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

Cyclic Polyolefins. XXXIV. 2,4-Diphenylbicyclo[3.3.0]octa-1,4-diene

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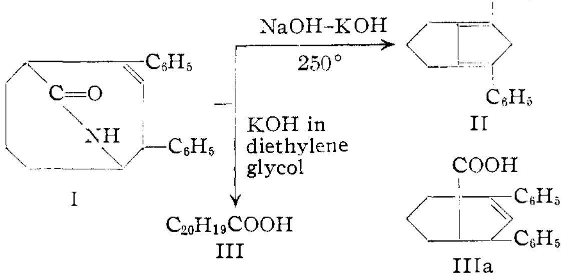
Alkali fusion of 5-amino-2,4-diphenylcyclooöct-2-enecarboxylic acid ε-lactam (I) has been found to result in elimination of the lactam bridge and formation in 72–92% yield of the crystalline hydrocarbon, 2,4-diphenylbicyclo[3.3.0]octa-1,4-diene (II). The ketone from which I was prepared by Beckmann rearrangement of the oxime, 2,4-diphenylbicyclo[3.3.1]non-2-en-9-one (IV), on alkali fusion yielded 58–91% of an aromatic hydrocarbon isomeric with II, 1,2-dimethyl-3,5-diphenylbenzene (V).

In an investigation of the utilization of carbonyl-bridged intermediates for the synthesis of eight-membered cyclic polyolefins substituted by phenyl groups, 5-amino-2,4-diphenylcyclooöct-2-enecarboxylic acid ε-lactam (I) was observed to be very resistant to hydrolysis by acids and bases but was hydrolyzed and decarboxylated without modification of the ring system by long boiling with hydrochloric acid.[1] Reaction of the lactam I with bases at high temperatures resulted in more drastic structural change, as described in this paper.

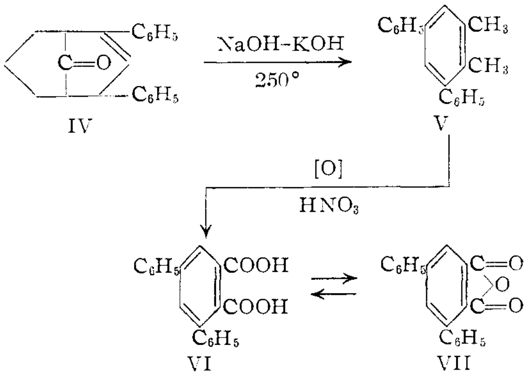
Fusion of the lactam I with a mixture of sodium hydroxide and potassium hydroxide at 250° formed a hydrocarbon II with the molecular formula $C_{20}H_{18}$ in a yield of 92%, or 72% after recrystallization, m.p. 132–132.4°. The following evidence established the structure of this hydrocarbon as 2,4-diphenylbicyclo[3.3.0]octa-1,4-diene (II). The hydrocarbon was yellow in color and showed blue fluorescence in solution. It gave unsaturation tests with potassium permanganate and bromine, and absorbed 101% of two molar equivalents of hydrogen in the presence of a palladium catalyst, forming a colorless crystalline saturated hydrocarbon (substituted by two phenyl groups), $C_{20}H_{22}$. These data indicate that II is a bicyclic diene. The hydrocarbon II formed a crystalline maleic anhydride adduct in 86% yield, indicating that the double bonds are conjugated. Conclusive evidence for the structure of II was obtained by ozonization, followed by decomposition of the ozonide with aqueous sodium bisulfite solution. Dibenzoylmethane was isolated in 32% yield, and oxidation of the material remaining in the aqueous phase with alkaline hydrogen peroxide yielded glutaric acid (39%). These data are sufficient to establish structure II, the glutaric acid being formed by oxidation of cyclopentane-1,2-dione produced initially from the ozonide.

The bridged diene II formed a dark purple picrate, m.p. 142.2–143°, and a brick-red adduct with 1,3,5-trinitrobenzene, m.p. 162–162.8°. Formation of such highly colored derivatives from II is to be expected from its structure, since corresponding derivatives with similar properties are formed from 1,4-diphenylcyclopenta-1,3-diene.[2] A bright orange monobromide of unknown structure (probably the 3-bromo derivative) was obtained from II and N-bromosuccinimide. The ultraviolet absorption spectrum of II contains maxima at 242 and 359 mμ, and is quite similar to the spectrum of 1,4-diphenylbuta-1,3-diene, which has maxima at 230, 328 and 345 mμ.[3]

The bridged diene II also was formed in 62% yield by alkali fusion of an isomer of the lactam I, m.p. 194–195.2°, obtained by heating I with potassium hydroxide in methanol.[1] Hydrolysis of I with potassium hydroxide in aqueous diethylene glycol at 215–220° resulted in formation of a small amount (10%) of an unsaturated monocarboxylic acid (III), $C_{21}H_{20}O_2$. Hydrogenation of III showed the presence of one double bond, and alkali fusion of III yielded 11% of the bridged diene II. No further evidence was obtained concerning the the structure of the acid III; formula IIIa represents one possibility.



Since the lactam grouping of I was eliminated in its conversion to II by alkali fusion, the reaction of 2,4-diphenylbicyclo[3.3.1]non-2-en-9-one (IV) with fused alkali was investigated. It seemed possible that II also would be formed from IV, since the oxime of IV was the precursor of I, formed by a Beckmann rearrangement. Alkali fusion of the ketone IV formed an isomer of II, $C_{20}H_{18}$, which proved to be 1,2-dimethyl-3,5-diphenylbenzene (V). The ultraviolet spectrum of V is very similar to the spectrum of *m*-terphenyl. Oxidation of V with dilute nitric acid formed a dicarboxylic acid VI that



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[1] A. C. Cope, F. S. Fawcett and G. Munn, THIS JOURNAL, **72**, 3399 (1950).

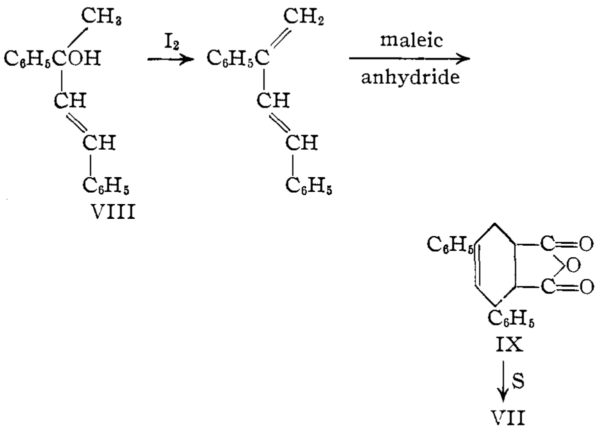
[2] N. L. Drake and J. R. Adams, Jr., *ibid.*, **61**, 1326 (1939).

[3] E. K. Blout and V. W. Eager, *ibid.*, **67**, 1315 (1945).

was isolated as the anhydride VII formed on sublimation under reduced pressure. Saponification of the anhydride re-formed the dicarboxylic acid VI. Conclusive evidence for the structure of the hydrocarbon V was obtained by an independent synthesis of the acid and anhydride, VI and VII.

In this synthesis, benzalacetone was treated with phenyllithium, forming 2,4-diphenyl-3-buten-2-ol (VIII) in 85% yield. The diene obtained from VIII on dehydration polymerized readily, but it proved possible to prepare a Diels–Alder adduct from the diene without isolating it by heating a mixture of the alcohol VIII, iodine and maleic anhydride in toluene. The adduct IX had a melting range of 142.2–149°, indicating that it probably was a mixture of stereoisomers. Dehydrogenation of the anhydride IX by heating with sulfur yielded 3,5-diphenylphthalic anhydride (VII), which on saponification formed 3,5-diphenylphthalic acid (VI). The anhydride and acid from this source were proved to be identical with the anhydride and acid obtained by oxidation of the hydrocarbon V by comparison of melting points, mixed melting points and infrared spectra.

Only speculative routes can be proposed for the formation of the hydrocarbons II and V from I and IV, respectively.



Experimental[4]

2,4-Diphenylbicyclo[3.3.0]octa-1,4-diene (II).—A finely pulverized mixture of 12.5 g. of sodium hydroxide, 12.5 g. of potassium hydroxide and 10.0 g. of the lactam I (prepared by the procedure described in ref. 1, p. 3403) was placed in an iron test-tube and evacuated to a pressure of 1 mm. The tube was placed in a bath at 130°, heated to 250° during a period of 25 minutes (some gas evolution occurred) and kept at 250° for 1 hour. The mixture was cooled at 1 mm., and rinsed from the tube with 400 ml. of water. The granular solid was triturated with water, collected on a filter and dried. The yield of crude II, m.p. 129.2–131.6°, was 7.89 g. (92%). A solution of the crude product in 50 ml. of hot carbon tetrachloride was boiled with Norit, filtered through filter aid and diluted with 75 ml. of boiling absolute ethanol. The diene II was collected in two crops as light yellow needles, m.p. 132–132.6°; yield 6.23 g. (72%). An analytical sample that was recrystallized from 95% ethanol melted at 132.3–133.0°; λ_{max} 242 mμ (ϵ 32,000) and 359 mμ (ϵ 52,300) in 95% ethanol.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02; mol. wt., 258. Found: C, 93.04; H, 6.87; mol. wt., 244 (Rast method in camphor).

The picrate of II was prepared by treating a solution of 10 mg. of II in 1 ml. of ether with 2–3 ml. of a saturated solution of picric acid in ether. Chilling caused precipitation of the picrate as dark purple needles in a yield of 20 mg. (74%), m.p. 142.2–143°.

Anal. Calcd. for $C_{32}H_{24}N_6O_{14}$: C, 53.62; H, 3.38; N, 11.74. Found: C, 53.32; H, 3.26; N, 11.96.

The trinitrobenzene adduct of II was prepared by treating a solution of 10 mg. of II in 3 ml. of 95% ethanol with 1–2 ml. of a hot saturated solution of 1,3,5-trinitrobenzene in 95% ethanol. The adduct precipitated as brick-red needles which were recrystallized from 95% ethanol. The yield was 15 mg. (58%), m.p. 162–162.8°.

Anal. Calcd. for $C_{32}H_{24}N_6O_{12}$: C, 56.14; H, 3.53; N, 12.26. Found: C, 56.00; H, 3.59; N, 11.92.

The lactam isomeric with I, m.p. 194–195.2°, obtained by heating I with potassium hydroxide in methanol (ref. 1, p. 3403) was converted to II (identical by mixed melting point with a sample prepared from I) in a similar manner in 62% yield. The hydrocarbon II also was obtained in 11% yield by alkali fusion (by the procedure described above) of a 1.0-g. sample of an unsaturated acid III prepared from I by the following procedure.

Monocarboxylic Acid $C_{21}H_{20}O_2$ (III) Derived from I.—A suspension of 3.85 g. of the lactam I in a solution of 100 ml. of diethylene glycol and 19 ml. of water containing 19 g. of potassium hydroxide was heated in a bath at 215–220° for 1 hour under nitrogen in a flask arranged for distillation (some water distilled during this period). After cooling, the dark residue was poured into 800 ml. of water and digested with Norit on a steam-bath. The hot mixture was filtered using a filter aid, and the filtrate was washed with ether, acidified and extracted with benzene. The benzene solution was extracted with 10% sodium bicarbonate solution, which was acidified and extracted with benzene.

The benzene extracts were dried over anhydrous sodium sulfate, concentrated under reduced pressure and diluted with cyclohexane. On further concentration and dilution with pentane 0.4 g. (10%) of a yellow crystalline monocarboxylic acid was obtained. After several recrystallizations from methylcyclohexane the product was colorless and melted at 208–209.5°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62; neut. equiv., 304. Found: C, 82.86; H, 6.63; neut. equiv., 304.

Reduction of a 0.25-g. sample of the acid III in 10 ml. of dioxane in the presence of 0.05 g. of 10% palladium-on-Norit was complete in 3 hours and 103% of one molar equivalent of hydrogen was absorbed. The reduction product was not isolated, and no further evidence concerning the structure of the acid III was obtained other than conversion to the hydrocarbon II described above.

Hydrogenation of II.—A solution of 2.01 g. of the hydrocarbon II in 75 ml. of cyclohexane was hydrogenated in the presence of 0.9 g. of 10% palladium-on-Norit. The reduction was complete in 10 hours and 101% of 2 molar equivalents of hydrogen was absorbed. The catalyst was separated and the product, a white wax-like solid (1.78 g., 88%, m.p. 49–52°) was isolated by a short-path distillation. Recrystallization from 95% ethanol yielded 2,4-diphenylbicyclo[3.3.0]octane as a white solid, m.p. 54.3–54.7°, which did not decolorize potassium permanganate or dissolve in cold concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.46; H, 8.52.

Maleic Anhydride Adduct of II.—A solution of 0.36 g. of II and 0.14 g. of maleic anhydride in 10 ml. of dry benzene was allowed to stand at room temperature overnight. Evaporation of the solvent and trituration of the residue with 20 ml. of ether yielded 0.43 g. (86%) of a gray solid, m.p. 156.2–157°. Recrystallization from a mixture of chloroform and cyclohexane yielded the pure adduct, m.p. 164.4–165°.

Anal. Calcd. for $C_{24}H_{20}O_3$: C, 80.87; H, 5.66. Found: C, 80.49; H, 5.53.

Bromination of II.—The hydrocarbon II (100 mg.) was dissolved in 25 ml. of reagent grade carbon tetrachloride. N-Bromosuccinimide (70 mg.) was added, and the resulting suspension was stirred at room temperature for 5.5 hours. The succinimide formed was separated by filtration, and the filtrate was concentrated under reduced pressure. The residual material was dissolved in 2 ml. of chloroform, approximately 10 ml. of 95% ethanol was added to the dark

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[4] Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

orange solution and the mixture was chilled at 5° for 12 hours. A bright orange solid, m.p. 112–114° dec., was separated by filtration and recrystallized from a mixture of chloroform and 95% ethanol, yielding 50 mg. (38%) of a monobromo derivative of II, m.p. 127–128° dec. A sample crystallized to a constant melting point of 126.6° dec. from chloroform–ethanol was analyzed.

Anal. Calcd. for $C_{20}H_{17}Br$: C, 71.22; H, 5.08; Br, 23.70. Found: C, 70.80; H, 5.23; Br, 23.61.

Ozonization of II.—The hydrocarbon II (1.0 g.) was dissolved in 40 ml. of chloroform and ozonized at −30° in a stream of oxygen delivering 22.5 mg. of ozone per minute for 17 minutes. The yellow solution was allowed to come to room temperature and poured into 10 ml. of water which contained 0.75 g. of sodium bisulfite. The chloroform was removed under reduced pressure, and the resulting aqueous solution was extracted with three 40-ml. portions of pentane. The pentane solution was washed with water and concentrated under reduced pressure. Recrystallization of the resulting oily white solid from 95% ethanol yielded 0.13 g. (32%) of dibenzoylmethane, m.p. and mixed m.p. with an authentic sample 75.8–76.4°. The dibenzoylmethane also was characterized by conversion to 3,5-diphenylisoxazole, m.p. 139.8–140.8°, by treatment with hydroxylamine.

To the aqueous solution above from which the dibenzoylmethane had been extracted was added at room temperature a solution containing 0.06 g. of hydrogen peroxide in 2 ml. of 10% aqueous sodium hydroxide. The solution was allowed to stand at room temperature for 2 hours and evaporated to dryness. The resulting white solid was treated with an excess of dilute sulfuric acid, and the acidic solution was extracted with ether in a continuous extractor for 18 hours. Concentration of the extract under reduced pressure yielded 0.12 g. of crude glutaric acid, which after recrystallization from benzene amounted to 0.09 g. (39%), m.p. 90.6–91.2°. The glutaric acid was identified by mixed melting point and by conversion to the di-*p*-bromophenacyl ester, m.p. 135.2–136.2°, which also was identical with a known sample (mixed melting point).

1,2-Dimethyl-3,5-diphenylbenzene (V).—A finely pulverized mixture of 12.5 g. of sodium hydroxide, 12.5 g. of potassium hydroxide and 10.0 g. of 2,4-diphenylbicyclo-[3.3.1]non-2-en-9-one (IV, prepared by the procedure described in ref. 1, p. 3402) was heated at 220–250° for 1 hour in an iron test-tube evacuated to a pressure of 2 mm. The product was cooled under reduced pressure and washed from the tube with 200 ml. of water, collected on a büchner funnel and air-dried; yield 8.28 g. (91%), m.p. 98.5–100°. Recrystallization from 95% ethanol yielded 5.23 g. (58%) of white crystalline V, m.p. 101.3–102.8°. A sample crystallized to a constant melting point of 100.8–101.8° from 95% ethanol was analyzed; λ_{max} 247 (ϵ 51,400) in 95% ethanol.

Anal. Calcd. for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.17; H, 6.81.

The hydrocarbon V was soluble in cold, concentrated sulfuric acid, but did not decolorize potassium permanganate and was not hydrogenated in the presence of 10% palladium-on-Norit.

3,5-Diphenylphthalic Anhydride (VII).—A suspension of 2.57 g. of the hydrocarbon V was heated under reflux with 65 ml. of dilute nitric acid (sp. gr. 1.075) for 8 hours.[5] The hot reaction mixture was poured into a mixture of ice and water, and the red solid that precipitated (3.18 g., m.p. 70–100°) was ground in a mortar and warmed on a steam-bath for 10 minutes with 60 ml. of 10% aqueous sodium hydroxide solution. The dark brown solution that resulted was filtered, and the filtrate was poured into 100 ml. of a mixture of ice and concentrated hydrochloric acid. The tan solid that was obtained was sublimed at 1 mm. with a heating block temperature of 155–170°. The white sublimate of 3,5-diphenylphthalic anhydride amounted to 0.95 g. (32%), m.p. 163–166°. An analytical sample with a constant melting point of 175.8–177.4° was obtained by resublimation. The compound also can be purified by recrystallization from benzene–pentane.

Anal. Calcd. for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03; sapon. equiv., 150. Found: C, 80.05; H, 4.25; sapon. equiv., 152.

3,5-Diphenylphthalic Acid (VI).—The anhydride VII (0.24 g.) was heated under reflux with 0.08 g. of sodium hydroxide in 35 ml. of ethanol for 1.5 hours. The solution was poured into a mixture of ice and hydrochloric acid, and the product was extracted with ether. Evaporation of the solvent under reduced pressure and recrystallization of the crude acid from benzene yielded 0.10 g. (40%) of VI, m.p. 192.4–193°.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43; neut. equiv., 160. Found: C, 75.51; H, 4.44; neut. equiv., 162.

Synthesis of VI and VII. 2,4-Diphenyl-3-buten-2-ol (VIII).—A solution of 22 g. of benzalacetone in 45 ml. of dry ether was added dropwise with stirring during 1.3 hours in a nitrogen atmosphere to the phenyllithium prepared from 2.3 g. of lithium and 23.5 g. of bromobenzene in 100 ml. of ether. The mixture was heated under reflux for 0.5 hour and poured into 300 ml. of ice and water. The ether layer was separated, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The orange liquid residue was distilled in a short-path still at 1–2 mm. with a heating block temperature of 80–110°. The distillate solidified and was recrystallized from pentane. The yield of VIII was 28.5 g. (85%), m.p. 57.2–58°. This compound has been described previously as a liquid.[6]

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.69; H, 7.18. Found: C, 85.71; H, 7.14.

3,5-Diphenyl-1,2,3,6-tetrahydrophthalic Anhydride (IX).—2,4-Diphenyl-3-buten-2-ol (VIII) (3.22 g.), 35 mg. of iodine, 2.74 g. of freshly sublimed maleic anhydride and a small amount of hydroquinone were dissolved in 300 ml. of toluene. The resulting red solution was heated under reflux for 6 hours. The solution was washed with water, saturated sodium bisulfite solution, again with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residual yellow solid was purified by recrystallization from ether and by sublimation at 1 mm. with a heating block temperature of 160°. The yield of IX was 1.1 g. (26%), m.p. 142.2–149°.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.94; H, 5.29. Found: C, 79.09; H, 5.31.

3,5-Diphenylphthalic Anhydride (VII) from Dehydrogenation of IX.—A mixture of 0.10 g. of IX and 0.021 g. of sulfur was heated at 210° for 1 hour. At the end of this time evolution of hydrogen sulfide had ceased, and the residue was sublimed at 1 mm. with a heating block temperature of 165–180°. The sublimate (0.070 g.) after recrystallization from benzene–pentane yielded 0.050 g. (50%) of 3,5-diphenylphthalic anhydride (VII), m.p. 176.4–177°. The anhydride VII prepared by this route and a sample obtained by oxidation of 1,2-dimethyl-3,5-diphenylbenzene (V) were proved to be identical by mixed melting point and comparison of infrared spectra.

The anhydride VII (50 mg.) prepared by dehydrogenation of IX was hydrolyzed by the procedure described above for the preparation of 3,5-diphenylphthalic acid (VI). The acid thus obtained (40 mg., 74%, m.p. 190.8–191.6°) was proved to be identical by mixed melting point with 3,5-diphenylphthalic acid obtained by oxidation of 1,2-dimethyl-3,5-diphenylbenzene (V).

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(5) A procedure similar to one used for the oxidation of 3,5-diphenyltoluene by C. Gastaldi and F. Cherchi, *Gazz. chim. ital.*, **45**, II, 266 (1915).

(6) E. P. Kohler, *Am. Chem. J.*, **31**, 659 (1904).