and the aqueous layer was extracted with two 200-ml. portions of ether. The combined oil and ethereal extracts were dried over sodium sulfate. The solution was concentrated, and the residue was distilled through a 20 × 1.2-cm. column packed with glass helices. The yield of V was 54.8 g. (86%), b.p. 118–119° (1 mm.). A redistilled analytical sample from another preparation was obtained as a colorless liquid b.p. 113–115° (0.45 mm.), m.p. 13–14°, n^{25}_{D} 1.5777, d^{25}_{4} 1.0481; M_D calcd. 62.32, found 62.93.

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.06; H, 8.51; N, 6.91.

3-Phenyltropidine Methiodide (VII).—An excess of methyl iodide (60 g.) was added to a solution of 54.8 g. of 3-phenyltropidine in 600 ml. of absolute ethanol with cooling in an ice-bath. After a few minutes the methiodide VII started to crystallize, and the mixture was allowed to stand overnight at 0–5°. The product was collected on a filter and washed with small portions of cold ethanol. The first crop after drying amounted to 87.5 g., m.p. 260–261° (dec., introduced at 200° and heated 2–3° per minute). Addition of small portions of methyl iodide to the filtrate followed by concentration yielded an additional 4.2 g. of VII, m.p. 259–261° (dec.), making the total yield 91.7 g. (98%). An analytical sample was recrystallized from absolute ethanol; m.p. 260–261° (dec., introduced at 200° and heated 2–3° per minute).

Anal. Calcd. for $C_{15}H_{20}IN$: C, 52.79; H, 5.91; N, 4.11; I, 37.19. Found: C, 52.71; H, 5.98; N, 3.95; I, 37.49.

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[6] A. C. Cope and F. A. Hochstein, THIS JOURNAL, **72**, 2515 (1950).

[7] Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy and his associates for analyses.

3-Phenyl-α-des-methyltropidine (IX).—3-Phenyltropidine methiodide (6.0 g.) and 50 ml. of water were warmed on a steam-bath and stirred until the solid dissolved, and the alkali-free silver hydroxide freshly prepared from 5.98 g. of silver nitrate was added. The mixture was stirred and heated on a steam-bath for 1.5 hours. The mixture was filtered, and the silver iodide and silver hydroxide were digested with 25 ml. of water on a steam-bath for 15 minutes. The solids were separated again by filtration, and the filtrates were combined and concentrated at 1–2 mm. with a bath temperature which did not exceed 45°. The concentrated solution of the quaternary base was dissolved in a small volume of methanol, filtered to remove a small amount of solid, and placed in a molecular-type still. The solvent was removed by distillation, and the residual quaternary base was decomposed by heating for 44 hours at 0.2–1.0 mm. with a bath temperature which did not exceed 58°. The product (IX) collected during the period of heating as a light yellow liquid in four fractions ($n^{25}\mathrm{D}$ 1.5724, 1.5715, 1.5725, 1.5719) with a total weight of 2.40 g. (64%). The second fraction was analyzed; d^{25}_{4} 1.0032; *M*D calcd. 68.68, found 69.93 (exaltation 1.25).

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.63; H, 9.06; N, 6.88.

Hydrogenation of a solution of 0.3 g. of IX in 20 ml. of absolute ethanol in the presence of 100 mg. of pre-reduced Adams platinum oxide was complete in seven hours and required 104.2% of two molar equivalents of hydrogen. The picrate of the reduction product failed to crystallize.

A 2.0-g. sample of IX was converted to the methiodide (XII) by treatment with an excess of methyl iodide in benzene solution. The product separated as an oil which crystallized on standing at 0–5°. Filtration separated a quantitative yield (3.35 g.) of XII as a light yellow powder, m.p. 130–131° (the preparation and properties of pure XII are described below).

3-Phenyl-α-des-methyltropidine Methiodide (XII).—3-Phenyltropidine methiodide (40 g.) and 320 ml. of water were warmed on a steam-bath and stirred mechanically until the solid dissolved. The alkali-free silver hydroxide freshly prepared from 40 g. of silver nitrate was added, and the mixture was stirred and heated on a steam-bath for one hour. The mixture was filtered, the solids were digested with 50 ml. of water on a steam-bath for 15 minutes, and again separated by filtration. The combined filtrates were concentrated in a nitrogen atmosphere at 1 mm. until nearly all of the water was removed with a bath temperature which did not exceed 55°. The residual quaternary base was decomposed by heating in a nitrogen atmosphere at 1 mm. with a bath temperature of 45–55° for three hours. The liquid residue was dissolved in 150 ml. of benzene and washed with 100 ml. of water. The water layer was extracted with 150 ml. of benzene, and the combined benzene solutions were concentrated under reduced pressure in a nitrogen atmosphere to a volume of 200 ml. (the bath temperature did not exceed 55°). The benzene solution was filtered if it was not clear, 35 g. of methyl iodide was added, and the solution was cooled to 0–5°. The methiodide XII began to crystallize in a few minutes, and was collected on a filter after the mixture had stood overnight at 0–5°. It was washed with 100 ml. of hexane and dried to a constant weight of 40.5 g. (97%) in a vacuum desiccator. XII was obtained as a yellow powder, m.p. 131.5–132.5°. An analytical sample that was recrystallized from a mixture of ethanol and hexane formed white crystals, m.p. 133.5–134.5° (introduced at 110° and heated 2–3° per minute).

Anal. Calcd. for $C_{16}H_{22}IN$: C, 54.09; H, 6.24; N, 3.94; I, 35.72. Found: C, 54.03; H, 6.34; N, 4.04; I, 35.88.

3-Phenyl-β-des-methyltropidine (XI).—A solution of 6.0 g. of 3-phenyltropidine methiodide in 30 ml. of water and 35 ml. of methanol was stirred and heated in a bath at 60° for 1.25 hours with the alkali-free silver hydroxide freshly prepared from 5.98 g. of silver nitrate. The solids were collected on a filter, digested with 20 ml. of methanol on a steam-bath for ten minutes, and again separated by filtration. The combined filtrates were concentrated under reduced pressure and the residual quaternary base was decomposed by heating in a short-path still at 0.6–1.5 mm. with a heating block temperature of 55–120°. Three fractions of the light yellow distillate (3.23 g., 87%) were separated at arbitrary intervals; $n^{25}\mathrm{D}$ 1.5802, 1.5950, 1.5954. Two redistillations in which only mechanical losses occurred yielded XI as a light yellow liquid, b.p. 133–134° (1.05 mm.), $n^{25}\mathrm{D}$ 1.5958, d^{25}_{4} 1.0142; *M*D calcd. 68.68, found 71.56 (exaltation 2.88).

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.54; H, 8.88; N, 6.15.

Hydrogenation of a solution of 0.305 g. of XI in 15 ml. of absolute ethanol in the presence of 100 mg. of prereduced Adams platinum oxide added in two portions was complete in four hours and required 107% of two molar equivalents of hydrogen. The methiodide of the reduction product failed to crystallize.

A solution of 5.5 g. of 3-phenyl-β-des-methyltropidine (XI) in 60 ml. of dry methanol and 8.0 g. of methyl iodide was warmed in a bath at 40–45° for 16 hours. A white crystalline solid separated, and the solution turned brown. The solid was collected on a filter and triturated with ethanol to remove a sticky impurity. An additional quantity of the white solid was obtained by concentrating the filtrate and crystallizing the residue from a mixture of ethanol and hexane, making the total yield 2.55 g. This solid was recrystallized from dry methanol. It was identified as tetramethylammonium iodide by the fact that it did not melt below 300°, and by analysis. The other products of the reaction were not isolated.

Anal. Calcd. for $C_4H_{12}IN$: C, 23.89; H, 6.02. Found: C, 23.97; H, 5.99.

Thermal Rearrangement of 3-Phenyl-α-des-methyltropidine (IX) to 3-Phenyl-β-des-methyltropidine (XI).—A solution of 6.0 g. of 3-phenyltropidine methiodide in 50 ml. of hot water was treated with the alkali-free silver hydroxide freshly prepared from 5.98 g. of silver nitrate, and the quaternary base was concentrated and decomposed in the manner described under the preparation of XII. The benzene solution of the α-des base IX was concentrated and distilled in a short-path still at 0.17–0.24 mm. with a heating block temperature of 42–53°, and the light yellow distillate (3.15 g., 84%) was separated into four fractions. The refractive indices ($n^{25}\mathrm{D}$ 1.5740, 1.5778, 1.5837, 1.5881) and ultraviolet absorption spectra (Fig. 1) of the fractions showed that they were mixtures of IX and XI containing amounts of XI that increased from the first to the last fraction (indicating that IX was rearranging to XI during the distillation). The four fractions were combined and redistilled slowly through a Vigreux column at 0.17 mm. The last of three fractions which were collected was the analytically pure β-des base XI, $n^{25}\mathrm{D}$ 1.5959, $\lambda_{\max.}$ 253 mμ (log ε 4.24).

Phenylcycloheptatriene (XIV).—3-Phenyl-α-des-methyltropidine methiodide (XII) (8.0 g.) and 50 ml. of water were warmed in a water-bath at 50–55° and stirred mechanically until the solid dissolved. The alkali-free silver hydroxide freshly prepared from 7.65 g. of silver nitrate was added, and the mixture was stirred at 50–55° for one hour. The solids were separated by filtration and washed with small portions of water. The filtrate was concentrated in a nitrogen atmosphere at 0.5–0.9 mm. with a bath temperature of 45–50° until nearly all of the water had distilled, and the residual quaternary base was decomposed by heating at the same temperature and pressure for 2.5 hours. The residue was dissolved in 50 ml. of benzene, and the solution was washed with 70 ml. of water. The water washing was extracted with 50 ml. of benzene, and the combined benzene solutions were concentrated. The residue was distilled in a nitrogen atmosphere and yielded 2.58 g. (68%) of XIV as a colorless liquid, b.p. 100–103° (1.8–1.9 mm.), $n^{25}\mathrm{D}$ 1.6202, d^{25}_{4} 1.0217, *M*D calcd. 55.03, found 57.86 (exaltation 2.83).

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 93.22; H, 7.18.

Phenylcycloheptatriene (XIV) also was prepared by thermal decomposition of the methiodide XII. The methiodide (5.0 g.) was placed in a small flask attached to a semi-micro column,[8] and heated slowly in a nitrogen atmosphere under reduced pressure. Decomposition began when the bath temperature reached 136°, and a colorless distillate was collected during a period of 25 minutes, with a maximum bath temperature of 157°. The yield of XIV was 1.36 g. (58%), b.p. 71–72° (0.16 mm.), $n^{25}\mathrm{D}$ 1.6202. A redistilled sample boiled at 92–93° (0.45 mm.), $n^{25}\mathrm{D}$ 1.6203, d^{25}_{4} 1.0219, and had the same ultraviolet absorption spectrum as a sample prepared from the quaternary base.

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[8] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.81; H, 7.06.

The solid residue obtained by thermal decomposition of XII (2.25 g. after trituration with ethanol and drying) was identified as trimethylamine hydroiodide; m.p. after two crystallizations from 95% ethanol 259–261° (dec., introduced at 250° and heated 2–3° per minute) (lit.[9] 263°). Treatment with picric acid yielded trimethylamine picrate, which was recrystallized from 95% ethanol; m.p. 214–217° (sl. dec.) (lit.[10] 216°).

Hydrogenation of a solution of 1.03 g. of phenylcycloheptatriene in 35 ml. of absolute ethanol in the presence of 0.1 g. of 10% palladium-on-carbon[11] was complete in 5.5 hours, and required 97.7% of three molar equivalents of hydrogen. The catalyst was separated by filtration, the filtrate was concentrated, and the residue was distilled through a semi-micro column.[8] Phenylcycloheptane distilled as a colorless liquid (0.90 g., 84%), b.p. 80–82° (0.65 mm.), n^{25}_D 1.5287, n^{20}_D 1.5309, d^{25}_4 0.9484; *M*D calcd. 56.43, found 56.65 (lit.[4] n^{20}_D 1.5309, d^{20}_4 0.9482).

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.43; H, 10.27.

The phenylcycloheptane obtained by this method was converted into a diacetamido derivative by nitration, reduction of the dinitro compound and acetylation of the diamine.[12] The hydrocarbon (0.43 g.) yielded 0.57 g. (85%) of the diacetamido derivative, which after two crystallizations from a mixture of ethanol and hexane formed white plates, m.p. 240.5–241° (lit.[4] 241°).

The phenylcycloheptane was also characterized by conversion into the sulfonamido derivative by treating a 0.40-g. sample with chlorosulfonic acid and subsequently with ammonium carbonate.[13] The crude derivative (0.5 g., 86%), m.p. 125–131°, was purified by three crystallizations from aqueous ethanol to a constant melting point of 142.9–143.5°. Since this melting point does not agree with the reported value[4] of 131°, the compound was analyzed.

Anal. Calcd. for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56; N, 5.53; S, 12.65. Found: C, 61.71; H, 7.76; N, 5.74; S, 12.63.

3-Phenyl-N-methylgranatoline (IV).—A solution of phenyllithium was prepared in the manner described under the preparation of III from 9.0 g. of lithium and 104.2 g. of bromobenzene in 675 ml. of dry ether. A solution of 76.5 g. of resublimed pseudopelletierine[5] in 500 ml. of dry ether was added dropwise during one hour. The heat of reaction maintained reflux, and after the addition the mixture was heated under reflux for 30 minutes. The product was isolated in the same manner as III. The yield of IV, m.p. 169.5–171°, was 41.3 g. (36%). An analytical sample was recrystallized from hexane as fluffy white needles, m.p. 170.5–171°.

Anal. Calcd. for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06. Found: C, 78.02; H, 9.33; N, 5.93.

A total of 37.7 g. (49%) of pseudopelletierine was recovered by a short-path distillation of the mother liquor from the ether extract of the reaction mixture (after hydrolysis), and from the methylene chloride extract.

3-Phenyl-N-methylgranatenine (VI).—VI was prepared by adding 41.3 g. of IV to 60 ml. of thionyl chloride and 150 ml. of dry ether, and treating the crude chloro compound with a solution of 50 g. of potassium hydroxide in 75 ml. of water and 150 ml. of ethanol with cooling, by a procedure analogous to the one used for preparing V. The mixture was made strongly basic by adding a solution of 20 g. of potassium hydroxide in 500 ml. of water. The product was isolated by extraction with ether, and purified by distillation through a 20-cm. Vigreux column. The yield of VI was 32.9 g. (86%), collected as a very pale yellow liquid, b.p. 137–139° (2 mm.). A sample from a similar preparation was analyzed; b.p. 138–139° (1 mm.), n^{25}_D 1.5720, d^{25}_4 1.0456, *M*D calcd. 66.94, found 67.14.

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.67; H, 9.07; N, 6.37.

3-Phenyl-N-methylgranatenine Methiodide (VIII).—An excess of methyl iodide (45 g.) was added to a solution of 32.8 g. of VI in 300 ml. of absolute ethanol with cooling in an ice-bath. The methiodide VIII began to crystallize after a few minutes, and was collected on a filter after the mixture had stood at 0–5° overnight. The solid was washed with small portions of cold ethanol, and the filtrate was treated with an additional 5 g. of methyl iodide and concentrated to obtain a second crop of VIII. The total yield was 53.8 g. (98%), m.p. 288–289° (dec., darkening at 275°). An analytical sample which was recrystallized from dry methanol melted at 288–289° (dec., darkening at 275°).

Anal. Calcd. for $C_{16}H_{22}IN$: C, 54.09; H, 6.24; N, 3.94; I, 35.72. Found: C, 54.02; H, 6.22; N, 3.94; I, 35.54.

3-Phenyl-α-des-dimethylgranatenine Methiodide (XIII).—3-Phenyl-N-methylgranatenine methiodide (VIII) (53.8 g.) and 1300 ml. of water were stirred and warmed on a steam-bath until the solid dissolved. The alkali-free silver hydroxide freshly prepared from 51.34 g. of silver nitrate was added, and the mixture was stirred and heated on a steam-bath for one hour. The mixture was filtered, and the solids were washed with small portions of water on the funnel. The filtrate was concentrated at 30–40 mm. with a bath temperature of 50–60° until nearly all of the water had distilled, and the residual quaternary base was decomposed by heating at 45–50° in a nitrogen atmosphere at 4–6 mm. for 2.5 hours. The residual oil was dissolved in 150 ml. of benzene and the solution was filtered and washed with 100 ml. of water. The water washing was extracted with 150 ml. of benzene, and the combined benzene extracts were concentrated to a volume of 200 ml. under reduced pressure in a nitrogen atmosphere. Methyl iodide (45 g.) was added. The methiodide XIII began to separate as an oil which soon crystallized. The mixture was allowed to stand at 0–5° overnight, and then was filtered to separate XIII, which was obtained as a white powder (after washing on the funnel with benzene and drying) in a yield of 55.2 g. (99%), m.p. 149–151°. An analytical sample was recrystallized from a mixture of ethanol and hexane as very pale yellow crystals, m.p. 151.5–152.5°.

Anal. Calcd. for $C_{17}H_{24}IN$: C, 55.29; H, 6.55; N, 3.79; I, 34.37. Found: C, 55.61; H, 6.54; N, 3.77; I, 34.41.

Phenylcycloöctatriene (XV).—A mixture of 8.0 g. of the methiodide XIII and 100 ml. of water was stirred and warmed in a water-bath at 45° until the solid dissolved. The alkali-free silver hydroxide freshly prepared from 7.31 g. of silver nitrate was added, and the mixture was stirred and heated at 45° for one hour. The solids were removed by filtration, washed on the funnel with small portions of water, and the filtrate was concentrated in a nitrogen atmosphere at 2 mm. with a bath temperature of 45–50° until nearly all of the water had distilled. The residual quaternary base was decomposed by heating under nitrogen at the same temperature and pressure for two hours. The residue was dissolved in 50 ml. of benzene, washed with 50 ml. of water, and the water washing was extracted with two 50-ml. portions of benzene. The combined benzene solutions were concentrated under reduced pressure and the residue was distilled through a semi-micro column, yielding 3.02 g. (77%) of phenylcycloöctatriene, b.p. 117–118° (1.7 mm.), n^{25}_D 1.6072, d^{25}_4 1.0198; *M*D calcd. 59.65, found 61.73 (exaltation 2.08).

Anal. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.47; H, 7.80.

Hydrogenation of a solution of 2.78 g. of XV in 40 ml. of cyclohexane in the presence of 0.8 g. of 10% palladium-on-carbon[11] was complete in 2.5 hours, and required 90.1% of three molar equivalents of hydrogen. The catalyst was separated by filtration and the filtrate was concentrated under reduced pressure. Distillation of the residue through a semi-micro column yielded 2.51 g. (88%) of phenylcyclooctane as a colorless liquid, b.p. 98° (0.75 mm.). Retreatment with hydrogen and palladium-on-carbon in acetic acid and a second retreatment with hydrogen and prereduced Adams platinum oxide catalyst in absolute ethanol resulted in no further uptake of hydrogen. The phenylcycloöctane obtained in this manner boiled at 79.5° (0.2 mm.), d^{25}_4 0.9586; *M*D calcd. 61.05, found 60.84, m.p. −1.7 to +1.5°, mixed melting point with a authentic sample of XVII described below, 2.0–7.3°.

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Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.71; H, 10.28.

1-Phenyl-1-cycloöctene (XVI).—Pure cycloöctanone, b.p. 113–113.5° (60 mm.), was regenerated from its semicarbazone.[14] A solution of phenylmagnesium bromide was prepared from 17.3 g. of bromobenzene and 2.67 g. of magnesium turnings in 75 ml. of dry ether. A solution of 12.6 g. of cycloöctanone in 75 ml. of dry ether was added with stirring during 30 minutes at a rate which maintained reflux. The mixture was stirred and heated under reflux for an additional period of 30 minutes, and then was cooled in ice. A solution of 50 g. of ammonium chloride in 150 ml. of water was added, slowly at first, and the mixture was stirred at room temperature for four hours and allowed to stand overnight. The ether layer was separated, the aqueous layer was extracted with 125 ml. of ether, and the combined ethereal solutions were dried over sodium sulfate. The ether was distilled, and the residue was dissolved in 150 ml. of benzene and heated in a bath at 100–110° for five hours. This treatment did not result in complete dehydration of the tertiary alcohol, for concentration and distillation yielded 4.1 g. (32%) of recovered cycloöctanone and 10.74 g. of a mixture of 1-phenyl-1-cycloöctanol and 1-phenyl-1-cycloöctene, b.p. 94.5–107° (0.55–1.5 mm.), n^{25}D 1.5582–1.5608. A 5.71-g. portion of this mixture was converted to pure 1-phenyl-1-cycloöctene by heating a solution in 100 ml. of benzene with 50 mg. of iodine under reflux in a flask attached to a Dean and Stark water separator[15] for three hours. The benzene solution was washed with sodium thiosulfate solution to remove iodine, and the light yellow product obtained by distillation under reduced pressure was rewashed with sodium thiosulfate and redistilled through a semi-micro column.[8] The yield of 1-phenyl-1-cycloöctene[16] (XVI) was 3.57 g., b.p. 82–83.5° (0.2 mm.), n^{25}D 1.5612, d^{25}_4 0.9781; *M*D calcd. 60.58, found 61.69 (exaltation 1.11).

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.59; H, 9.83.

Phenylcycloöctane (XVII).—An authentic sample of phenylcycloöctane was prepared by hydrogenating a solution of 2.24 g. of 1-phenyl-1-cycloöctene in 40 ml. of glacial acetic acid in the presence of 0.4 g. of 10% palladium-on-carbon.[11] The reduction was complete in 20 minutes and required 102.9% of one molar equivalent of hydrogen. The catalyst was separated by filtration, and the filtrate was concentrated under reduced pressure. A solution of the residue in ether was washed with 10% sodium carbonate solution and water, and was dried over magnesium sulfate. The extracts were concentrated, and the residue was distilled through a semi-micro column, yielding 1.88 g. (83%) of phenylcycloöctane as a colorless liquid, b.p. 86–87.5° (0.29 mm.) m.p. 7.3–8.5°, n^{25}D 1.5299, d^{25}_4 0.9525; *M*D calcd. 61.05, found 61.05.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.36; H, 10.71.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra shown in Figs. 1 and 3 were determined for solutions of the compounds in purified cyclohexane[17] with a Beckman model DU quartz ultraviolet spectrophotometer. The following maxima were observed: In Fig. 1: Curve 1 (mixture of IX and XI), $\lambda_{max.1}$ 226 mμ (log ε 4.21), $\lambda_{max.2}$ 259 mμ (log ε 3.92); Curve 2 (mixture of IX and XI), $\lambda_{max.1}$ 229 mμ (log ε 4.17), $\lambda_{max.2}$ 254 mμ (log ε 4.10); Curve 3 (mixture of IX and XI, $\lambda_{max.1}$ 232 mμ (log ε 4.11), $\lambda_{max.2}$ 254 mμ (log ε 4.15); Curve 4 (XI), $\lambda_{max.}$ 252 mμ (log ε 4.27). In Fig. 3: Curve 1 (XIV), $\lambda_{max.1}$ 231 mμ (log ε 4.23), $\lambda_{max.2}$ 284 mμ (log ε 3.99); XIV prepared by thermal decomposition of the methiodide XII (not shown), $\lambda_{max.1}$ 232 mμ (log ε 4.20), $\lambda_{max.2}$ 284 mμ (log ε 4.00); Curve 2 (XV), $\lambda_{max.1}$ 232 mμ (log ε 4.23), $\lambda_{max.2}$ 284 mμ (log ε 3.94); Curve 3 (XVI), $\lambda_{max.}$ 248 mμ (log ε 4.07).

CAMBRIDGE, MASS.

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

Cyclic Polyolefins. XVII. Preparation of Arylcycloöctatetraenes from Cycloöctatetraene and Organometallic Compounds[1]

BY ARTHUR C. COPE AND MARK R. KINTER[2]

The reaction of phenyllithium with cycloöctatetraene has been found to proceed by addition, followed by a process equivalent to the transfer of lithium hydride from the addition compound to another molecule of cycloöctatetraene. The products isolated after hydrolysis were phenylcycloöctatetraene, phenylcycloöctatriene, a mixture of 1,3,5- and 1,3,6-cycloöctatrienes and recovered cycloöctatetraene. Phenylsodium reacted in the same way, yielding phenylcycloöctatetraene and cycloöctatrienes. Likewise *p*-dimethylaminophenyllithium yielded *p*-dimethylaminophenylcycloöctatetraene and cycloöctatrienes. The reaction of phenylmagnesium bromide with cycloöctatetraene resulted in the formation of biphenyl- and cycloöctatrienes.

Phenylcycloöctatetraene has been characterized by the preparation of a 1:1 complex with silver nitrate, addition compounds with maleic anhydride and *p*-benzoquinone, and by quantitative hydrogenation to phenylcycloöctane. *p*-Dimethylaminophenylcycloöctatetraene was reduced quantitatively to *p*-dimethylaminophenylcycloöctane. A crystalline salt was obtained from *p*-dimethylaminophenylcycloöctatetraene and *d*-camphor-10-sulfonic acid, but recrystallization of the salt failed to result in the separation of diastereomeric forms.

In a recent communication[3] the reactions of phenyllithium and *p*-dimethylaminophenyllithium with cycloöctatetraene were reported to form phenylcycloöctatetraene (I) and *p*-dimethylaminophenylcycloöctatetraene (IV), respectively. This paper presents additional information concerning these unusual reactions and the properties of I and IV, and in addition describes the reactions of cycloöctatetraene with phenylsodium and phenylmagnesium bromide.

Organolithium compounds are known to add to the carbon–carbon double bonds of aryl-substituted olefins[4] and fulvenes,[5] and to conjugated dienes in the initiation of polymerization.[6] A study of the reaction of organolithium compounds with cycloöctatetraene accordingly was undertaken, in order to determine whether substituted

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[2] du Pont Fellow, 1950–1951.

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