

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

Cyclic Polyolefins. I. Synthesis of Cycloöctatetraene from Pseudopelletierine<sup>1</sup>BY ARTHUR C. COPE AND C. G. OVERBERGER<sup>2</sup>

This paper presents data amplifying our recent communication<sup>3</sup> which reported duplication of the Willstätter synthesis of cycloöctatetraene from pseudopelletierine.<sup>4,5</sup> Indirect evidence of three kinds had been interpreted as indicating that the Willstätter product might not have been 1,3,5,7-cycloöctatetraene<sup>6</sup>: Similarity of the product to styrene; the fact that catalytic dehydrogenation of cycloöctene at 425–455° yielded styrene; proof that application of the Hofmann exhaustive methylation procedure to diaminobutanes (investigated as open chain models of intermediates in the Willstätter synthesis) yielded ethylacetylene and methylallene in addition to the conjugated 1,3-butadiene. Development of a catalytic synthesis of cycloöctatetraene from acetylene<sup>7</sup> has renewed interest in the hydrocarbon. A correspondence in properties<sup>7</sup> made it appear likely that the catalytic and Willstätter products were identical. This has now been fully established by repetition of the Willstätter synthesis and direct comparison of the product with cycloöctatetraene prepared catalytically from acetylene.

Our synthesis began with the preparation of pseudopelletierine (I) from glutaraldehyde, methylamine and acetonedicarboxylic acid.<sup>8</sup> Subsequent steps are shown in the equations, which include yields and a comparison of the melting points of solid intermediates with those recorded previously. The following evidence was obtained for the structures of intermediates. N-Methylgranatenine (III) was hydrogenated quantitatively in the presence of Adams platinum catalyst to the corresponding saturated compound, N-methylgranatanine, m. p. 47–48.5° (lit. 49–50°).<sup>9</sup> The diene resulting from the first Hofmann exhaustive methylation step ( $\alpha$ -des-dimethyl-granatenine, V) also was hydrogenated quantitatively and yielded dimethylaminocycloöctane, which was identified by its physical properties and also converted to the methiodide, m. p. 274–275° (dec.) (lit. 270–271°).<sup>4</sup> The ultraviolet absorption curve of V (Fig. 1) showed a maximum at approxi-

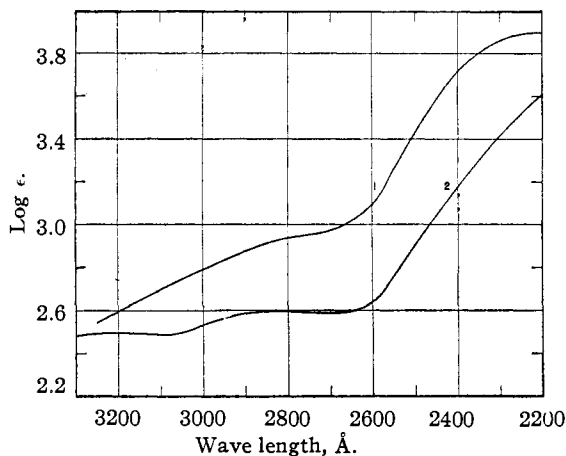


Fig. 1.—Curve 1, absorption spectrum of  $\alpha$ -des-dimethylgranatenine (V); curve 2, absorption spectrum of 1,6-bis-(dimethylamino)-2,4-cycloöctadiene (VIII).

mately 2200 Å. ( $\log \epsilon$  3.9) indicating conjugation of the two double bonds; compare  $\lambda_{\max}$  2170 Å. ( $\log \epsilon$  4.32) for 1,3-butadiene.<sup>10</sup> 1,3,5-Cycloöctatriene (VII), the product of the second exhaustive methylation step in the synthesis, absorbed three molar equivalents of hydrogen in a quantitative hydrogenation and yielded cycloöctane. The ultraviolet absorption spectrum of VII (Fig. 2) showed a maximum at 2650 Å. ( $\log \epsilon$  3.57) indicating conjugation of the three double bonds. The absorption maximum for an open-chain conjugated triene, 2,4,6-octatriene, is cited as 2600 Å. ( $\log \epsilon$  3.90).<sup>11</sup>

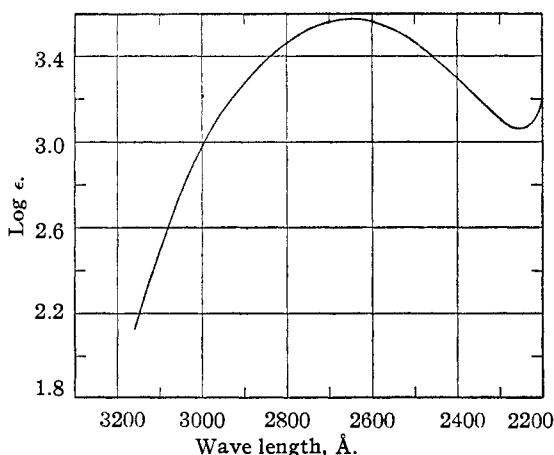


Fig. 2.—Absorption spectrum of 1,3,5-cycloöctatriene (VII).

(1) Presented at the Tenth National Organic Chemistry Symposium, Boston, Massachusetts, June 13, 1947.

(2) du Pont Postdoctorate Fellow, 1946–1947.

(3) Cope and Overberger, *THIS JOURNAL*, **69**, 976 (1947).

(4) Willstätter and Waser, *Ber.*, **44**, 3423 (1911).

(5) Willstätter and Heidelberger, *ibid.*, **46**, 517 (1913).

(6) The argument has been summarized well by Baker, *J. Chem. Soc.*, 258 (1945).

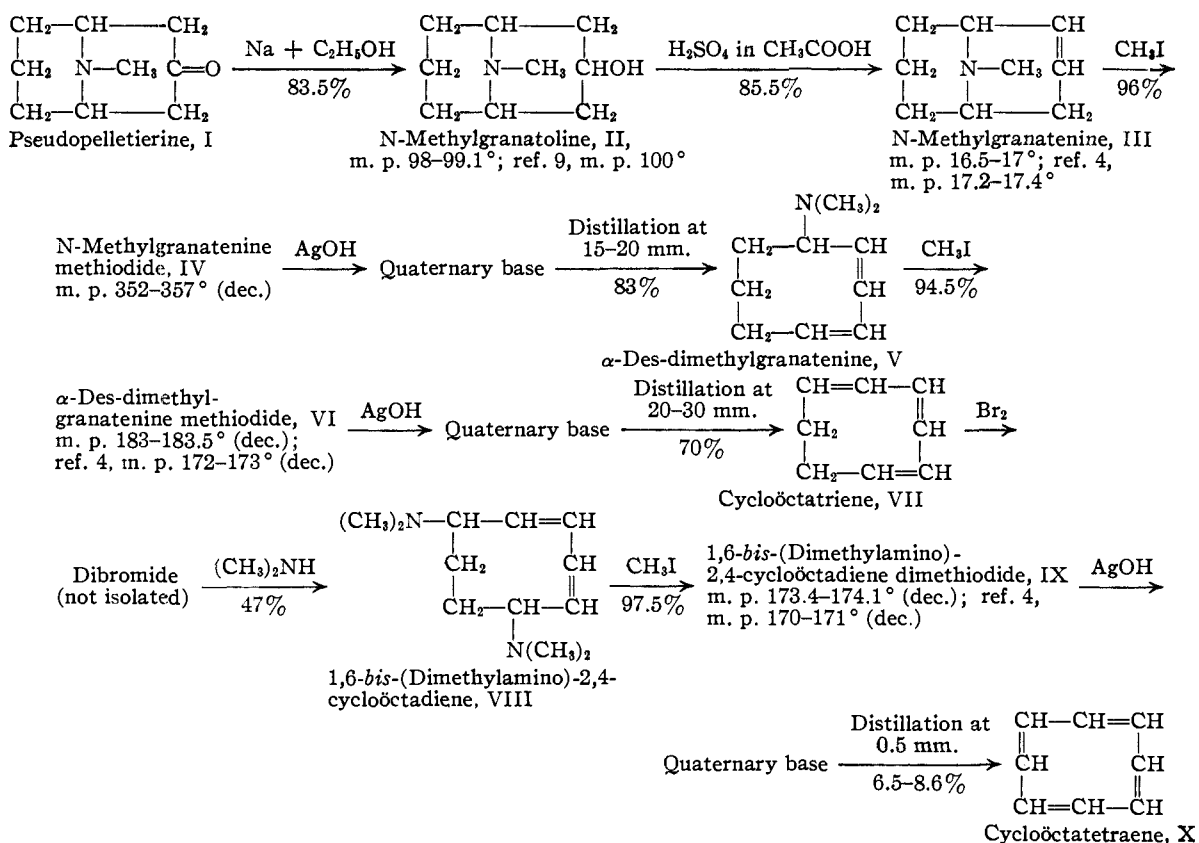
(7) Described in Department of Commerce reports of German technological developments, including a translation of a paper by W. J. Reppe reprinted in "German Synthetic Fiber Developments," p. 631. Textile Research Institute, New York, N. Y., 1946 (P. B. 7416).

(8) By modifications of the procedure described by Schöpf and Lehmann, *Ann.*, **518**, 1 (1935); Cope, D'Addieco and Overberger, to be published.

(9) Ciamician and Silber, *Ber.*, **26**, 2738 (1893).

(10) Dimroth, *Angew. Chem.*, **52**, 549 (1939).

(11) R. A. Morton, "The Application of Absorption Spectra to the Study of Vitamins, Hormones and Coenzymes," 2d ed., Adam Hilger Ltd., London, 1942, p. 25.



The dibromide prepared by adding bromine to VII was not isolated, but was treated directly with dimethylamine to form a bis-(dimethylamino)-cycloöctadiene which was formulated by Willstätter and Waser<sup>4</sup> as VIII. Our data support but do not rigorously prove this structure, in the absence of information definitely establishing the relative positions of the two dimethylamino groups. Quantitative hydrogenation of VIII yielded a bis-(dimethylamino)-cycloöctane believed to be the 1,4-isomer, which was converted to a dimethiodide, m. p. 258-259° (dec.). The purification of VIII included treatment with warm, dilute hydrochloric acid, which would eliminate easily hydrolyzed vinylamine type isomers. The ultraviolet absorption spectrum of VIII (Fig. 1) approached a maximum below but near 2200 Å., indicating conjugation of the two double bonds. These data appear to eliminate all possible isomeric structures derivable from VII except VIII and 1,2-bis-(dimethylamino)-3,5-cycloöctadiene. It should be noted that both bromines would be allylic in type in the product of 1,6-, 1,4- or 3,4-addition of bromine to 1,3,5-cycloöctatriene, and that the displacement reaction with dimethylamine could proceed with rearrangement, so that the diamine does not necessarily have the same arrangement of groups as the dibromide. Through a combination of displacement with and without rearrangement any of the four possible dibromides (products of 1,2-, 1,4-, 1,6- or 3,4-addi-

tion) could lead to either structure VIII or to 1,2-bis-(dimethylamino)-3,5-cycloöctadiene, and accordingly the dibromide could have any of these structures or be a mixture. The diamine (VIII) reacted with methyl iodide to give an excellent yield of a pure, crystalline dimethiodide (IX), and accordingly is homogeneous rather than a mixture of isomers.

The final exhaustive methylation gave a low yield of cycloöctatetraene (X), and a high proportion of polymer. After purification by distillation through a Craig micro-fractionating column<sup>12</sup> the cycloöctatetraene was obtained in 6.5-8.6% yield as a light yellow liquid,  $n_D^{25}$  1.5342. The melting point of the product was -5.8 to -5.4°, and was not depressed on mixture with a sample prepared catalytically from acetylene.<sup>13</sup> The maleic anhydride adducts obtained from cycloöctatetraene from the two sources also were identical (m. p. and mixed m. p.). Both samples of cycloöctatetraene had practically identical ultraviolet (Fig. 3) and infrared absorption spectra.<sup>14</sup> The synthetic

(12) Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

(13) By the German procedure described by Copeland and Youker in Fiat Final Report No. 720, 1946, p. 26 (distributed by the Office of the Publication Board, U. S. Department of Commerce).

(14) We are indebted to Dr. R. C. Lord, Jr., and Mr. R. S. McDonald for the infrared data, which will be published separately. Infrared spectra also were determined for intermediates I, II, III, V, VII and VIII. The spectra contain nothing inconsistent with the structures assigned to these compounds, and have no features which would indicate the presence of allene or acetylene structures.

sample absorbed four molar equivalents of hydrogen in the presence of Adams platinum catalyst and yielded cyclooctane.

The melting point observed for the synthetic cyclooctatetraene is of interest, because Willstätter and Heidelberger<sup>6</sup> had reported a freezing point of about  $-27^{\circ}$  for their product, which was purified by vacuum distillation without fractionation. The molal freezing point depression constant of cyclooctatetraene was determined to be approximately 5.5. Using this value and assuming a m. p. of  $-5^{\circ}$  for pure cyclooctatetraene, a m. p. of  $-27^{\circ}$  would correspond to the presence of approximately 30% of an isomeric impurity. Infrared spectra<sup>14</sup> indicated the presence of small amounts of styrene (in the neighborhood of 3%) in our samples of cyclooctatetraene prepared by the Willstätter synthesis and in most samples prepared from acetylene. This impurity may have been responsible for the low freezing point originally reported for cyclooctatetraene, and may have been removed from our product during the fractional distillation, possibly by polymerization.

#### Experimental<sup>15</sup>

**N-Methylgranatoline (II).**<sup>9</sup>—A solution of 78.9 g. of pseudopelletierine (b. p.  $101^{\circ}$  (7 mm.), m. p.  $45-46^{\circ}$ )<sup>8</sup> in 1550 ml. of commercial absolute ethanol was placed in a 3-liter three-necked flask equipped with an efficient reflux condenser. The solution was heated to the boiling point and 120 g. of sodium was added in small pieces during two to three hours, as rapidly as possible without flooding the condenser. After all of the sodium had reacted, the mixture was cooled, diluted with 600 ml. of water and concentrated under reduced pressure until the residue contained an aqueous phase of approximately 100 ml. After cooling, 300 ml. of water and 500 ml. of ether were added to the residue and the ether solution was separated. The aqueous solution was extracted with 500 and 200 ml. portions of ether, and the combined ether extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure and the brown solid residue recrystallized from commercial hexane, b. p.  $60-66^{\circ}$ . II was obtained as brown plates in two crops; yield 66.6 g. (83.5%), m. p.  $86-95^{\circ}$ . The average yield in four preparations was 82%. The crude product was sufficiently pure for use in preparing III. Several recrystallizations from ligroin (b. p.  $74-93^{\circ}$ ) gave II as small, white plates, m. p.  $98-99.1^{\circ}$ .

*Anal.* Calcd. for  $C_9H_{17}NO$ : C, 69.60; H, 11.04; N, 9.02. Found: C, 69.88; H, 11.06; N, 9.31.

Willstätter and Waser<sup>4</sup> stated that II was obtained from natural pseudopelletierine in a yield corresponding to 80%.

**N-Methylgranatenine (III).**—Glacial acetic acid (34 g.) was added with cooling to 66.6 g. of N-methylgranatoline (II). Concentrated sulfuric acid (122 g.) was added slowly with cooling to the resulting sirup. The solution was placed in a flask attached to a reflux condenser and heated in a bath at  $165^{\circ}$  for six and one-half hours. The mixture was cooled, 400 ml. of water was added and the solution was made basic by adding a 20% sodium hydroxide solution with good cooling. The dark oil which separated was taken up in 200 ml. of ether and the aqueous layer was extracted with four 300-ml. portions of ether. In some cases emulsions were formed during the extraction. Water was added if necessary to keep inorganic salts in solution. The extracts were dried over magnesium

(15) Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy, Mr. Philip H. Towle and Mrs. Louise W. Spencer for analyses.

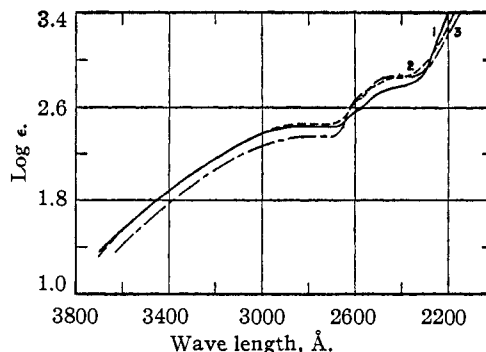


Fig. 3.—Absorption spectrum of cyclooctatetraene. Curve 1, sample prepared from acetylene, freshly distilled; curve 2, sample prepared from pseudopelletierine; curve 3, sample prepared from acetylene, four days after distillation.

sulfate and the product was distilled through a column with a  $20 \times 1.2$  cm. section packed with glass helices. The yield of III was 50.3 g. (85.5%), b. p.  $71-72^{\circ}$  (17 mm.). The average yield in four preparations was 85.5%. A sample purified by redistillation had the following physical constants: b. p.  $56^{\circ}$  (10 mm.); m. p.  $16.5-17^{\circ}$ ;  $n_D^{25}$  1.4945;  $d_4^{25}$  0.9549.

*Anal.* Calcd. for  $C_9H_{15}N$ : C, 78.77; H, 11.01; N, 10.20. Found: C, 78.77; H, 11.09; N, 10.55.

This procedure is based upon the preparation of tropidine from tropine described by Ladenburg<sup>16</sup> and Willstätter,<sup>17</sup> Willstätter and Waser<sup>4</sup> reported b. p.  $62-62.2^{\circ}$  (9 mm.) and m. p.  $17.2-17.4^{\circ}$  for III prepared in a similar manner in unspecified yield.

Hydrogenation of 1 g. of III in 16 ml. of absolute ethanol in the presence of 0.3 g. of pre-reduced Adams platinum catalyst was complete in two hours and required 103.6% of one molar equivalent of hydrogen. The product, N-methylgranatanine, was isolated by distillation under reduced pressure. It crystallized as a hygroscopic solid and was purified by sublimation at  $40^{\circ}$  and 3 mm.; m. p.  $47-48.5^{\circ}$ .

*Anal.* Calcd. for  $C_9H_{17}N$ : C, 77.39; H, 12.30; N, 10.06. Found: C, 77.34; H, 12.35; N, 10.00.

Ciamician and Silber<sup>9</sup> reported the m. p. of N-methylgranatanine obtained by the phosphorus and hydroiodic acid reduction of III as  $49-50^{\circ}$ . Willstätter and Veraguth<sup>18</sup> reported m. p.  $55-58^{\circ}$  for the compound, prepared by electrolytic reduction of pseudopelletierine. Their product was not analyzed and may have contained some N-methylgranatoline, which also was obtained from the electrolytic reduction.

N-Methylgranatanine was converted to the methiodide by heating to reflux with an excess of methyl iodide in cyclohexane solution. The salt which separated on cooling was recrystallized from 80% ethanol as a white powder, m. p.  $353-359^{\circ}$  (dec.).

*Anal.* Calcd. for  $C_{10}H_{20}NI$ : I, 45.13. Found: I, 45.06.

**N-Methylgranatenine Methiodide (IV).**—N-Methylgranatenine (III) (50.3 g.), methyl iodide (78 g.) and 500 ml. of cyclohexane were placed in a 1-liter flask attached to a reflux condenser and heated to  $40^{\circ}$  for three hours. After addition of 5 g. of methyl iodide the mixture was heated at  $40^{\circ}$  for an additional two hours. Filtration separated 96.5 g. of IV, a white crystalline salt. The filtrate was warmed with 10 g. of methyl iodide for three hours at  $40^{\circ}$ . An additional 2 g. of IV was obtained, making the yield 98.5 g. (96%). The average yield in

(16) Ladenburg, *Ann.*, **217**, 118 (1882).

(17) Willstätter, *ibid.*, **326**, 28 (1902).

(18) Willstätter and Veraguth, *Ber.*, **39**, 1984 (1905).

four preparations was 96.5%. An analytical sample was recrystallized from 95% ethanol; m. p. 352–357° (dec.) after partial sublimation at 280°.

*Anal.* Calcd. for  $C_{10}H_{18}NI$ : C, 43.02; H, 6.49; N, 5.01; I, 45.46. Found: C, 42.79; H, 6.59; N, 4.88; I, 45.15.

**$\alpha$ -Des-dimethylgranatenine (V).**—Silver hydroxide was prepared by adding a solution of 28.3 g. of sodium hydroxide in 150 ml. of water to 120 g. (0.706 mole) of silver nitrate in 400 ml. of water. The precipitate was washed until free from alkali and added to 98.5 g. (0.353 mole) of the methiodide (IV) and 400 ml. of water in a 1-l. flask. After mechanical stirring and heating at 60° for one hour, the mixture was filtered. The silver iodide-silver hydroxide mixture was washed with water on the filter and then heated with 100 ml. of water at 60–70° with intermittent shaking for fifteen minutes. After again filtering, the combined filtrates were concentrated under reduced pressure. The concentrate was transferred to a 250-ml. Claisen flask attached to a well-cooled receiver and the quaternary base was decomposed (with some foaming) by heating in a bath at 100–110° at 15–20-mm. pressure. The upper parts of the flask were rinsed with 10 ml. of water to dissolve any remaining quaternary base, and the solution was again distilled to dryness in the same manner.

The colorless oil was separated from the water in the distillate by extraction with 50 and 100 ml. portions of ether. The ether extracts were dried over magnesium sulfate and distilled through a column with a 20 × 1.2 cm. section packed with glass helices. Foaming interfered with the distillation, which yielded 44.3 g. (83%) of V, b. p. 80° (12 mm.). The average yield in four preparations was 81.5%. An analytical sample had the following properties:  $n^{25}_D$  1.4988;  $d^{25}_4$  0.9038;  $M_D$  calcd. 49.18, found 49.12.

*Anal.* Calcd. for  $C_{10}H_{17}N$ : C, 79.40; H, 11.33; N, 9.26. Found: C, 79.46; H, 11.20; N, 9.25.

Willstätter and Waser<sup>4</sup> reported a 90% yield of V, b. p. 71–71.5° (8 mm.);  $d^{20}_4$  0.910.

Hydrogenation of 1.5 g. of V in the presence of 0.2 g. of pre-reduced Adams platinum catalyst in 16 ml. of absolute ethanol was complete in four hours and required 101% of two molar equivalents of hydrogen. After separation of the catalyst, distillation yielded 1.3 g. (85%) of dimethylaminocyclooctane. After redistillation, its properties were b. p. 110° (40 mm.);  $n^{25}_D$  1.4707;  $d^{25}_4$  0.877;  $M_D$  calcd. 50.14, found 49.76.

*Anal.* Calcd. for  $C_{10}H_{21}N$ : C, 77.34; H, 13.63; N, 9.02. Found: C, 77.41; H, 13.45; N, 9.04.

The methiodide of dimethylaminocyclooctane obtained in this manner, prepared in cyclohexane solution and purified by recrystallization from a mixture of acetone and commercial hexane (b. p. 60–66°), had m. p. 274–275° (dec., slight darkening at 270°).

*Anal.* Calcd. for  $C_{11}H_{24}NI$ : C, 44.44; H, 8.13; N, 4.71; I, 42.70. Found: C, 44.39; H, 8.13; N, 4.49; I, 42.82.

Willstätter and Waser<sup>4</sup> reported b. p. 86–86.5° (11 mm.),  $n^{20}_D$  1.4790,  $d^{20}_4$  0.883 and  $M_D$  49.78 for dimethylaminocyclooctane and m. p. 270–271° for its methiodide.

**$\alpha$ -Des-dimethylgranatenine Methiodide (VI).**—VI was prepared from 44.3 g. of V and 80 g. of methyl iodide in 500 ml. of cyclohexane. The conditions of reaction were similar to those described for the preparation of IV, and the product was obtained in two crops as slightly pink, chloroform soluble crystals; yield 81 g. (94.5%). The average yield in three preparations was 92.3%. An analytical sample was recrystallized from a mixture of acetone and commercial hexane; m. p. 183–183.5° (dec.).

*Anal.* Calcd. for  $C_{11}H_{23}NI$ : C, 45.05; H, 6.88; N, 4.77; I, 43.28. Found: C, 44.96; H, 7.05; N, 4.69; I, 42.90.

**1,3,5-Cyclooctatriene (VII).**—The freshly prepared, alkali-free silver hydroxide obtained from 77.6 g. of silver nitrate and 18.3 g. of sodium hydroxide was added to a

solution of 67 g. of VI in 100 ml. of water. The reaction conditions were similar to those described under V. Foaming occurred during concentration and also during the decomposition of the quaternary base, which was conducted in a 500-ml. Claisen flask at a bath temperature of 90–110° and 20–30 mm. pressure. The organic layer which separated in the receiver, which was cooled with Dry Ice, was extracted with ether, dried over magnesium sulfate and distilled through a column with a 20 × 1.2 cm. section packed with glass helices. A trace of picric acid was added as a polymerization inhibitor before distillation. The yield of VII was 16.8 g. (70%), b. p. 65–66° (60 mm.). After redistillation its properties were: b. p. 45° (18 mm.);  $n^{25}_D$  1.5248;  $d^{25}_4$  0.9042;  $M_D$  calcd. 35.65, found 35.94.

*Anal.* Calcd. for  $C_8H_{10}$ : C, 90.50; H, 9.50. Found: C, 90.49; H, 9.51.

VII proved to be somewhat unstable and accordingly was used at once.

Willstätter and Waser<sup>4</sup> reported a 72% yield of VII.

Hydrogenation of 1 g. of VII in the presence of 0.2 g. of Adams platinum catalyst in 25 ml. of absolute ethanol was complete in one hour and required 99.5% of three molar equivalents of hydrogen. The cyclooctane formed could not be separated from ethanol by distillation. The alcohol solution was diluted with water and extracted with ether. The extracts were dried over magnesium sulfate, distilled and redistilled through a Craig micro fractionation column<sup>12</sup>;  $n^{25}_D$  1.4562; m. p. 11.7°.

*Anal.* Calcd. for  $C_8H_{16}$ : C, 85.62; H, 14.37. Found: C, 85.57; H, 14.18.

**1,6-bis-(Dimethylamino)-2,4-cyclooctadiene (VIII).**—A solution of 28 g. (0.175 mole) of dry bromine in 130 ml. of dry, alcohol-free chloroform was added dropwise during five hours to 18.5 g. (0.175 mole) of VII in 250 ml. of dry chloroform at –20° with mechanical stirring in a flask protected from atmospheric moisture. The solution remained colorless throughout the addition and no hydrogen bromide was evolved. The chloroform was removed under reduced pressure at room temperature and 500 ml. of a benzene solution containing 1.48 moles of dry dimethylamine was added to the residue with cooling. Dimethylamine hydrobromide began to separate after a few minutes. After standing for eleven hours, the mixture was cooled and extracted with an excess of 15% hydrochloric acid. The acid extracts were made basic by adding an excess of 20% sodium hydroxide solution with cooling and extracted with four 200-ml. portions of ether. The ether was removed under reduced pressure, and approximately 300 ml. of 2 *N* hydrochloric acid was added to the residue. The acid solution was heated at 55–70° for three to five minutes to hydrolyze any substituted vinyl amine types present in the crude product. After cooling, the solution was extracted with 100 ml. of ether, made basic with 20% sodium hydroxide solution with cooling, and extracted with three 125-ml. portions of ether. The ether extracts of the basic solution were dried over magnesium sulfate for one hour and distilled under nitrogen through a column with a 20 × 1.2 cm. section packed with glass helices. VIII was obtained as a light straw-yellow liquid which was kept under nitrogen and cooled to prevent rapid darkening which occurred otherwise; yield 15.9 g. (47%); b. p. 116° (8 mm.),  $n^{25}_D$  1.4990;  $d^{25}_4$  0.9317.

*Anal.* Calcd. for  $C_{12}H_{22}N_2$ : C, 74.16; H, 11.41; N, 14.41. Found: C, 74.38; H, 11.13; N, 14.53.

The above procedure is similar to the one used by Willstätter and Waser.<sup>4</sup> These investigators purified their product by acid hydrolysis to remove vinyl amine types after distillation of VIII, before conversion to quaternary salts, and do not report physical constants for VIII after purification.

A sample of VIII was treated with picric acid in alcohol solution and converted into the dipicrate, which was recrystallized from a large volume of absolute alcohol containing 5–10% acetone; m. p. 194.6–195.2° (dec.).

*Anal.* Calcd. for  $C_{24}H_{28}N_8O_{14}$ : C, 44.17; H, 4.33; N, 17.17. Found: C, 44.41; H, 4.51; N, 16.97.

Hydrogenation of 0.879 g. of VIII in the presence of 0.3 g. of pre-reduced Adams catalyst was complete in seventeen hours and required 108% of two molar equivalents of hydrogen. Distillation followed by redistillation through the Craig micro column gave 1,4-bis-(dimethylamino)-cyclooctane, b. p.  $105^\circ$  (6 mm.),  $n_D^{25}$  1.4823;  $d_4^{25}$ , 0.9166.<sup>19</sup>

*Anal.* Calcd. for  $C_{12}H_{16}N_2$ : C, 72.65; H, 13.21; N, 14.13. Found: C, 72.53; H, 13.12; N, 14.08.

The product of a similar quantitative hydrogenation, in which 1.5 g. of VIII absorbed 103% of two molar equivalents of hydrogen in twenty-two hours, was distilled through the Craig micro column. Methyl iodide (4 g.) in 25 ml. of absolute ethanol was added to several fractions from this distillation (0.85 g.), and the mixture was boiled under reflux for three minutes. The yield of 1,4-bis-(dimethylamino)-cyclooctane dimethiodide was 1.98 g. (96%), m. p. after recrystallization from absolute ethanol  $258-259^\circ$  (dec.).

*Anal.* Calcd. for  $C_{14}H_{22}N_2I_2$ : C, 34.86; H, 6.69; N, 5.81; I, 52.64. Found: C, 35.07; H, 6.67; N, 5.60; I, 52.99.

Another sample of 1,4-bis-(dimethylamino)-cyclooctane obtained by hydrogenation of VIII was converted to the dipicrate, which was recrystallized from absolute ethanol; m. p.  $171.5-172.2^\circ$  (dec.).

*Anal.* Calcd. for  $C_{24}H_{32}N_8O_{14}$ : C, 43.90; H, 4.90; N, 17.07. Found: C, 43.96; H, 5.07; N, 16.88.

**1,6-bis-(Dimethylamino)-2,4-cyclooctadiene Dimethiodide (IX).**—Methyl iodide (35 g.) was added to 10.1 g. of VIII in 300 ml. of absolute ethanol. The reaction mixture was boiled under reflux for five minutes, 2 g. of methyl iodide was added, and the mixture was allowed to cool slowly. IX separated as colorless to light yellow crystals in three crops in a total yield of 24.2 g. (97.5%), m. p. after recrystallization from absolute ethanol  $173.4-174.1^\circ$  (dec.).

*Anal.* Calcd. for  $C_{14}H_{22}N_2I_2$ : C, 35.16; H, 5.90; N, 5.86; I, 53.08. Found: C, 35.27; H, 6.14; N, 5.87; I, 52.76.

**Cyclooctatetraene (X).**—The freshly prepared silver hydroxide obtained from 25.5 g. of silver nitrate and 6 g. of sodium hydroxide was added to 23 g. of the dimethiodide (IX) in 100 ml. of water. The suspension was stirred and heated at  $30-40^\circ$  for twenty-five minutes, cooled and filtered. The mixture of silver iodide and silver hydroxide was warmed with 75 ml. of water and shaken intermittently for ten minutes. The mixture was filtered and the combined filtrates were concentrated to a volume of 75 ml. by warming in a bath at  $30-35^\circ$  under reduced pressure. The residue was transferred to a 500-ml. Claisen flask and distilled at 0.5 mm. into a receiver cooled with a Dry Ice-solvent mixture. The decomposition of the quaternary base occurred with foaming at a bath temperature of  $40-65^\circ$  and 0.5 mm. pressure. The light yellow liquid which separated when the distillate was allowed to come to room temperature in a nitrogen atmosphere was extracted with a small volume of ether

(19) Willstätter and Waser<sup>4</sup> reported b. p.  $259-261^\circ$  (718 mm.),  $d_4^{25}$ , 0.913 for 1,4-bis-(dimethylamino)-cyclooctane prepared in the same way.

and dried over magnesium sulfate. The ether solution was concentrated and the product distilled through a Craig micro distillation column under nitrogen at 50 mm. The yellow product was separated from a polymeric distillation residue as six fractions; yield 0.43 g. (8.6%),  $n_D^{25}$  1.5342; m. p.  $-5.8$  to  $-5.4^\circ$ ; mixed m. p. with a sample of cyclooctatetraene prepared from acetylene (melting at  $-5.9$  to  $-5.3^\circ$ )  $-6.0$  to  $-5.3^\circ$ .

*Anal.* Calcd. for  $C_8H_8$ : C, 92.26; H, 7.74. Found: C, 92.47; H, 7.91.

A repetition of this preparation gave a 6.5% yield of X with the same physical properties.

A maleic anhydride adduct was prepared by heating 30 mg. of the sample of cyclooctatetraene described above and 20 mg. of maleic anhydride under nitrogen until refluxing occurred for two minutes. On cooling the mixture solidified, and was recrystallized from chlorobenzene. The adduct melted at  $166.2-167.8^\circ$  (m. p. determined by the hot-stage microscope technique) and showed no depression in mixed m. p. ( $165.4-167^\circ$ , hot stage) with a sample of the adduct prepared from X obtained from acetylene (described below).

Hydrogenation of 0.165 g. of this sample of cyclooctatetraene in the presence of 0.2 g. of pre-reduced Adams catalyst in 20 ml. of glacial acetic acid was complete in seventy-five minutes and required 101.5% of four molar equivalents of hydrogen. After separation of the catalyst, the solution was made alkaline by adding 10% sodium carbonate solution and extracted with ether. The ether solution was dried and distilled through a Craig micro column. The last of three fractions of the cyclooctane obtained melted at  $8.8^\circ$ , presumably depressed by slight contamination with solvent.

**Cyclooctatetraene-Maleic Anhydride Adduct.**—Cyclooctatetraene (0.5 g.) prepared from acetylene<sup>18</sup> and maleic anhydride (0.48 g.) were heated under nitrogen at a temperature which caused refluxing for five minutes. The solid which separated on cooling was crystallized from 8 ml. of chlorobenzene. The crystalline adduct (0.4 g.) was recrystallized from 6 ml. of chlorobenzene; m. p.  $166.5-167.6^\circ$  (lit.  $166^\circ$ ).<sup>20</sup>

*Anal.* Calcd. for  $C_{12}H_{10}O_3$ : C, 71.27; H, 4.95. Found: C, 71.10; H, 5.03.

**Ultraviolet Absorption Spectra.**—Ultraviolet absorption spectra of compounds V, VII, VIII and X were determined with a Beckmann quartz ultraviolet spectrophotometer. Purified cyclohexane<sup>21</sup> was used as the solvent in each case. The spectra are shown in Figs. 1-3, in which logarithms of the molar extinction coefficients are plotted against the wave lengths in ångström units.

### Summary

The Willstätter synthesis of cyclooctatetraene from pseudopelletierine has been duplicated, and the product has been shown to be identical to cyclooctatetraene prepared catalytically from acetylene. Evidence supporting the structures of intermediates in the synthesis has been obtained.

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(20) Ref. 7, p. 650.

(21) Maclean, Jencks and Acree, *J. Research Natl. Bur. Standards*, **34**, 271 (1945).