

Reaction of 2-Isohexylcyclohexanone (IIIg) with Phenylmagnesium Bromide.—The reaction of 5.00 g. (0.0274 mole) of IIIg with the Grignard reagent from 0.80 g. (0.0329 mole) of magnesium and 5.17 g. (0.0329 mole) of bromobenzene was carried out as described for IIIf. Distillation of the products gave these various fractions: (1) 0.67 g., b.p. 62–64° (0.11–0.08 mm.); (2) 0.34 g., b.p. 64–120° (0.20 mm.); (3) 5.68 g., b.p. 120–122° (0.08 mm.). Fraction 1 was recovered IIIg (13%); fraction 3 represented an 80% yield of 2-(4-methylpentyl)-1-phenylcyclohexanol. Fraction 3 was redistilled and a middle cut, b.p. 120° (0.08 mm.), n_D^{25} 1.5142, was taken for analysis. The infrared spectrum (liquid film) contained a hydroxyl band at 2.86 μ .

Anal. Calcd. for $C_{15}H_{26}O$: C, 83.02; H, 10.84. Found: C, 83.62; H, 10.96.

2-Dimethylaminomethyl-1-phenyl-1-propionyloxycyclohexane (XIIIc) Hydrochloride.—A mixture of 2.00 g. (0.0857 mole) of XIIc, m.p. 54–56°, 0.96 g. (0.01 mole) of sodium propionate and 20 ml. of propionic anhydride was placed in a 50-ml. round-bottom flask equipped with a reflux condenser carrying a drying tube. The mixture was heated for 8 hours on the steam-bath, after which it was poured into 50 ml. of water and allowed to stand until the anhydride had all dissolved. The solution was saturated with potassium carbonate and extracted with four 20-ml. portions of ether. The ether solution was dried over anhydrous potassium carbonate and a solution of dry hydrogen chloride in ether was added dropwise until no more precipitate formed. The resulting white solid was filtered off, washed with ether, dried and recrystallized from ethanol–ethyl acetate to give 2.44 g. (88%) of XIIIc hydrochloride, m.p. 182–183.5° dec. A sample was recrystallized two more times for analysis, m.p. 183–185° dec. The infrared spectrum (mull) had a strong carbonyl band at 5.78 μ ; no hydroxyl band was present.

Anal. Calcd. for $C_{15}H_{25}O_2NCl$: C, 66.34; H, 8.66; Cl, 10.9. Found: C, 66.51; H, 8.59; Cl, 10.8

When this preparation was carried out as above, except that heating was continued for only 3 hours, the product consisted largely of unchanged carbinol XIIc.

When the acylation was carried out as above on 13.4 g. (0.0574 mole) of the mixture of isomers of XIIc obtained from the Grignard reaction, 16.3 g. (87%) of XIIIc hydrochloride, m.p. 170–181°, resulted. Fractional crystallization from ethanol–ethyl acetate gave 9.9 g. of colorless prisms, m.p. and mixed m.p. with above product 183–185° dec., and 1.89 g. of colorless needles, m.p. 180–182° dec. The salt, m.p. 180–182°, when mixed with the 185° salt, melted at 170–180° dec. The lower melting salt was analyzed: C, 66.33; H, 8.66; Cl, 10.8. The infrared spectrum (mull) contained a strong carbonyl band at 5.78 μ . This spectrum was similar, but not identical, to the spectrum of the 185° salt.

2-(2-Dimethylaminoethyl)-1-phenyl-1-propionyloxycyclohexane (XIIIId) Hydrochloride.—One gram of XIIId, m.p. 71–72°, 0.48 g. of sodium propionate and 25 ml. of propionic anhydride were placed in a 50-ml. round-bottom flask equipped with a reflux condenser carrying a drying tube.

The mixture was stirred magnetically and heated at 115–120° in an oil-bath for 24 hours, after which it was cooled to room temperature and poured into 50 ml. of water. After the solution had become homogeneous, it was saturated with potassium carbonate and extracted with five 15-ml. portions of ether. After drying over anhydrous potassium carbonate, the ether solution was treated with a solution of dry hydrogen chloride in ether (dropwise addition) until no more precipitate formed. The resulting white solid was washed with ether, dried and crystallized from ethyl acetate, which gave 0.76 g. (55.5%) of XIIIId hydrochloride as colorless plates, m.p. 180–181°. Recrystallization from ethyl acetate resulted in recovery of nearly all of this material as colorless plates, m.p. 181–182° dec. Further recrystallization did not raise the melting point. The infrared spectrum (mull) contained a strong ester carbonyl band at 5.79 μ . No hydroxyl band was present.

Anal. Calcd. for $C_{19}H_{30}O_2NCl$: C, 67.14; H, 8.90; Cl, 10.4. Found: C, 67.31; H, 8.90; Cl, 10.4.

Lower reaction temperatures or shorter heating times gave very little of the ester. Recovered carbinol XIIId was the main product in every case.

The preparation of XIIIId hydrochloride also could be carried out in 46% yield by heating XIIId hydrochloride in propionic anhydride at 115–120° for 24 hours.

Attempted Preparation of the Propionate of XIIe.—Conversion of the carbinol XIIe to this ester was attempted by the following methods: (a) heating XIIe with propionic anhydride and sodium propionate at 115° for 24 hours; (b) same as (a), except heated at 125°; (c) addition of propionyl chloride to a benzene solution of XIIe; (d) treatment of XIIe in ether with one equivalent of phenyllithium to form the lithium salt, followed by addition of propionyl chloride. The main product of each of these reactions was the carbinol XIIe, recovered as the hydrochloride. In no case was any other pure compound isolated.

A fifth method, heating XIIe hydrochloride in propionic anhydride at 135–140° for 24 hours, gave a 9.6% yield of 1 (or 6)-(3-dimethylaminopropyl)-2(or 1)-phenylcyclohexene hydrochloride, m.p. 173–175°, as the only crystalline product. The infrared spectrum had a band of medium intensity at 6.27 μ (probably the conjugated double bond). No hydroxyl or carbonyl bands were present.

Attempted Propionylation of 2-(4-Methylpentyl)-1-phenylcyclohexanol.—A mixture of 3.0 g. (0.115 mole) of this carbinol, 1.1 g. (0.115 mole) of sodium propionate and 30 ml. of propionic anhydride was stirred magnetically and heated at 125° for 24 hours. The excess propionic anhydride was removed under reduced pressure (bath temperature 100°) and the residue was taken up in 40 ml. of dry ether. The ether solution was filtered to remove the sodium propionate, the ether removed under reduced pressure, and the product distilled to give 2.0 g. (67%) of recovered carbinol, b.p. 121–124° (0.1 mm.), n_D^{25} 1.5130. The remainder of the reaction was a brown gum which would not distil.

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

Cyclic Dienes. XXIV. 1,2-Dimethylenedecalin¹

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The cyclic diene 1,2-dimethylenedecalin was synthesized in five steps from 3,4-dihydro-1,2-naphthalic anhydride in an over-all yield of 61%. In the final step, a diacetate was pyrolyzed to give an 81% yield of the desired diene. The structure of the 1,2-dimethylenedecalin was proved by analysis, vapor phase chromatography, infrared and ultraviolet absorption spectra and conversion to solid Diels–Alder adducts with maleic anhydride and benzoquinone. The structure of the maleic anhydride adduct was further proved by hydrolysis to the corresponding diacid and by simultaneous dehydrogenation and decarboxylation to phenanthrene.

In a previous article in this series³ a general method for the synthesis of linear condensed poly-

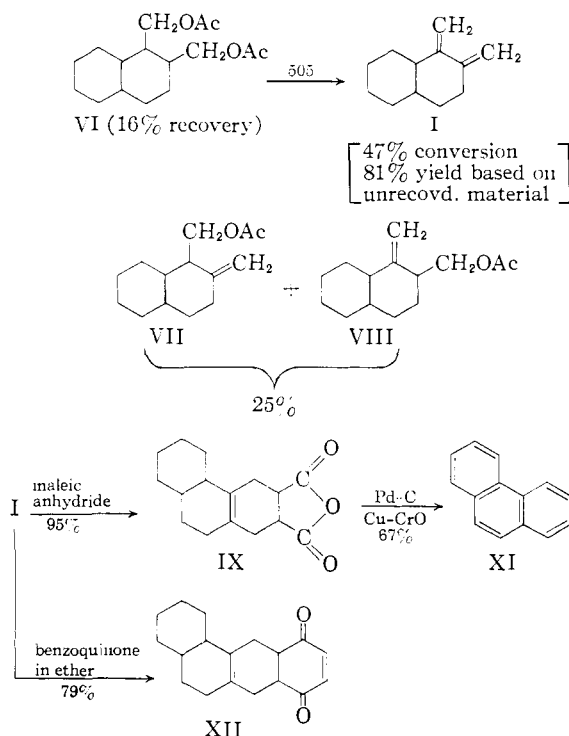
nuclear aromatic hydrocarbons was described. For example, pentacene was prepared from 1,2-dimethylenecyclohexane and heptacene and hexacene from 2,3-dimethylenedecalin.⁴ An interest-

(1) Previous paper in this series, *THIS JOURNAL*, **81**, 5393 (1959).
(2) National Cancer Institute Fellow (U. S. Public Health Service), 1955–1957.

(3) W. J. Bailey and M. Madoff, *THIS JOURNAL*, **75**, 5603 (1953).

(4) W. J. Bailey and C.-W. Liao, *ibid.*, **77**, 992 (1955).

ing extension of this series of dienes appeared to be 1,2-dimethylenedecalin (I). The use of this diene in the general scheme previously developed would allow the synthesis of linear condensed ring systems containing one or two angular benzo substituents, such as dibenzo[a,1]pentacene. In addition, the polymerization of such a diene should give information on the effect of steric hindrance on the reactivity of the diene system.



The starting material for the preparation of the diene I was 3,4-dihydro-1,2-naphthalic anhydride (II),⁵ which was esterified to give a 97% yield of diethyl 3,4-dihydro-1,2-naphthalate (III). Catalytic hydrogenation of III in the presence of W-5 Raney nickel catalyst⁶ produced erratic results. In the best run an 80% yield of 1,2-dicarbethoxydecalin (IV) was obtained. In most cases the principal product was accompanied by a partially reduced product containing one double bond. It is likely that the remaining double bond was in the relatively inert 9,10-position, since Nazarov⁷ noted that the *cis*- $\Delta^{9(10)}$ -octahydronaphthalene-1,2-dicarboxylic acid does not hydrogenate under usual conditions. The presence of a lower boiling fore-run (6 to 25% by weight) indicated that some hydrogenolysis had taken place. More consistent and satisfactory results were observed when III was hydrogenated in the presence of nickel-on-kieselguhr.⁸ This procedure consistently gave an 88% yield of IV, which undoubtedly was a mixture

of various stereoisomeric forms. An alternate route that gave equally satisfactory results was the hydrogenation of diethyl naphthalate over nickel-on-kieselguhr to give an 88% yield of IV.

Reduction of the diester IV with lithium aluminum hydride gave a 95% yield of 1,2-dimethylenedecalin (V), which was in turn acetylated in a 93% yield to give 1,2-di-(acetoxymethyl)-decalin (VI).

When the diacetate VI was pyrolyzed at 505°C under such conditions that no appreciable charring occurred and 75% of two molar equivalents of acetic acid was liberated, a 47% conversion to 1,2-dimethylenedecalin (I) was realized. At the same time a 25% yield of presumably a mixture of the two possible olefin acetates, 2-methylene-1-acetoxymethyldecalin (VII) and 1-methylene-2-acetoxymethyldecalin (VIII), and a 16% recovery of unchanged starting diacetate VI were obtained. The yield of diene I, based on unrecovered VI, VII and VIII, was, therefore, 81%.

The ultraviolet absorption spectrum of 1,2-dimethylenedecalin (I) did not possess a maximum or minimum above 220 m μ , but appeared to reach an ϵ maximum of 5700 just below 220 m μ . Such a spectrum is indicative of conjugated double bonds exocyclic to a six-membered ring (1,2-dimethylenecyclohexane⁹ and 2,3-dimethylenedecalin⁴ both possess maxima below 220 m μ). The infrared spectrum of the diene I showed strong absorption bands at 895, 1450 and 2980 cm.⁻¹, characteristic of a methylene group, and a medium absorption band at 1635 cm.⁻¹, characteristic of a conjugated system. A Diels-Alder adduct, $\Delta^{4a(10a)}$ -dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX), was formed in a 95% yield from 1,2-dimethylenedecalin (I) and maleic anhydride. The structure of the adduct IX was proved by hydrolysis to the corresponding $\Delta^{4a(10a)}$ -dodecahydrophenanthrene-2,3-dicarboxylic acid (X) and by simultaneous dehydrogenation and decarboxylation to phenanthrene (XI). A second adduct, $\Delta^{6(12a),9}$ -tetradecahydrobenz[a]anthracene-8,10-dione (XII), was obtained in a 79% yield from equimolar quantities of I and benzoquinone.

All attempts to obtain a high molecular weight homopolymer from 1,2-dimethylenedecalin (I) by a peroxide-catalyzed system failed. Even though the extra ring on I would be expected to make the steric requirement of the adjacent methylene group¹⁰ less than that of the methyl group in the related 3-methyl-1,2-dimethylenecyclohexane,¹¹ apparently this steric factor is still quite large. However, with an ionic catalyst the diene I did give a homopolymer with a softening point of 102-112°C.

Experimental¹²

Diethyl 3,4-Dihydro-1,2-naphthalate (III).—A mixture of 200 g. (1.0 mole) of 3,4-dihydro-1,2-naphthalic anhydride

(5) E. B. Hershberg and L. F. Fieser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 194.

(6) H. Adkins and H. R. Billica, *THIS JOURNAL*, **70**, 695 (1948).

(7) I. N. Nazarov, V. F. Kucherov and V. M. Andreev, *Doklady Akad. Nauk, S.S.S.R.*, **102**, 751 (1955) [*C. A.*, **50**, 4881 (1956)].

(8) Similar improvement of results was observed when diethyl terephthalate was hydrogenated with the less active W-2 Raney nickel catalyst rather than with the more active W-5 catalyst; W. J. Bailey and R. Barclay, *THIS JOURNAL*, **81**, 5393 (1959).

(9) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

(10) R. T. Arnold, V. J. Webers and R. M. Dodson, *ibid.*, **74**, 368 (1952).

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

(12) The authors are indebted to Dr. Mary H. Aldrich, Miss Kathryn Gerdeman and Miss Jane Swan for the microanalyses and to Miss Gerdeman, Dr. Rudolph A. Schroeder and Dr. Ellis R. Lippincott for the infrared spectrum and aid in its interpretation. The infrared spectrum was determined on the pure liquid with a Beckman IR-4

(II),⁸ m.p. 125–126°, 350 ml. of absolute ethanol, 900 ml. of benzene and 20 g. of concentrated sulfuric acid was heated under reflux for 4 days until the theoretical amount of ternary azeotrope had been collected in a Dean–Stark trap. After the solution was washed with a 10% sodium bicarbonate solution and then with water, the excess alcohol, benzene and water were removed by distillation under reduced pressure. The residue was distilled through a 12-inch Vigreux column to yield 266 g. (97%) of diethyl 3,4-dihydro-1,2-naphthalate (III), b.p. 171–175° (0.65–0.75 mm.). This ester solidified on cooling, and recrystallization from absolute ethanol gave 244 g. of white crystals, m.p. 74–75° (reported¹³ m.p. 73°).

Anal. Calcd. for C₁₆H₁₆O₄: C, 70.05; H, 6.61. Found: C, 70.30; H, 6.76.

Diethyl 1,2-Naphthalate.—A mixture of 82.4 g. (0.41 mole) of 1,2-naphthalic anhydride, 160 ml. of absolute ethanol, 500 ml. of benzene and 15 ml. of concentrated sulfuric acid was heated under reflux for 4 days, until the theoretical amount of alcohol–water–benzene mixture had been collected in a Dean–Stark trap. The reaction mixture was washed with three 350-ml. portions of 10% sodium bicarbonate solution and three 350-ml. portions of water. The aqueous extracts were then re-extracted with three 250-ml. portions of ether. After the combined organic layer and ether extracts were dried over magnesium sulfate, the ether was removed by distillation at atmospheric pressure. The residue was then concentrated to approximately 250 ml. by distillation through a 12-inch Vigreux column under reduced pressure. When the residue was allowed to cool with stirring, light yellow crystals precipitated. These crystals were removed by filtration, washed with methanol and dried *in vacuo* to yield 107 g. (95%) of diethyl 1,2-naphthalate, m.p. 86–87°. Two recrystallizations from methanol with treatment with decolorizing charcoal produced white crystals, m.p. 88.5–89.5°.

Anal. Calcd. for C₁₈H₁₈O₄: C, 70.57; H, 5.92. Found: C, 70.80; H, 5.75.

1,2-Dicarbethoxydecalin (IV). A. By Hydrogenation of Diethyl 3,4-Dihydro-1,2-naphthalate (III) with Raney Nickel.—A mixture of 50 g. (0.19 mole) of diethyl 3,4-dihydro-1,2-naphthalate (III), 60 ml. of absolute ethanol (distilled from Raney nickel) and 6 g. of W-5 Raney nickel catalyst was placed in a high pressure hydrogenation vessel which was filled with hydrogen under a pressure of 185 atmospheres at 23°. When the hydrogenation was carried out at 196°, 0.71 mole (97%) of hydrogen was absorbed. After the catalyst was removed by filtration, the filtrate was fractionally distilled through an 8-inch, helix-packed column to yield 41 g. (80%) of 1,2-dicarbethoxydecalin (IV), b.p. 118–119° (0.30 mm.), *n*_D²⁵ 1.4795.

Anal. Calcd. for C₁₆H₂₀O₄: C, 68.05; H, 9.28. Found: C, 68.32; H, 9.20.

B. By Hydrogenation of Diethyl 3,4-Dihydronaphthalate (III) with Nickel-on-Kieselguhr.—A hydrogenation vessel containing 58.5 g. (0.22 mole) of diethyl 3,4-dihydro-1,2-naphthalate (III), 60 ml. of absolute ethanol (distilled from Raney nickel) and 18 g. of reduced nickel-on-kieselguhr catalyst (Harshaw Chemical Co.) was filled with hydrogen under a pressure of 240 atmospheres at 22°. After the mixture had been shaken at 200° for 7 hours, 0.97 mole (110%) of hydrogen was absorbed. After the catalyst was removed by filtration, the filtrate was fractionated through an 8-inch, helix-packed column to yield 53 g. (88%) of 1,2-dicarbethoxydecalin (IV), b.p. 115° (0.25 mm.), *n*_D²⁵ 1.4792.

C. By Hydrogenation of Diethyl Naphthalate with Nickel-on-Kieselguhr.—When 56.4 g. (0.2 mole) of diethyl naphthalate, 60 ml. of absolute ethanol and 18 g. of reduced nickel-on-kieselguhr (Harshaw Chemical Co.) was hydrogenated at 240 atmospheres pressure and 200° for 7 hours, 110% of the theoretical amount of hydrogen was absorbed. After the catalyst was removed by filtration, fractionation through an 8-inch, helix-packed column gave 53 g. (88%) of 1,2-dicarbethoxydecalin (IV), b.p. 115° (0.25 mm.), *n*_D²⁵ 1.4792.

1,2-Dimethyloldecalin (V).—To a slurry of 24 g. (0.63 mole) of lithium aluminum hydride in 900 ml. of ether was

added dropwise with vigorous stirring a solution of 124.3 g. (0.44 mole) of 1,2-dicarboxydecalin (IV) in 400 ml. of ether at such a rate as to maintain gentle reflux. After the reaction mixture was heated under reflux for an additional 40 hours, the excess hydride was decomposed by the dropwise addition of 25 ml. of water. A sufficient amount of 10% hydrochloric acid was added to decompose the complex in such a way that the pH of the solution always was above 2. Most of the ether layer was removed by decantation and the aqueous layer was exhaustively extracted with ether. The combined extracts and original ether layer were dried over anhydrous potassium carbonate and magnesium sulfate. After the ether was removed by flash distillation under reduced pressure, the residue was fractionally distilled through a 30-cm. Vigreux column to yield 83 g. (95%) of highly viscous 1,2-dimethyloldecalin (V), b.p. 142° (0.25 mm.), *n*_D²⁵ 1.5190.

Anal. Calcd. for C₁₂H₂₂O₂: C, 72.68; H, 11.19. Found: C, 72.46; H, 11.13.

1,2-Di-(acetoxymethyl)-decalin (VI).—To a refluxing solution of 74 g. (0.37 mole) of 1,2-dimethyloldecalin (V) in 325 ml. of glacial acetic acid was added dropwise over a period of 75 minutes 280 g. (2.8 moles) of acetic anhydride. After the mixture had been heated for an additional 72 hours, the excess acetic anhydride and acetic acid were removed from the reddish-brown solution by distillation through a 12-inch Vigreux column under reduced pressure. Fractionation of the residue through the same column gave 97 g. (93%) of 1,2-di-(acetoxymethyl)-decalin (VI), b.p. 137.5° (0.5 mm.), *n*_D²⁵ 1.4829.

Anal. Calcd. for C₁₆H₂₆O₄: C, 68.05; H, 9.28. Found: C, 68.29; H, 9.09.

1,2-Dimethylenedecalin (I).—At the rate of 1 g. per minute, 81 g. (0.29 mole) of 1,2-di-(acetoxymethyl)-decalin (VI) was added dropwise to a vertical Vycor tube packed with Pyrex helices and externally heated at 505° by a FD 303A Hoskins electric furnace as described previously.¹⁴ In order to minimize charring, the system was continuously flushed with a slow stream of oxygen-free nitrogen. The pyrolysate was collected in a side-arm flask which contained 20 mg. of 1,3,5-trinitrobenzene and which was cooled in a Dry Ice–acetone-bath. An ether solution of the pyrolysate was washed with 50-ml. portions of cold water until the washings were neutral to litmus. (Titration of an aliquot of the aqueous extracts indicated that 75% of two molar equivalents of acetic acid had been liberated.) After the ether solution had been washed with 5% sodium carbonate solution, a saturated sodium chloride solution and then with water, it was dried over anhydrous sodium carbonate. After the ether had been removed by distillation under reduced pressure, the residue was fractionated through an 8-inch, helix-packed column to yield 22 g. (47%) of 1,2-dimethylenedecalin (I), b.p. 112–113° (26 mm.), *n*_D²⁵ 1.5061, *d*₄²¹ 0.9050; 16 g. (25%) of presumably a mixture of the two possible olefin acetates, 2-methylene-1-acetoxymethyldecalin (VII) and 1-methylene-2-acetoxymethyldecalin (VIII); and 13 g. (16% recovery) of the starting diacetate VI. The yield of diene I, based on unrecovered VI, VII and VIII, was, therefore, 81%. A vapor-phase chromatogram of the diene I through a column packed with silicone grease on Chromosorb at 209° showed only one symmetrical peak.

Anal. Calcd. for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.60; H, 11.09.

Δ^{4a(10a)} Dodecahydrophenanthrene-2,3-dicarboxylic Anhydride (IX).—A solution of 1.6 g. (0.01 mole) of 1,2-dimethylenedecalin (I) and 1.0 g. (0.01 mole) of maleic anhydride in 25 ml. of ether was heated under reflux for 18 hours. The reaction mixture was concentrated to approximately 10 ml. and allowed to cool. The resulting white solid was removed by filtration and washed with cold petroleum ether (30–60°) to give 2.5 g. (95%) of slightly impure adduct, m.p. 121–123°. Recrystallization from a mixture of ether and petroleum ether gave an analytically pure sample of Δ^{4a(10a)}-dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX), m.p. 126.5–128°.

Anal. Calcd. for C₁₆H₂₀O₃: C, 73.82; H, 7.69. Found: C, 73.63; H, 7.57.

Δ^{4a(10a)}-Dodecahydrophenanthrene-2,3-dicarboxylic Acid (X).—After a mixture of 0.5 g. (0.009 mole) of potassium

spectrophotometer. The ultraviolet spectrum was determined in cyclohexane with a Cary recording spectrophotometer, model 11. All melting points are corrected.

(13) K. v. Auwers and K. Moller, *J. prakt. Chem.*, **109**, 124 (1925).

(14) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

hydroxide in 25 ml. of water and 0.3 g. (0.0012 mole) of $\Delta^{4a(10a)}$ -dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX) was heated on a steam-bath for 10 minutes, the reaction mixture was neutralized carefully with 10% hydrochloric acid. The mixture was extracted with ether and the extracts were dried over magnesium sulfate. The dried ether solution was concentrated and cooled to yield 0.27 g. (85%) of slightly impure $\Delta^{4a(10a)}$ -dodecahydrophenanthrene-2,3-dicarboxylic acid (X), m.p. 182–183°. Recrystallization from an ether-petroleum ether mixture gave an analytically pure sample, m.p. 184–185°.

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.00; H, 7.99.

Dehydrogenation and Decarboxylation of $\Delta^{4a(10a)}$ -Dodecahydrophenanthrene-2,3-dicarboxylic Anhydride (IX).—Simultaneous dehydrogenation and decarboxylation of 0.20 g. (0.0077 mole) of $\Delta^{4a(10a)}$ -dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX) was carried out in the presence of 0.1 g. of a 10% palladium-on-carbon catalyst and 0.07 g. of a copper-chromite catalyst. When the mixture had been heated for 3.5 hours at 275°, 92 mg. (67%) of crude phenanthrene (XI), m.p. 80–89°, had sublimed to the cold finger of the dehydrogenation apparatus. Resublimation produced a fairly pure sample of phenanthrene (XI), m.p. 98–100°. A mixed melting point determination with an authentic sample of phenanthrene showed no depression.

$\Delta^{6a(12a),9}$ -Tetradecahydrobenz[a]anthracene-8,11-dione (XII).—A solution of 1.08 g. (0.01 mole) of benzoquinone

and 1.62 g. (0.01 mole) of 1,2-dimethylenedecalin (I) in 30 ml. of anhydrous ether was heated under reflux for 8 hours. When the reaction mixture was cooled, a white solid precipitated from the solution. The precipitate, which was removed by filtration, was recrystallized from absolute alcohol to yield 2.13 g. (79%) of white $\Delta^{6a(12a),9}$ -tetradecahydrobenz[a]anthracene-8,11-dione (XII), m.p. 139.5–140.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 80.05; H, 8.09.

Ionic Polymerization of 1,2-Dimethylenedecalin (I).—In a test-tube, 2.1 g. of 1,2-dimethylenedecalin (I) was thoroughly mixed with approximately 5 g. of powdered Dry Ice and the mixture was cooled in additional Dry Ice. After a few drops of boron trifluoride etherate had been added, the mixture was stored for 3 days at -20° and then for 2 days at 5° before it was allowed to warm to room temperature. The viscous mixture was dissolved in benzene containing a trace of N-phenyl- β -naphthylamine and the resulting solution was poured into cold methanol. The light-tan precipitate was removed by filtration, washed thoroughly with methanol, and dried under partial vacuum to yield 1.21 g. (57%) of crude poly-1,2-dimethylenedecalin (XIII). Fractional precipitation of this crude polymer from a benzene solution into a large excess of methanol gave 0.22 g. of a white, powdery polymer, softening point 102–112°. A viscosity determination in a benzene solution with a modified Ubbelohde viscometer at 30° indicated an intrinsic viscosity of 0.03.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Hydrophenanthrenecarboxylic Esters¹

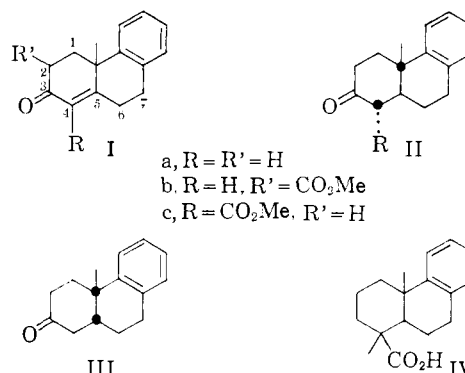
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A synthetic route from hydrophenanthrones to the resin acids is developed. A rate-controlled formation of enolate ion of unsymmetrical ketones is described. The position of keto-enol equilibrium of cyclic β -ketoesters is discussed.

The ready availability of hydrophenanthrones Ia, IIa and III by standard synthesis or by any of three recently developed synthetic routes² and the easy access to hydrophenanthrenecarboxylic acids of various stereochemical configurations (IV)³ made a conversion of any of the ketones into the acids most attractive. Since one of the acids of structure IV has been transformed into a naturally occurring resin acid already and similar partial syntheses of other resin acids seemed assured, a transformation of I-III into IV appeared to lead the way to a stereospecific total synthesis of the most abundant diterpenic natural products. The present communication describes attempts in this direction, and reveals new data on two important points in organic synthesis, the site of alkylation of unsymmetrical ketones and the position of keto-enol equilibrium of cyclic β -ketoesters.

At first a base-catalyzed carbonation of the tricyclic ketone Ia came under consideration. While prior to our study the only alkylations of systems comparable to Ia had led to substitution at C-4,⁴



our desired position, it was decided to carry out our reaction under conditions of irreversible enolate anion formation so as to learn more about the mechanistic detail of this first step of the alkylation process. The carbonation therefore was conducted by the interaction of Ia with triphenylmethylsodium, followed by the introduction of dry CO₂ gas and, finally, by reaction with diazomethane.⁵ Whereas enolates V and/or VI might lead to three esters, *i.e.*, carbomethoxylation at C-2, 4 and 6, the reaction gave only two crystalline products.

Ives and R. B. Kelley, *ibid.*, **76**, 2853 (1954); for a complete description of this work *cf.* *J. Chem. Soc.*, 1131 (1957); (b) G. Stork and J. W. Schulenberg, *THIS JOURNAL*, **78**, 250 (1956).

(5) *Cf.* H. M. E. Cardwell, J. W. Cornforth, S. R. Duff, H. Halterman and R. Robinson, *J. Chem. Soc.*, 373 (1953). A similar carbonation had been carried out successfully on cholestenone by T. E. Stevens in this Laboratory.

(1) This work was presented at the 16th International Congress of Pure and Applied Chemistry, Paris, France, July 18–24, 1957, and constitutes an excerpt from the Ph.D. dissertation of B. G. J., Iowa State College, June, 1957.

(2) (a) and (b) E. Wenkert and T. E. Stevens, *THIS JOURNAL*, **78**, 2318, 5627 (1956); (c) E. Wenkert and R. D. Youssefyeh, unpublished data, *cf.* Ph.D. dissertation of R. D. Youssefyeh, Iowa State University, June, 1959.

(3) (a) and (b) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211, 217 (1958); (c) E. Wenkert and J. W. Chamberlin, *ibid.*, **81**, 488 (1959).

(4) (a) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J.