Synthesis of Resin Acid Intermediates. 4β,9β-Dimethyl-4α-carboxy-8β-hydroxy-*trans*-decalin from 4-Carboethoxy-9-methyl-$\Delta^{4,10}$-octalin-3,8-dione

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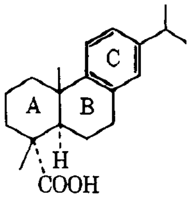
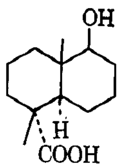
4β,9β-Dimethyl-4α-carboxy-8β-hydroxy-*trans*-decalin (II), an intermediate for the synthesis of diterpene resin acids and related compounds, has been prepared from 4-carboethoxy-9-methyl-$\Delta^{4,10}$-octalin-3,8-dione (III) in 13% over-all yield.

Total synthesis of the hydrophenanthrenoid diterpene resin acids, *e.g.*, dehydroabietic acid (I), has been accomplished previously by addition of ring A to a preformed B–C bicyclic unit[2] or by ring closure of a suitable A–C system.[3] Our efforts have been directed toward synthesis of an A–B bicyclic intermediate suitable for elaboration to a variety of natural substances.[4] This paper describes one preparation of such an intermediate, 4β,9β-dimethyl-4α-carboxy-8β-hydroxy-*trans*-decalin (II).[5]



I

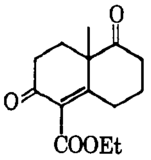


II

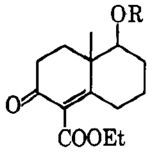
4-Carboethoxy-9-methyl-$\Delta^{4,10}$-octalin-3,8-dione (III)[6] was an attractive starting material for synthesis of II, since it already contained the carboxyl portion of the difficultly accessible C-4 *gem*-methyl carboxyl grouping found in the resin acids,[7] as well as the carbonyl group at C-8 for eventual use in elaboration of the C ring. Selective reduction of this unconjugated ketone with sodium borohydride[8] afforded the alcohol IV, m.p. 101–102.5°, in 77% yield. Reduction of III with excess sodium borohydride, followed by oxidation of the resulting product, presumably V, with manganese dioxide, also produced IV, but in lower yield.

Introduction of the C-4 methyl group was attempted by treatment of the benzoate VI with potassium *t*-butoxide and methyl iodide, but no pure methylation product was isolated.[9] Accordingly, attention was turned to prior reduction of the $\Delta^{4,10}$ double bond of IV. Since a *trans* ring juncture was desired, chemical reduction was investigated first. Brief treatment of IV with lithium in ammonia afforded as the only crystalline product 10% of a substance, m.p. 83–84°, which was subsequently shown to be the desired VII. One attempt to reduce IV with sodium amalgam[10] failed and one attempt with aluminum amalgam[11] to reduce the corresponding acetate VIII, m.p. 83–84°, likewise afforded only recovered starting material.

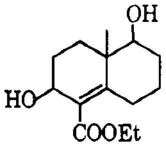
Catalytic hydrogenation of IV afforded a mixture of VII and the oily *cis*-fused IX. The *trans*-fused β-keto ester was, as expected,[9] completely nonenolic, in contrast to IX which gave a strong positive ferric chloride test and exhibited strong ultraviolet absorption at 258 mμ. Similarly, hydrogenation of acetate VIII afforded a mixture of the *trans* dihydro compound X, m.p. 100–101° (nonenolic), and the *cis*-fused XI, m.p. 55–56°, [$\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 10,000)]. The assignment of stereochemistry to the two pairs of hydrogenation products was confirmed by conversion of X, by hydrolysis and decarboxylation, to the known 8β-hydroxy-9β-methyl-*trans*-decalone-3 (XII), m.p. 70–71°, which was compared with an authentic sample.[12] Evidence consistent with assignment of the α configuration to the 4-carboethoxy group of VII and X was ob-



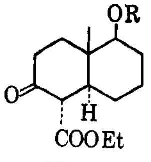
III



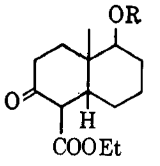
IV, R = H
VI, R = Bz
VIII, R = Ac



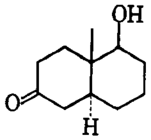
V



VII, R = H
X, R = Ac



IX, R = H
XI, R = Ac



XII

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[1] Goodyear Foundation Fellow, 1963–1964.

[2] See, *e.g.*, (a) G. Stork and J. W. Schulenberg, *J. Am. Chem. Soc.*, **78**, 250 (1956); **84**, 284 (1962); (b) E. Wenkert, *et al.*, *ibid.*, **86**, 2038 (1964).

[3] See, *e.g.*, (a) R. E. Ireland and R. C. Kierstead, *J. Org. Chem.*, **27**, 703 (1962); (b) F. E. King, T. J. King, and J. G. Topliss, *Chem. Ind.* (London), 113 (1956); (c) U. R. Ghatak, D. K. Datta, and S. C. Ray, *J. Am. Chem. Soc.*, **82**, 1728 (1960).

[4] See T. A. Spencer, M. A. Schwartz, and K. B. Sharpless, *J. Org. Chem.*, **29**, 782 (1964), for a previous report of some of these investigations; see C. T. Mathew, G. Sen Gupta, and P. C. Dutta, *Proc. Chem. Soc.*, 336 (1964), and C. T. Mathew and P. C. Dutta, *ibid.*, 135 (1963), for synthesis of a stereoisomer of II.

[5] For a preliminary report of part of this work see T. A. Spencer, T. D. Weaver, M. A. Schwartz, W. J. Greco, Jr., and J. L. Smith, *Chem. Ind.* (London), 577 (1964).

[6] I. N. Nazarov and S. I. Zav'yalov, *J. Gen. Chem. USSR*, **25**, 477 (1955).

[7] See ref. 2b for similar use of a substance prepared *via* a carboalkoxymethyl vinyl ketone as a source of ring A of resin acids.

[8] C. B. C. Boyce and J. S. Whitehurst, *J. Chem. Soc.*, 2680 (1960).

[9] E. Wenkert and B. G. Jackson [*J. Am. Chem. Soc.*, **81**, 5601 (1959)] initially reported difficulty in methylating a similar α,β-unsaturated β'-keto ester. Accordingly we did not pursue our attempts to methylate VI as diligently as Wenkert's subsequent report of success[2b] would have led us to do. Since the podocarpic acid stereochemistry was obtained in Wenkert's case,[2b] reinvestigation of methylation of VI (or analog) might prove to be a route to bicyclic intermediates with axial carboxyl, as opposed to the obtainment of abietic acid stereochemistry reported in this paper.

[10] A. A. L. Challis and G. R. Clemo, *J. Chem. Soc.*, 1692 (1947).

[11] U. Ghatak, N. N. Saha, and P. C. Dutta, *J. Am. Chem. Soc.*, **79**, 4487 (1957).

[12] A. J. Birch, E. Pride, and H. Smith, *J. Chem. Soc.*, 4688 (1958).

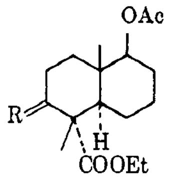
tained by recovery of VII from its reaction with sodium ethoxide in ethanol, which would be expected to effect epimerization of a hindered 4β-carboethoxyl group.

It was obviously desirable to obtain as high a *trans-cis* ratio as possible in the catalytic hydrogenation of IV or VIII. Accordingly, various conditions were tried in the hope of maximizing the yield of VII or X. The *trans-cis* ratio was virtually unaffected, however, by changes in the pH of the reducing medium or the concentration of palladium-on-carbon catalyst; approximately a 1:1 mixture was obtained in all cases. These results contrast with those of Wenkert[9] and Augustine,[13] who found that the stereochemistry of hydrogenation of similar systems showed considerable dependence on such variables.

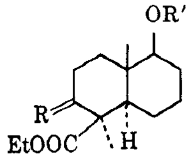
The yield of pure VII from IV or X from VIII was consistently about 40%. In preparative runs it proved most convenient to hydrogenate IV, acetylate the crude reduction product, and separate X from XI in 40% over-all yield.

Introduction of the C-4 methyl group was accomplished by treatment of X with sodium hydride in benzene, followed by methyl iodide.[14] Only a very small amount of one crystalline methylation product, m.p. 80–81°, was obtained. This substance is presumably the predominant methylation isomer[15] XIII (which gives rise to II) rather than XIV, but this has not been established experimentally.

The C-3 carbonyl group was reduced by treatment of the crude methylation mixture with ethanedithiol and boron trifluoride etherate, followed by Raney nickel desulfurization of the crude thioketal mixture. The product from this sequence had spectral properties consistent with the desired XV, or XVI. One attempted reduction by the Clemmensen method[16] gave unidentified material exhibiting different infrared absorption.



XIII, R = O
XV, R = H_2



XIV, R = O; R′ = Ac
XVI, R = H_2; R′ = Ac
XVII, R = H_2; R′ = H

The well-known[17] resistance to hydrolysis of axial carboxylates of the podocarpic acid type, such as XVI, allowed facile separation of the C-4 stereoisomers. Ordinary saponification conditions afforded an acidic product that was almost entirely hydroxy acid II. Pure II, m.p. 216–218°, could thus be obtained in 42% over-all yield from acetate X. Its methyl ester melted at 95–96°.

The neutral material from the hydrolysis was chromatographed to afford an oil (*ca.* 10%) which was homogeneous by v.p.c. analysis and had infrared and n.m.r.[18] spectra consistent with the axial ethyl ester XVII. Evidence confirming the assignment of stereochemistry to II will be delineated in a subsequent publication describing another synthesis of this substance.[5] The utility of II as an intermediate for resin acid synthesis has been demonstrated by its conversion to methyl ±-dehydrodeisopropylabietate.[5]

Experimental Section[19]

4-Carboethoxy-9-methyl-$\Delta^{4,10}$-octalin-3,8-dione (III).—β-Ethoxypropionyl chloride was prepared from commercially available β-ethoxypropionitrile by hydrolysis with concentrated hydrochloric acid to β-ethoxypropionic acid (63%), followed by conversion to the acyl chloride with phosphorus trichloride (75%). Carboethoxymethyl vinyl ketone was prepared from β-ethoxypropionyl chloride by the method of Nazarov,[20] in comparable yield. The condensation of carboethoxymethyl vinyl ketone with methyldihydroresorcinol was conducted as prescribed,[6] except that isolation of III by vacuum distillation proved troublesome; unreacted methyldihydroresorcinol usually contaminated the product. Elution chromatography on acid-washed alumina with 3:1 ether–hexane afforded III as white crystals: m.p. 76–78°; $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (ε 11,000); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.79, 5.93, and 6.14 μ; $\tau_{\max}^{\mathrm{CS_2}}$ 8.70 (center of triplet, CH_3CH_2O), 8.52 (singlet, $CH_3C<$), and 5.73 p.p.m. (quartet, CH_3CH_2O). The yield of III, m.p. 58–75°, obtained by this method was 52%. Nazarov[6] reports a 73% yield of a distilled oil which partially solidified to afford crystals with m.p. 65–66°. A solid, m.p. 60–65°, was isolated in our laboratory from distilled III, and it had a solution infrared spectrum identical with our 76–78° material.

4-Carboethoxy-8β-hydroxy-9β-methyl-$\Delta^{4,10}$-octalone-3 (IV).—According to the procedure of Boyce and Whitehurst,[8] a stirred and ice-cooled solution of 42.5 g. (0.170 mole) of diketone III, m.p. 75–79°, in 750 ml. of absolute ethanol was treated with a solution of 1.59 g. (0.042 mole) of purified[21] sodium borohydride in 200 ml. of absolute ethanol. Dropwise addition of the sodium borohydride solution was completed in 30 min. and the resulting wine-red solution was allowed to stir at 0° for an additional 15 min. One liter of water was added, and the solution was acidified with 1 *M* hydrochloric acid, causing the color to change to yellow. This solution was extracted with two 1-l. portions of chloroform, and the aqueous layer was saturated with sodium chloride and again extracted with 1 l. of chloroform. The chloroform extracts were stripped of solvent, yielding a residue of 44 g. of brown oil which crystallized to afford 33 g. (77%), of IV, m.p. 98–101°. Recrystallization from acetone–hexane gave 28.6 g. (67%) of IV, m.p. 100–102°. The analytical sample had m.p. 101.0–102.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ 244 mμ (ε 12,000); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.91, 5.78, 5.96, and 6.17 μ; $\tau_{\max}^{\mathrm{CS_2}}$ 8.87 (singlet, $CH_3C<$), 8.79 (center of triplet, CH_3CH_2O), and 5.94 p.p.m. (center of quartet, CH_3CH_2O).

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.83; H, 8.04.

4-Carboethoxy-8β-benzoyloxy-9β-methyl-$\Delta^{4,10}$-octalone-3 (VI) was prepared from IV with benzoyl chloride in pyridine. Although this substance was nicely crystalline, its melting point was always very broad, typically 122–161°; $\lambda_{\max}^{\mathrm{EtOH}}$ 231 mμ (ε 25,000); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.76–5.80, 5.96, and 6.15 μ; $\tau_{\max}^{\mathrm{CS_2}}$ 8.77 (center of triplet, CH_3CH_2O), 8.60 (singlet, $CH_3C<$), 5.90 (center of

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(13) R. L. Augustine, *J. Org. Chem.*, **28**, 152 (1963); R. L. Augustine and A. D. Brown, *ibid.*, **25**, 802 (1960); R. L. Augustine, *ibid.*, **23**, 1853 (1958).

(14) Methylation of these nonenolizable β-keto esters has proved capricious in our hands. The optimum conditions will be described in a subsequent publication reporting another synthesis of II.[4]

(15) Stereoelectronic control to give predominantly the axially methylated product has also been observed in a similar β-keto ester system by E. Wenkert and A. Tahara [*J. Am. Chem. Soc.*, **82**, 3229 (1960)]; *cf.* ref. 2b for a discussion of the stereochemistry of alkylation reactions of this and related systems.

(16) Ref. 2b describes successful use of the Clemmensen method for reduction of similar ring A ketones. Possibly the reaction failed in the case of XV + XVI because the strongly acidic conditions permitted strain-relieving migration of the angular methyl to a positive center generated at the site of the hydroxyl group.

(17) See, *e.g.*, C. L. Graham, F. J. McQuillin, and P. L. Simpson, *Proc. Chem. Soc.*, 136 (1963).

(18) We thank Professor W. L. Meyer of the University of Arkansas for determining this n.m.r. spectrum.

(19) Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken either in an open capillary or on a micro hot stage; those of analytical samples are corrected. Boiling points are uncorrected. Ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 spectrometer. Infrared spectra were determined on a Perkin-Elmer Model 21 spectrometer.

(20) I. N. Nazarov and S. I. Zav'yalov, *J. Gen. Chem. USSR*, **23**, 1793 (1953).

(21) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.* **77**, 6209 (1955).

quartet, $\mathrm{CH_3C}H_2\mathrm{O}$), and 1.9–2.7 p.p.m. (multiplets, aromatic hydrogens).

Anal. Calcd. for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.74; H, 6.88.

4-Carboethoxy-8β-acetoxy-9β-methyl-$\Delta^{4,10}$-octalone-3 (**VIII**) was prepared from IV with acetic anhydride in pyridine in 90% yield and had m.p. 83–84°; $\lambda_{\max}^{\mathrm{EtOH}}$ 240 mμ (ε 11,500); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.75, 5.95, and 6.14 μ; $\tau_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 8.70 (center of triplet, $\mathrm{C}H_3\mathrm{CH_2O}$), 8.68 (singlet, $\mathrm{C}H_3\mathrm{C}<$), 7.93 (singlet $\mathrm{C}H_3\mathrm{COO}$), and 5.73 p.p.m. (center of quartet, $\mathrm{CH_3C}H_2\mathrm{O}$).

Anal. Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.08; H, 7.32.

Hydrogenation of Alcohol IV.—Catalytic reduction of IV was run in acidic, neutral, and basic media with amounts of 10% palladium on carbon varying from 10 to 50% of the weight of IV. A typical procedure was the following, adapted from a method of Wenkert.[9] To a solution of 1.70 g. (0.0067 mole) of IV, m.p. 102–104°, in 500 ml. of ethyl acetate, was added 0.80 g. of 10% palladium-on-carbon catalyst (Sargent) and a mixture of 2.5 ml. of concentrated sulfuric acid and 1 ml. of water. Hydrogen was bubbled through this magnetically stirred mixture for 30 min. The mixture was then filtered, and the clear filtrate was washed with 10% sodium bicarbonate solution until the aqueous washings were basic. The organic layer was washed with saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to afford 1.35 g. of oil which was chromatographed on acid-washed alumina. Elution with 1:1 ether–hexane afforded 0.585 g. (34%) of VII, m.p. 60–75°. Recrystallization from hexane gave 0.480 g. (28%), m.p. 78–82°, and an analytical sample: m.p. 83–84°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.79, 5.73, and 5.83 μ; $\tau_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 8.95 (singlet, $\mathrm{C}H_3\mathrm{C}<$), 8.74 (center of triplet, $\mathrm{C}H_3\mathrm{CH_2O}$), and 5.79 p.p.m. (center of quartet, $\mathrm{CH_3C}H_2\mathrm{O}$).

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.18; H, 8.74.

The residual oil had $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 7000), $\lambda_{\max}^{\mathrm{film}}$ 2.80, 5.70, 5.80, 6.10, and 6.20 μ, and was presumably largely the enolic **4-carboethoxy-8β-hydroxy-9β-methyl-*cis*-decalone-3** (**IX**). The strength of ultraviolet absorption at 258 mμ of the crude reduction products from IV under varying conditions was used to estimate the relative amounts of VII and IX formed. Although completely reproducible values were not, for unknown reasons, obtained, it was evident that variations in reaction conditions did not alter the approximately 1:1 product ratio to any great extent. Isolation of crystalline *trans* product was facilitated by acetylation of the crude reduction product from IV and separation of acetates X and XI (vide infra).

Hydrogenation of Acetate VIII.—A 250-ml. erlenmeyer flask was charged with 3.325 g. (0.0113 mole) of acetate VIII, m.p. 82.5–84.0°, 150 ml. of ethyl acetate, 1.5 g. of 10% palladium on carbon, and a mixture of 2 ml. of concentrated sulfuric acid and 0.5 ml. of water.[9] While this mixture was stirred magnetically, hydrogen was bubbled through it from a gas-dispersion tube for 30 min. The mixture was filtered by suction and the filtrate was washed with 10% sodium bicarbonate solution until the washes were basic, and then was washed with saturated sodium chloride solution, dried over sodium sulfate, and evaporated to yield 3.387 g. of colorless oil, $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 5000). Upon standing, the oil crystallized to afford 1.414 g. of oily solid which was recrystallized from hexane to give 0.919 g. of **4α-carboethoxy-8β-acetoxy-9β-methyl-*trans*-decalone-3** (**X**), m.p. 99–102.5°.

All material except this recrystallized product was chromatographed on 80 g. of acid-washed alumina. Elution with 1:4 ether–hexane gave 1.460 g. of oil which crystallized on standing in the freezer. Characterization of this material is described below. Elution with ether gave 0.541 g. of a solid which yielded, upon recrystallization from hexane, 0.397 g. of X, m.p. 98–102°. The total yield of X was 1.316 g. (39%). In subsequent runs X could be isolated consistently in *ca.* 40% yield by direct crystallization without chromatography. The analytical sample of X was prepared by recrystallization from hexane and had m.p. 100–101°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.72–5.81 μ; $\tau_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 8.92 (singlet, $\mathrm{C}H_3\mathrm{C}<$), 8.81 (center of triplet, $\mathrm{C}H_3\mathrm{CH_2O}$), 8.08 (singlet, $\mathrm{C}H_3\mathrm{COO}$), and 5.98 p.p.m. (center of quartet, $\mathrm{CH_3C}H_2\mathrm{O}$); ferric chloride test, negative, even on long standing.

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.96; H, 8.23.

The material eluted with 1:4 ether–hexane was recrystallized from hexane in the freezer to give 1.362 g. (41%) of **4-carboethoxy-8β-acetoxy-9β-methyl-*cis*-decalone-3** (**XI**), m.p. 53–55.5°. The analytical sample, obtained by recrystallization in large clusters from hexane, had m.p. 55.0–56.0; $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ε 10,300); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.79, 6.05, and 6.19 μ; $\tau_{\mathrm{TMS}}^{\mathrm{CS_2}}$ 9.16 (singlet, $\mathrm{C}H_3\mathrm{C}<$), 8.70 (center of triplet, $\mathrm{C}H_3\mathrm{CH_2O}$), 7.96 (singlet, $\mathrm{C}H_3\mathrm{COO}$), and 5.80 p.p.m. (center of quartet, $\mathrm{CH_3C}H_2\mathrm{O}$); ferric chloride test, strongly positive immediately.

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.84; H, 8.16. Found: C, 64.96; H, 8.11.

From the ε for pure XI and for the crude reaction product the ratio of *trans–cis* hydrogenation can be seen to be close to 1:1. As in the case of the reduction of IV, this ratio was not appreciably affected by changes in pH or catalyst concentration, and there is no real advantage to the use of an acidic medium.

Lithium–Ammonia Reduction of IV.—To a solution of 70 mg. (0.01 mole) of lithium wire in 30 ml. of liquid ammonia was added a solution of 494 mg. (0.00184 mole) of IV in 30 ml. of anhydrous ether. After 10 min., 1.0 g. of ammonium chloride was added, the ammonia was allowed to evaporate, and the mixture was partitioned between water and ether. The dried organic layers yielded 358 mg. of oil which was chromatographed on acid-washed alumina to afford as the only crystalline product 52 mg. of crude VII. Recrystallization afforded 27 mg. of VII, m.p. 83.5–86°.

4β,9β-Dimethyl-4α-carboxy-8β-hydroxy-*trans*-decalin (**II**).—Methylation of acetoxy β-keto ester X was accomplished[14] by a procedure like that of Banerjee and Mahapatra.[22] To a cooled solution of 3.00 g. (0.010 mole) of X in 15 ml. of dried benzene, under nitrogen, was added 0.256 g. (0.011 mole) of sodium hydride. The mixture was stirred overnight (until after hydrogen evolution ceased). To the resulting white suspension was added 2.0 ml. of redistilled methyl iodide, and the mixture was refluxed for 6 hr., with 2.0 ml. more of methyl iodide being added every 2 hr. The mixture was then poured into 50 ml. of water, the benzene layer was separated, and the water layer was extracted with three 30-ml. portions of ether. The combined organic layers were washed with 10 ml. of saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to yield 2.64 g. of clear oil.

Chromatography on acid-washed alumina of one methylation product afforded (with 1:4 ether–hexane) a small amount of crystalline material, which was recrystallized from ether–hexane to give an analytical sample of, presumably, **4β,9β-dimethyl-4α-carboethoxy-8β-acetoxy-*trans*-decalone-3** (**XIII**), m.p. 80–81°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.71–5.82 μ.

Anal. Calcd. for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.56; H, 8.58.

The separation of XIII was not efficient and the entire methylation product was customarily carried through the steps next described to yield II.

To a solution of the 2.64 g. of methylation product in 10 ml. of ethanedithiol was added 1.8 ml. of freshly distilled boron trifluoride etherate, according to the procedure of Fieser[23] for thioketal preparation. The clear mixture was allowed to stand overnight at room temperature and then was diluted with 50 ml. of ether. The ethereal solution was extracted with three 10-ml. portions of 1 *M* sodium hydroxide solution, washed with saturated sodium chloride solution, dried over magnesium sulfate, evaporated, and dried *in vacuo* to give 2.96 g. of an amorphous solid.

A solution of this 2.96 g. of crude thioketal in 250 ml. of absolute ethanol was added to 30 g. (50 ml. of settled material under ethanol) of W-4 Raney nickel.[24] The mixture was refluxed and stirred overnight, then cooled, and filtered. The filtrate was evaporated under reduced pressure to yield 2.17 g. (94%) of light yellow oil, $\lambda_{\max}$ 5.78 μ.

To this material was added 25 ml. of 6 *N* sodium hydroxide solution and 5 ml. of 95% ethanol, and the resulting mixture was refluxed for 12 hr., cooled, and extracted with ether. The ether layers were dried and evaporated to yield 0.828 g. of oil. The aqueous layer was poured slowly into a well-stirred ice-cold solution of 6 *N* hydrochloric acid, yielding 0.807 g. of white precipitate, m.p. 205–217°. Extraction of the acidic aqueous filtrate with ether gave 0.415 g. of oily crystals smelling strongly of acetic acid.

The neutral oil (0.828 g.) was subjected to 24 hr. more of the same hydrolysis conditions. Similar work-up afforded 0.587

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[22] D. K. Banerjee and S. N. Mahapatra, *Tetrahedron*, **11**, 234 (1960).

[23] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[24] A. A. Pavlic and H. Adkins, *ibid.*, **68**, 1471 (1946).

g. of neutral material and 0.188 g. of acidic material. From the combined acidic products there was obtained, by recrystallization from acetone–hexane, a total of 0.952 g. (42% from X) of II, m.p. 216–218°, $\lambda_{\max}^{KBr}$ 3.0 and 5.95 μ.

Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80; neut. equiv., 226. Found: C, 69.06; H, 9.87; neut. equiv., 225.

Treatment of II with ethereal diazomethane afforded **4β,9β-dimethyl-4α-carbomethoxy-8β-hydroxy-*trans*-decalin,** m.p. 95–96° (from hexane), $\lambda_{\max}^{CHCl_3}$ 2.8–2.9 and 5.80 μ.

Anal. Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06; Found: C, 70.08; H, 10.12.

The oily neutral material from the hydrolysis was subjected to a further 6 days of reflux with sodium hydroxide solution. The neutral material which remained after this hydrolysis was chromatographed on acid-washed alumina to afford an oil (*ca.* 10% from acetate X) which gave one broad peak on v.p.c. analysis (250°, column packing unrecorded) and exhibited $\lambda_{\max}^{film}$ 2.8–2.9 and 5.79 (shoulder at 5.82) μ; $\tau_{\max}^{CCl_4}$ 9.32 (singlet, CH_3-C<), 8.87 (singlet, $CH_3CCOOCH_2CH_3$), 8.74 (center of triplet, CH_3CH_2O), and 5.92 p.p.m. (center of quartet, CH_3CH_2O), consistent with its being **4α,9β-dimethyl-4β-carboethoxy-8β-hydroxy-*trans*-decalin (XVII)**.

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Electron-Transfer Polymers. XXVII. Solvent Effects on the Absorption Spectra of Partially Oxidized Oligomeric Hydroquinones

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The charge-transfer bands that appear when ethylhydroquinone, 1,3-bis(2,5-dihydroxyphenyl)propane (I), 1,5-bis(2,5-dihydroxyphenyl)pentane (II), and 1,3,5-tris(2,5-dihydroxyphenyl)pentane (III) are partially oxidized were investigated. Ethylquinhydrone shows two peaks at 360 and 450 mμ. Neither obeys the Beer–Lambert law, and both must be due to intermolecular quinhydrone. The three oligomers show absorption centering at about 440 mμ, due to intermolecular quinhydrone. In addition they show shorter wave length absorptions centering at about 370 mμ for I, 330 mμ for II, and 330 and 370 mμ for III. These obey the Beer–Lambert relation and are intramolecular. In the case of I, the position of the band also shifts from *ca.* 370 to *ca.* 350 mμ in going from 1 to 90% acetic acid. The intensities of these shorter wave length bands are sensitive to solvent composition. In highly aqueous solvent the intensity is markedly higher than in more highly organic mixtures. The increase in intensity, bespeaking an increase in complexation, increases proportionately with the value of the surface tension of the pure solvent. This is explained, following the hypothesis of Sinanoğlu and Abdulnur for the analogous behavior of the double helix of DNA, as being due to the loss in solvent-cage surface area upon complex formation. A driving force of complex formation, in this view, then must be directly correlated with the change in free energy, which is proportional to the surface tension of the solvent multiplied by the change in solvent-cage surface area. Reasonable support for this hypothesis was found.

When hydroquinone, ethylhydroquinone, and the three oligomeric hydroquinones described in a previous paper,[1] namely, 1,3-bis(2,5-dihydroxyphenyl)propane (I), 1,5-bis(2,5-dihydroxyphenyl)pentane (II), and 1,3,5-tris(2,5-dihydroxyphenyl)pentane (III) are oxidized in 90% acetic acid, the solutions, initially colorless, gradually become yellow as the fraction of solute converted to quinone increases. When, however, the compounds are oxidized in dilute solution in 1% aqueous acetic acid, the solutions of the 1,3-bis and of the 1,3,5-tris compounds take on a deep red coloration with the first addition of oxidizing agent. The color reaches maximum intensity near the midpoint of the oxidation, then gradually, as quinone accumulates, gives way to the final clear yellow quinone color. This color production is reminiscent of the behavior observed when polyvinylhydroquinone is oxidatively titrated,[2-4] and also of the weaker dark color observed in relatively concentrated solutions of quinhydrone.[5] Dilute hydroquinone solutions show no visible quinhydrone color at the midpoint of an oxidative titration. It has been shown that the molar extinction coefficient of the quinhydrone charge-transfer complex does not vary appreciably from one solvent to another.[6] Thus, the conclusion must be that the 1,3-propylene-linked oligomers possess some property which promotes the donor–acceptor (charge-transfer) interaction that appears in a highly aqueous solvent.

This matter has been investigated. The absorption spectra of partially oxidized ethylhydroquinone and the three oligomeric hydroquinones have been examined in several solvents and mixtures. The spectrum of the ethylquinhydrone complex (not previously reported) was examined over the region 220 to 600 mμ in 50% aqueous tetrahydrofuran by volume. Solutions of ethylhydroquinone and ethyl-*p*-benzoquinone were mixed, the component absorptions were subtracted, and two new overlapping yet distinct maxima were found at 360 and 450 mμ. Both were of approximately the same intensity, though the longer wave length band was considerably broader. They were affected similarly by changes in the concentration of either component, and neither of them obeyed the Beer–Lambert law. An attempt was made to determine the association constant and the molar extinction coefficient from each peak, but without success.

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