0.57 g. (85% yield) of benzoic acid melting at 121–122°; identification was by the mixture melting point method.

(b) **α-Hydroperoxy-α-methoxypropiophenone (XXXIb).**—A suspension of 5.6 g. of XXXIb in 20 ml. of ethanol and 10 ml. of petroleum ether (b.p. 60–68°) was allowed to stand at room temperature for 5 min., during which time an exothermal reaction occurred. The solution was evaporated and the residue was extracted with ether and sodium carbonate solution. Upon acidification of the aqueous extract and partial evaporation, 2.8 g. (80% yield) of benzoic acid (m.p. 120–122°) was obtained. Evaporation of the ether extract gave a small residue which was treated with phenylhydrazine in the usual manner, yielding 0.1 g. of benzil phenylosazone (m.p. 225–227°).[15] Identifications were by the mixture melting point method.

Decompositions in Formic Acid.—In each case 1 g. of hydroperoxide (XXXIa or b) was added to 10–20 ml. of cold formic acid. An exothermal reaction ensued in case of XXXIa. The solutions were then heated on a steam-bath for 30 minutes after which they were evaporated under vacuum. The residues melted at 120–122° and were identified as benzoic acid by the mixture melting point method. The yields were 0.6 g. (90%) from α-hydroperoxy-α-methoxyacetophenone (XXXIa) and 0.52 g. (84%) from the corresponding propiophenone (XXXIb).

Decompositions in Sodium Hydroxide Solution.—In each case 1 g. of hydroperoxide (XXXIa or b) was added to 15 ml. of 10% sodium hydroxide solution. An exothermal reaction occurred in the case of XXXIa. After a few minutes it was poured into excess dilute hydrochloric acid. In the case of XXXIb the reaction mixture stood overnight before it was poured into excess dilute hydrochloric acid. Upon evaporation of these solutions and recrystallization of the residues from water, yields of benzoic acid (m.p. 120–122°) of 79% from the hydroperoxyacetophenone (XXXIa) and of 72% from the hydroperoxypropiophenone (XXXIb) were obtained. Identifications were by the mixture melting point method.

Decomposition of α-Hydroperoxy-α-methoxyacetophenone (XXXIa) with Pyridine.—To 3.8 g. of the hydroperoxide was added 15 ml. of pyridine. An exothermal reaction ensued. The mixture was then heated over a steam-bath for 20 min., after which it was evaporated by a stream of air. The residue was dissolved in ether, the ether extract was washed thoroughly and then extracted with sodium carbonate solution. Upon acidification of the aqueous layer with hydrochloric acid 1.1 g. (43% yield) of benzoic acid was obtained (m.p. 120–122°). The ether layer was evaporated and the residue was treated with phenylhydrazine in the usual way. The product was benzil phenylosazone (0.14 g., m.p. 224–226°).[15] Identifications were by the mixture melting point method.

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AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. XX. 4-*n*-Octyl-1,2-dimethylenecyclohexane[1]

BY WILLIAM J. BAILEY AND WILLIAM A. KLEIN[2]

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A convenient synthesis of a 2-alkyl-1,3-butadiene was developed from a commercially available alkenylsuccinic anhydride as the starting material. Thus 2-*n*-octyl-1,3-butadiene was prepared in four steps including a pyrolysis of a diacetate in an over-all yield of 53%. This 2-octylbutadiene was then converted in five steps to 4-*n*-octyl-1,2-dimethylenecyclohexane in an over-all yield of 40%. The final step in the synthesis involved the pyrolysis of a diacetate in a 55% yield. The structures of the dienes were proved by ultraviolet and infrared absorption spectra and conversion to solid Diels–Alder adducts.

A series of substituted 1,2-dimethylcyclohexanes[3-6] has been prepared in this Laboratory in an effort to determine the correlation between the molecular structure and the physical properties of the corresponding polymers. One of the objectives was the determination of the reason for the fact that the all-*cis* poly-1,2-dimethylenecyclohexane was a high melting crystalline polymer while the closely related all-*cis* natural rubber was an excellent rubber.[7] Since a methyl group located in the 4-position had very little effect on the softening point of an all-*cis* polymer, it was of interest to determine what effect a large group located in the 4-position would have on the physical properties of a poly-1,2-dimethylenecyclohexane. It had been shown previously that, as the size of the *n*-alkyl group in poly-*n*-alkyl methacrylates[8] and poly-*n*-alkylstyrenes[9] was increased, the softening point was decreased until a maximum depression occurred when the alkyl group contained eight to ten carbon atoms. Higher homologs reversed this trend and the softening points began to rise, presumably because the long alkyl side chains were capable of increasing the crystallinity of the polymers by the formation of crystallites involving only these side groups. For these reasons the synthesis of 4-*n*-octyl-1,2-dimethylenecyclohexane (I) was undertaken with the hope that a less crystalline and therefore a more rubbery all-*cis* polymer could be produced.

Since one of the key intermediates in the projected synthesis of I was 2-*n*-octyl-1,3-butadiene (II), an effort was made to find a convenient route to this diene. Previous work in this Laboratory has shown that the pyrolysis of esters is an excellent method for the preparation of unsaturated compounds and that, if charring is avoided, highly strained dienes, such as 1,2-dimethylene-4-cyclohexene, an isomer of *o*-xylene, can be prepared completely free of its aromatic isomer.[10] Marvel and

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(1) Previous paper in this series, THIS JOURNAL, **79**, 1444 (1957).

(2) Office of Naval Research Fellow, 1951–1954; Union Carbide Fellow, 1954–1955.

(3) W. J. Bailey, J. Rosenberg and L. J. Young, THIS JOURNAL, **76**, 2251 (1954).

(4) W. J. Bailey and R. L. Hudson, *ibid.*, **78**, 670, 2806 (1956).

(5) W. J. Bailey, C.-W. Liao and G. H. Coleman, *ibid.*, **77**, 990 (1955).

(6) W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955).

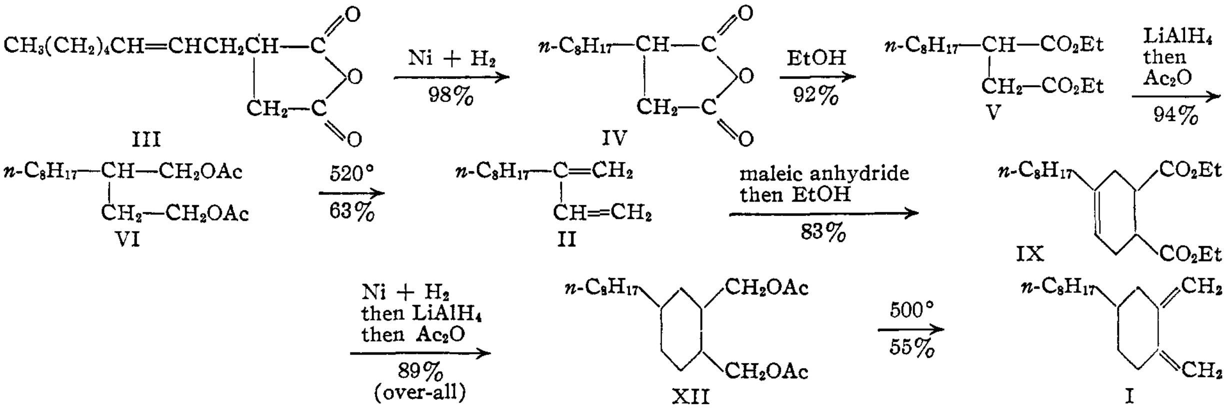
(7) W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

(8) C. E. Rehberg and C. H. Fisher, *Ind. Eng. Chem.*, **40**, 1431 (1948).

(9) C. G. Overberger, C. Frazier, J. Mandelman and H. F. Smith THIS JOURNAL, **75**, 3326 (1953).

(10) W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955); W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **77**, 1163 (1955).

co-workers have developed a method for the synthesis of 2-alkylbutadienes involving the pyrolysis of a monoacetate as the final step; however, this procedure, which involves a Mannich reaction on an aldehyde, deamination, a Grignard reaction and esterification, is fairly long and gives a rather low over-all yield.[11] Overberger and co-workers also have developed a synthesis of 2-alkylbutadienes involving the pyrolysis of a diacetate as a final step; however, their starting material was prepared by a Stobbe condensation, esterification and catalytic reduction in only a fair over-all yield.[12] Since a series of alkenylsuccinic anhydrides, addition products of 1-olefins and maleic anhydride, are now commercially available,[13] it appeared that these adducts would make excellent starting materials for the preparation of 2-alkylbutadienes.



Thus the commercially available octenylsuccinic anhydride (III) was reduced catalytically to produce a 98% yield of *n*-octylsuccinic anhydride (IV) which was then esterified to give ethyl 3-carbethoxyundecylate (V) in a 92% yield. By a procedure which is essentially a one-step reductive acetylation with lithium aluminum hydride and acetic anhydride,[14] the ester V was reduced and the intermediate glycol in the reaction mixture was acetylated to yield the 3-acetoxymethylundecyl acetate (VI) in a 94% yield. An alternative procedure for the preparation of VI by the reductive acetylation of IV did not give as high a yield. Apparently the intermediate reduction products from IV were so insoluble that, even when the reduction was carried out for 96 hr., only a 78% yield of VI was obtained.

Pyrolysis of the diacetate VI at 520° was conducted by the dropwise addition of the liquid through a Vycor tube packed with Pyrex helices under such conditions that only 77% of two molar equivalents of acetic acid was liberated. Under these conditions little or no charring that could cause isomerization occurred. From the pyrolysis were obtained a 46% conversion to 2-*n*-octyl-1,3-butadiene (II) plus a 28% yield of a mixture of the two possible intermediate olefin acetates. The yield of II, based on unrecovered olefin acetate, was 63%. The over-all yield for the four-step synthesis of II from the commercially available III was 53%.

The diene II was characterized by conversion to two solid Diels–Alder adducts. Thus the 2-*n*-octyl-1,3-butadiene (II) plus maleic anhydride gave a 47% yield of 4-*n*-octyl-1,2,3,6-tetrahydrophthalic anhydride (VII), while treatment with 1,4-naphthoquinone produced a 67% yield of 2-*n*-octyl-1,4,4a,9a-tetrahydroanthraquinone (VIII). The ultraviolet absorption spectrum possessed a maximum ϵ of 20,400 at 226 mμ which indicated the presence of a pair of conjugated double bonds. Although the maximum is slightly higher than predicted from Woodward's rules,[15] it is in excellent agreement with that reported for 2-*n*-heptyl-1,3-butadiene.[12] The structure of II also was indicated by its infrared absorption spectrum which possessed strong bands at 722, 883–913, 986, 1367, 1443, 1619, 1789, 2245 and 2860 cm.$^{-1}$ and somewhat weaker bands at 757, 1015, 1066, 1111, 1155, 1195, 1232, 1298 and 1644 cm.$^{-1}$. The absence of a band in the 800 to 850 cm.$^{-1}$ region indicated that very little if any of the isomeric 3-methyl-1,3-undecadiene was present.

The 4-*n*-octyl-1,2-dimethylenecyclohexane was then prepared from II in five steps in an over-all yield of 40%, essentially by a procedure developed earlier for the ascending of a diene series by the addition of a cyclohexane ring.[3] The *n*-octylbutadiene II was treated with maleic anhydride and the solid adduct VII was not isolated, but the crude reaction mixture was esterified directly to produce an 83% yield of the diethyl ester IX. IX was catalytically reduced in a 96% yield to give the diethyl 4-*n*-octylhexahydrophthalate (X) which, in turn, was reduced nearly quantitatively to the glycol XI with lithium aluminum hydride. Acetylation with acetic anhydride produced a 95% yield of the 4-*n*-octylhexahydrophthalyl diacetate (XII).

The diacetate XII was pyrolyzed at 500° by dropwise addition to the apparatus described above under such conditions that only 54% of two molar equivalents of acetic acid was liberated. These rel-

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(11) C. S. Marvel, R. L. Myers and J. H. Saunders, THIS JOURNAL, **70**, 1694 (1948); C. S. Marvel and J. L. R. Williams, *ibid.*, **70**, 3842 (1948).

(12) C. G. Overberger and C. W. Roberts, *ibid.*, **71**, 3618 (1949); C. G. Overberger, A. Fishman, C. W. Roberts, L. M. Arond and J. Lal, *ibid.*, **73**, 2540 (1951).

(13) Humphrey-Wilkinson, Inc., North Haven, Conn.

(14) W. J. Bailey and W. R. Sorenson, THIS JOURNAL, **78**, 2287 (1956); W. J. Bailey and J. Economy, *ibid.*, **77**, 1133 (1955).

(15) R. B. Woodward, *ibid.*, **63**, 1123 (1941); **64**, 76 (1942).

atively mild conditions were chosen in order to prevent charring that could cause the formation of any polymerization inhibitors. Under these conditions a 26% conversion to the 4-*n*-octyl-1,2-dimethylenecyclohexane (I) was realized. In addition a 40% yield of a mixture of the two possible intermediate olefin acetates and a 13% recovery of the starting diacetate XII were obtained. The yield of the diene I, based on unrecovered olefin acetate and starting diacetate, was 55%.

The diene I also was characterized by conversion to two solid Diels–Alder adducts. Thus the 4-*n*-octyl-1,2-dimethylenecyclohexane (I) was treated with maleic anhydride to produce a 47% yield of 6-*n*-octyl-$\Delta^{9(10)}$-octahydronaphthalene-2,-3-dicarboxylic anhydride (XIII) and with 1,4-naphthoquinone to produce a 38% yield of 2-*n*-octyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XIV). The ultraviolet absorption spectrum of the diene I showed no maximum or minimum above 220 mμ but appeared to reach a maximum just below 220 mμ. This is a definite indication of the presence of a pair of non-planar conjugated double bonds exocyclic to a cyclohexane ring. Although this maximum is much lower than that predicted from Woodward's rules,[15] it is in excellent agreement with the maxima reported for similar cyclic dienes which have a pair of conjugated double bonds slightly askew.[3–5,10,16] For instance, 4-methyl-1,2-dimethylenecyclohexane also possesses no maximum or minimum above 220 mμ but appears to reach a maximum just below 220 mμ. Only when the two exocyclic double bonds are forced into the same plane, as in 2,3-dimethylenebicyclo[2.2.1]heptane, does the absorption maximum occur at longer wave lengths. The infrared absorption spectrum of the diene I also was very similar to that of closely related dienes. The strong absorption at 890 cm.$^{-1}$ indicated the presence of a terminal methylene group.

The polymers from these interesting dienes will be reported separately.

Experimental[17]

***n*-Octylsuccinic Anhydride (IV).**—A solution of 368 g. (1.75 moles) of *n*-octenylsuccinic anhydride (III) (Humphrey–Wilkinson, Inc.) in 600 ml. of purified dioxane and 25 g. of W-5 Raney nickel catalyst were placed in a high pressure hydrogenation vessel. The hydrogenation was completed in 1 hr. at 100° and 160 atm. of hydrogen. After removal of the catalyst by filtration, the dioxane was removed by distillation under reduced pressure to yield 366 g. (98%) of *n*-octylsuccinic anhydride (IV), m.p. 62–64.5° (reported[8] m.p. 64–64.5°).

Ethyl 3-Carbethoxyundecylate (V).—A mixture of 3000 ml. of benzene, 1200 ml. of absolute ethanol, 775 g. (3.68 moles) of *n*-octylsuccinic anhydride (IV) and 10 ml. of concentrated sulfuric acid was heated under reflux until no further separation of an aqueous phase occurred (Dean–Stark trap). After the reaction mixture was washed with an aqueous sodium bicarbonate solution, the excess solvents were removed by distillation at atmospheric pressure through a 12-inch Vigreux column. The residue was fractionally distilled through the same column under reduced pressure to give 969 g. (92%) of ethyl 3-carbethoxyundecylate (V), b.p. 110° (0.07 mm.), n^{25}D 1.4350.

Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.12; H, 10.26.

3-Acetoxymethylundecyl Acetate (VI). A. From *n*-Octylsuccinic Anhydride (IV).—To a slurry of 68.4 g. (1.8 moles) of lithium aluminum hydride in 2 liters of anhydrous ether was added slowly a solution of 315 g. (1.5 moles) of *n*-octylsuccinic anhydride (IV) in 2 liters of anhydrous ether. (It was necessary periodically to warm the dropping funnel with a heat lamp in order to prevent the precipitation of the anhydride.) After the reaction mixture had been heated under reflux for 96 hr., 75 ml. of water was added dropwise to destroy the excess lithium aluminum hydride. The complexes were then decomposed by the addition of 432 g. (7.2 moles) of acetic acid. Most of the ethyl ether was removed by distillation and it was replaced by *n*-butyl ether. After the addition of 1530 g. (15 moles) of acetic anhydride and 30 g. of acetic acid, the mixture was heated under reflux for 72 hr. It was filtered while hot in order to remove the heavy deposit of inorganic salts. After the solvent was removed by flash distillation, the residue was fractionally distilled through a 12-inch Vigreux column to yield 336 g. (78%) of 3-acetoxymethylundecyl acetate (VI), b.p. 118° (0.04 mm.), n^{25}D 1.4396.

Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.39; H, 10.32.

B. From Ethyl 3-Carbethoxyundecylate (V).—To a cooled slurry of 160 g. (4.2 moles) of lithium aluminum hydride and 1.5 liters of dry ether was added slowly a solution of 962 g. (3.36 moles) of ethyl 3-carbethoxyundecylate (V) dissolved in 1.5 liters of dry ether. After addition had been completed, the reaction mixture was heated under reflux for an additional 72 hr. The excess lithium aluminum hydride was then destroyed by the dropwise addition of 100 ml. of water, and the complexes were decomposed with 1009 g. (16.8 moles) of acetic acid. The ethyl ether was replaced by *n*-butyl ether as described above, and the unisolated diol was heated under reflux for 120 hr. with 1500 ml. of acetic anhydride and 30 ml. of acetic acid. After the inorganic salts were removed by filtration of the hot mixture, the excess solvents were removed by flash distillation under reduced pressure. The residue was fractionally distilled through a 12-inch Vigreux column to yield 903 g. (94%) of 3-acetoxymethylundecyl acetate (VI), b.p. 127° (0.11 mm.), n^{25}D 1.4394.

2-*n*-Octyl-1,3-butadiene (II).—At the rate of 1.5 g. per minute, 100 g. (0.35 mole) of 3-acetoxymethylundecyl acetate (VI) was added dropwise to a vertical Vycor pyrolysis tube which was packed to a depth of 10 inches with 1/8-inch glass helices and heated externally at 520° by a FD 303 A Hoskins electric furnace as described previously.[18] The addition was conducted in an inert atmosphere by the introduction of a slow stream of oxygen-free nitrogen at the top of the tube. The pyrolysate was collected in a receiver cooled by a Dry Ice–cellosolve bath. (Titration of a 0.27-g. sample of the pyrolysate with standard sodium hydroxide solution indicated that 77% of two molar equivalents of acetic acid had been liberated.) Fractional distillation of the crude pyrolysate through a 6-inch, helix-packed column yielded 27 g. (46%) of 2-*n*-octyl-1,3-butadiene (II), b.p. 71° (4.3 mm.), n^{25}D 1.4514; and 22 g. (28%) of presumably a mixture of the two possible olefin acetates, 3-acetoxymethyl-1-undecene and 3-methylene-*n*-undecyl acetate. The yield of the diene II, based on the unrecovered olefin acetates, was 63%.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.66; H, 13.52.

4-*n*-Octyl-1,2,3,6-tetrahydrophthalic Anhydride (VII).—To a filtered solution of 1.60 g. (0.016 mole) of maleic anhydride in 50 ml. of dry benzene was added 3.5 g. (0.021 mole) of 2-*n*-octyl-1,3-butadiene (II). After the solution had been heated under reflux for 24 hr., the benzene was removed by distillation under reduced pressure to yield 2.36 g. (47%) of the crude adduct VII, m.p. 45–58°. Recrystallization from petroleum ether gave an analytically pure sample of 4-*n*-octyl-1,2,3,6-tetrahydrophthalic anhydride (VII), m.p. 51.3–51.8°. (A mixed melting point with maleic anhydride exhibited a large depression.)

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[16] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[17] The authors are grateful to Dr. Mary Aldridge and Miss Kathryn Gerdeman for the microanalyses and to Miss Gerdeman and Dr. Ellis R. Lippincott for the infrared spectra. The infrared spectra were determined on the pure liquids with a sodium chloride prism in a Perkin-Elmer model 12-C infrared spectrometer modified for double-pass operation. The ultraviolet absorption spectra were determined in purified cyclohexane in a Beckman model DU spectrophotometer. All melting points are corrected.

[18] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.41; H, 8.99.

2-*n*-Octyl-1,4,4a,9a-tetrahydroanthraquinone (VIII).—A solution of 1.58 g. (0.010 mole) of 1,4-naphthoquinone, 3.0 g. (0.018 mole) of 2-*n*-octyl-1,3-butadiene (II) and a few milligrams of N-phenyl-β-naphthylamine in 50 ml. of dry benzene was heated under reflux for 24 hr. The benzene was removed by distillation under reduced pressure to give 2.21 g. (67%) of the slightly impure adduct VIII, m.p. 84–86°. Recrystallization from ethanol produced analytically pure 2-*n*-octyl-1,4,4a,9a-tetrahydroanthraquinone (VIII), m.p. 85.8–86.4°.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70. Found: C, 81.65; H, 8.44.

Diethyl 4-*n*-Octyl-1,2,3,6-tetrahydrophthalate (IX).—After a filtered solution of 39.2 g. (0.40 mole) of maleic anhydride dissolved in 300 ml. of dry benzene and 50 g. (0.30 mole) of 2-*n*-octyl-1,3-butadiene (II) had been maintained at 55° for 20 hr., the unisolated adduct and excess maleic anhydride were esterified by the addition of 125 ml. of absolute ethanol and 1 ml. of concentrated sulfuric acid. The water formed in the esterification process was removed as the ternary azeotrope by means of a Dean–Stark receiver. After no more aqueous phase appeared in the distillate, the excess benzene and alcohol were removed by distillation through the Dean–Stark receiver. The residue, without further treatment, was fractionally distilled through a 12-inch Vigreux column to yield 84 g. (83%) of diethyl 4-*n*-octyl-1,2,3,6-tetrahydrophthalate (IX), b.p. 150° (0.15 mm.), $n^{25}\mathrm{D}$ 1.4636.

Anal. Calcd. for $C_{20}H_{34}O_4$: C, 70.97; H, 10.13. Found: C, 71.01; H, 9.95.

Diethyl 4-*n*-Octylhexahydrophthalate (X).—A mixture of 114 g. (0.34 mole) of diethyl 4-*n*-octyl-1,2,3,6-tetrahydrophthalate (IX), 35 ml. of absolute ethanol and 6 g. of W-5 Raney nickel catalyst was added to a high pressure hydrogenation vessel. The hydrogenation was completed in 4 hr. at 100° and 170 atm. of hydrogen. After the catalyst was removed by filtration, the ethanol was removed by distillation under reduced pressure. The residue was fractionally distilled through a 6-inch, helix-packed column to yield 112 g. (96%) of diethyl 4-*n*-octylhexahydrophthalate (X), b.p. 140° (0.10 mm.), $n^{25}\mathrm{D}$ 1.4562. (Similar results were obtained by the hydrogenation of IX in ethanol at 22° and atmospheric pressure by use of Adams catalyst, platinum oxide.)

Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.70; H, 10.38.

4-*n*-Octylhexahydrophthalyl Alcohol (XI).—To a slurry of 14 g. (0.37 mole) of lithium aluminum hydride in 1 liter of anhydrous ether was added dropwise a solution of 96 g. (0.28 mole) of diethyl 4-*n*-octylhexahydrophthalate (X) in 100 ml. of ether. Near the end of the addition the reaction mixture became so viscous that it was necessary to add an additional 200 ml. of ether in order to facilitate stirring. After the reduction mixture had been heated under reflux overnight, the excess lithium aluminum hydride was destroyed by the dropwise addition of 50 ml. of water. A sufficient amount of 10% hydrochloric acid was added to the ice-bath cooled reaction mixture to cause the formation of two distinct layers. The clear ether layer was removed by decantation before the remainder of the salts was dissolved by additional dilute acid. The aqueous phase was extracted several times with ether, and these extracts were combined with the initial ether layer. After the ethereal solution had been dried with anhydrous potassium carbonate and sodium sulfate, the ether was removed by flash distillation under reduced pressure to give 70 g. (97%) of crude 4-*n*-octylhexahydrophthalyl alcohol (XI), m.p. 61–65°. Recrystallization of a small quantity from ether–petroleum ether gave an analytically pure sample, m.p. 64.0–64.6°.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.58. Found: C, 74.77; H, 12.31.

4-*n*-Octylhexahydrophthalyl Diacetate (XII).—After a mixture of 104 g. (0.41 mole) of the crude 4-*n*-octylhexahydrophthalyl alcohol (XI), 250 g. of acetic anhydride and 30 g. of acetic acid was heated under reflux in a 1-liter flask for 24 hr., the excess acetic acid and acetic anhydride were removed by distillation under reduced pressure through a 12-inch Vigreux column. The residue was distilled through the same column to yield 132 g. (95%) of 4-*n*-octylhexahydrophthalyl diacetate (XII), b.p. 140° (0.03 mm.), $n^{25}\mathrm{D}$ 1.4605.

Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.35; H, 10.49.

4-*n*-Octyl-1,2-dimethylenecyclohexane (I).—By the use of the pyrolysis apparatus described for the preparation of II, 36 g. (0.105 mole) of 4-*n*-octylhexahydrophthalyl diacetate (XII) was pyrolyzed at 500° at the addition rate of 1.5 g. per minute. A few milligrams of antioxidant, N-phenyl-β-naphthylamine, was added to an ether solution of the pyrolysate. Removal of the acetic acid by extraction with water and titration of an aliquot of these washings with standard sodium hydroxide solution indicated that 54% of two molar equivalents of acetic acid had been eliminated. After the ether solution was dried over anhydrous sodium sulfate, most of the ether was removed by distillation through a 6-inch, helix-packed column. The residue was then fractionally distilled through the same column to yield 6.2 g. (26%) of the light yellow 4-*n*-octyl-1,2-dimethylenecyclohexane (I), b.p. 79° (0.11 mm.), $n^{25}\mathrm{D}$ 1.4707; 11.8 g. (40%) of presumably a mixture of the pair of intermediate olefin acetates, 1-methylene-2-acetoxymethyl-4-*n*-octylcyclohexane and 1-acetoxymethyl-2-methylene-4-*n*-octylcyclohexane, b.p. 106–118° (0.09 mm.), $n^{25}\mathrm{D}$ 1.4645; and 4.5 g. (13%) of recovered diacetate XII. The yield of I, based on unrecovered olefin acetates and XII, was 55%.

Anal. Calcd. for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 87.47; H, 12.80. Calcd. for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.80; H, 11.27.

6-*n*-Octyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic Anhydride (XIII).—After a mixture of a filtered solution of 0.59 g. (0.006 mole) of maleic anhydride in 50 ml. of dry benzene and 1.59 g. (0.007 mole) of 4-*n*-octyl-1,2-dimethylenecyclohexane (I) had been allowed to stand at 25° for 2 hr., it was heated under reflux for 15 hr. The benzene was partially removed by distillation under reduced pressure and the precipitate which formed was removed by filtration and was washed with 30–60° petroleum ether. The crude adduct XIII weighed 0.90 g. (47%) and had a melting range of 89–95°. Two recrystallizations from 60–80° petroleum ether gave analytically pure 6-*n*-octyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic anhydride (XIII), m.p. 103.8–105°.

Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50. Found: C, 75.41; H, 9.64.

2-*n*-Octyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XIV).—A mixture of 1.72 g. (0.008 mole) of 4-*n*-octyl-1,2-dimethylenecyclohexane (I), 0.95 g. (0.006 mole) of 1,4-naphthoquinone and 50 ml. of dry benzene was heated under reflux for 15 hr. After the benzene was partially removed by evaporation of the solution on the steam-bath, the resulting precipitate was removed by filtration and was washed with hot ethanol. The yield of the crude light tan adduct XIV, m.p. 141–144°, was 0.87 g. (38%). Recrystallization from 60–80° petroleum ether gave analytically pure 2-*n*-octyl-1,2,3,4,5,5a,6,11,11a,12-decahydronaphthacene-6,11-dione (XIV), m.p. 145.8–146.6°.

Anal. Calcd. for $C_{26}H_{34}O_2$: C, 82.49; H, 9.05. Found: C, 82.65; H, 8.87.

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