The red fractions, eluted with pentane–ether (1:1 to 1:3), contained unchanged starting material as evidenced by the main ultraviolet maxima at 387–389 mμ. Subsequently red fractions were eluted with ether–ethyl acetate (49:1 to 19:1) which all showed a maximum in the 414–417 mμ region, due to [30]annulene (spectroscopic yield, 18 mg., 3.9%). These fractions were combined, evaporated and the residue was crystallized from ether. The resulting [30]annulene (VII or isomer) (9.5 mg., 2.1%) was obtained as a dark brown-red crystalline powder, which decomposed on attempted m.p. determination. The ultraviolet spectrum is given in Table I and Fig. 3.[34] The infrared spectrum (Fig. 2)[33] showed bands at 3.31(m), 6.61(w), 7.77(w), 10.00(s), 10.51(w) and 10.67(w) μ. A benzene solution was dark red in concentrated solution and orange-red in dilute solution.

Anal. Calcd. for $C_{30}H_{30}$: C, 92.26; H, 7.74. Found: C, 88.82, 88.52; H, 7.36, 7.52 (C:H ratio = 30:29.63, 30:30.38).

[30]Annulene with essentially identical physical properties was obtained (in *ca.* 6% spectroscopic yield) when the crystalline pentadehydro-[30]annulene isomer[2] was subjected to partial hydrogenation and subsequent chromatography as described above.

Full hydrogenation of [30]annulene in dioxane over platinum,[41] followed by crystallization from methanol, yielded cyclotriacontane, m.p. 56–57°, undepressed on admixture with an authentic sample (m.p. 57–58°).

Stability Experiments with [30]Annulene.—A weighed sample of [30]annulene was allowed to stand at room temperature in diffuse day-light for 4 hr. and then crushed and triturated with warm benzene. Ultraviolet examination showed that less than 5% of starting material remained.

A solution of [30]annulene in chloroform (*ca.* 0.68 mg./l.) which initially showed λ_{max} 429 mμ (E 0.250) on being allowed to stand without protection from diffuse day-light after 24 hr. showed λ_{max} 423 mμ (E 0.145) (at least 42% destruction) and after 48 hr. the maximum had disappeared (λ 423 mμ, E 0.088).[47] Similarly a solution of [30]annulene in dioxane (*ca.* 2 mg./l.) which initially showed λ_{max} 428 mμ (E 0.740) after 24 hr. in day-light exhibited λ_{max} 413 mμ (E 0.168), indicating at least 77% decomposition.

A benzene solution of [30]annulene (*ca.* 1.8 mg./l.) on being boiled with a trace of iodine was 45% destroyed after 5 minutes and completely destroyed after 1.5 hr.

Acknowledgments.—We are indebted to Dr. Y. Gaoni for valuable help in connection with the synthesis of [30]annulene, and to Dr. J. Bregman for very kindly allowing us to quote the preliminary results of the X-ray work on [18]annulene.

(47) The instability in chloroform was first noticed when ether–chloroform was used to elute [30]annulene from the chromatography column, whereby extensive decomposition resulted.

[CONTRIBUTION FROM THE CHANDLER LABORATORIES, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

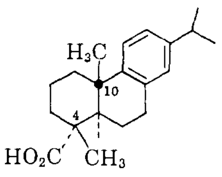
The Total Synthesis of *dl*-Dehydroabietic Acid[1]

BY GILBERT STORK AND JOHN W. SCHULENBERG

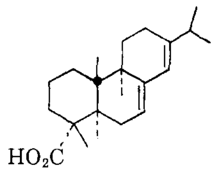
RECEIVED AUGUST 14, 1961

The total synthesis of *dl*-dehydroabietic acid is described.

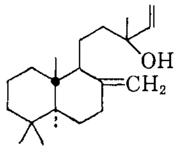
Dehydroabietic acid (I) has been shown by Harris[2] to constitute about 4% of the total acidic material obtained from the oleoresin of *Pinus palustris*. It is, however, because of its relationship to abietic acid (II), the major diterpene acid which is obtainable from rosin, that dehydroabietic acid derives its main interest. It is, in fact, from abietic acid that pure dehydroabietic acid was first obtained by Fieser and Campbell.[3] The extensive structural investigations which established the correct structure I of dehydroabietic acid have been reviewed in detail.[4] It is also known that the stereochemistry, both relative and absolute, is that shown in structure I. This last point was established by showing that dehydroabietic and abietic acids have the same relative and absolute stereochemistry of the A:B ring junction as manoöl (III)[5] which has in turn been correlated with lanosterol[6] (IV) and therefore with cholesterol.[7] The relative orientation of the methyl and the carboxyl groups at C_4 follows from the lack of optical activity of the tricarboxylic acid V obtained by nitric acid oxidation of abietic acid.[8]



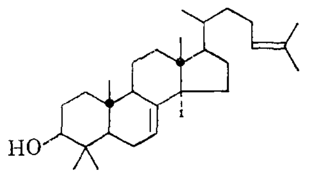
I



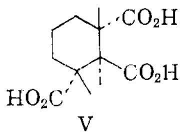
II



III



IV



V

We will describe in this paper the successful total synthesis of *dl*-dehydroabietic acid, but before we do this mention will be made of a few previous attempts.

Haworth and Barker[9] were the first to attempt the synthesis of dehydroabietic acid by a route

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(1) A preliminary report of this synthesis has been published, G. Stork and John W. Schulenberg, *J. Am. Chem. Soc.*, **78**, 250 (1956).

(2) G. C. Harris, *ibid.*, **70**, 3671 (1948).

(3) L. F. Fieser and W. P. Campbell, *ibid.*, **60**, 159 (1938).

(4) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Third Edition, Reinhold Publishing Corp., New York, N. Y., 1949; J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, 1951.

(5) O. Jeger, O. Durst and G. Büchi, *Helv. Chim. Acta*, **30**, 1853 (1947).

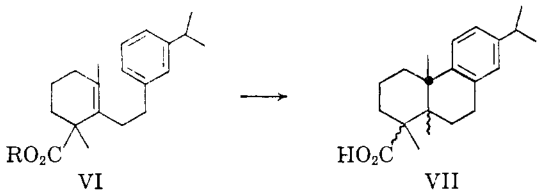
(6) E. Kyburz, B. Riniker, H. R. Schenk, H. H. Heusser and O. Jeger, *ibid.*, **36**, 1891 (1953).

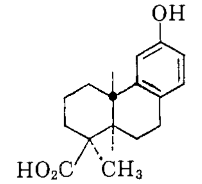
(7) R. B. Woodward, A. H. Patchett, D. H. R. Barton, D. A. Ives and R. B. Kelly, *J. Am. Chem. Soc.*, **76**, 2852 (1954).

(8) L. Ruzicka and L. Sternbach, *Helv. Chim. Acta*, **21**, 565 (1938).

(9) R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

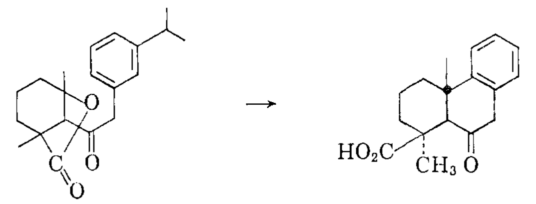
which included as its crucial step the transformation VI to VII. The substance obtained probably


VI VII

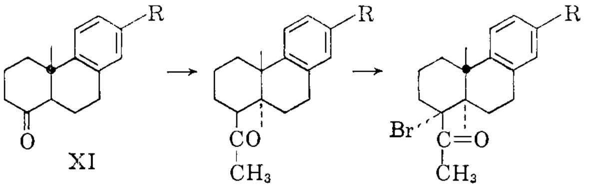

VIII

had the constitution of dehydroabietic acid, but the difference in the melting points of the acid and its methyl ester from those now known for *dl*-I and its methyl ester show that the substance was clearly an isomer, possibly related to podocarpic acid (VIII).[10]

Using a related synthetic scheme, Parham and Wheeler[11,12] cyclized the ketolactone IX with aluminum chloride to the desisopropyl ketone X. The latter after Wolff–Kishner reduction gave substances shown to have a stereochemistry different from that of dehydroabietic acid.

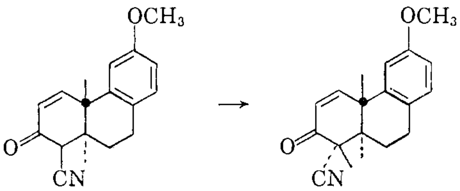

IX X

Also without success were experiments in this Laboratory designed to convert the tricyclic ketone XI, R = isopropyl,[13] to dehydroabietic acid. This particular approach[14] suffered from the configurational inhomogeneity of XI which, at equilibrium, is a mixture of *cis*- and *trans*-α-decalone derivatives.[15] This stereochemical difficulty made the methyl ketone XII, R = isopropyl, which we succeeded in constructing from the tricyclic system XI, of uncertain value for the synthesis of dehydroabietic acid for which we had envisaged the Favorskii rearrangement[16] of the bromoketone XIII. It is, however, interesting that more recently Barltrop[17] prepared from XI,

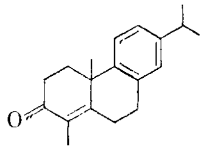

XI XII XIII

R = H, the methyl ketone XII, R = H, which must have contained at least some of the *trans* A/B isomer[18] since the Favorskii rearrangement of the corresponding bromoketone XIII, R = H, led to the isolation of *dl*-desisopropyldehydroabietic acid.

Finally, it has been shown by Kuehne[19] that the dehydroabietic acid stereochemistry at C_4 can be established by the methylation of the unsaturated ketonitrile system XIV.


XIV

It appeared to us that the tricyclic ketone XV would make an excellent starting point for the introduction of the desired asymmetry at C_4 and C_5 and it thus became our first synthetic objective. For this synthesis 1-methyl-6-isopropyl-2-tetralone (XXI) was needed and was prepared in two different fashions. The first route[20] involved the condensation of 3-(2-bromoethyl)-cumene[14] with malonic ester, followed by saponification and decarboxylation to the butyric acid XVIII. Conversion to the acid chloride, followed by stannic chloride cyclization, gave 6-isopropyl-1-tetralone (XIX) which was then treated with methylmagnesium iodide. Dehydration gave the dihydronaphthalene XX which upon treatment with monoperphthalic acid, followed by rearrangement of the resulting epoxide with hydrochloric acid, yielded the desired 1-methyl-6-isopropyl-2-tetralone (XXI).


XV

This rather long route had been chosen since at the time no suitable method was available for

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[10] This type of cyclization was indeed shown to give mainly the podocarpic stereochemistry (C_{10}-methyl and C_4-carboxyl *cis*) by F. E. King, T. J. King and J. G. Topliss, *Chemistry & Industry*, 113 (1956), who established the identity of a substance prepared in this manner by R. D. Haworth and B. P. Moore, *J. Chem. Soc.*, 633 (1946), to be *dl*-podocarpic acid. *Cf.* also J. A. Barltrop and A. C. Day, *ibid.*, 671 (1959), and U. R. Ghatak, *Tetrahedron Letters*, **No. 1**, 19 (1959).

[11] W. E. Parham, E. L. Wheeler, R. M. Dodson and S. W. Fenton, *J. Am. Chem. Soc.*, **76**, 5380 (1954).

[12] W. E. Parham, E. L. Wheeler and R. M. Dodson, *ibid.*, **77**, 1167 (1955).

[13] G. Stork and A. W. Burgstahler, *ibid.*, **73**, 3544 (1951).

[14] A. W. Burgstahler, Ph.D. Thesis, Harvard University, 1952.

[15] W. H. Reusch, Ph.D. Thesis, Columbia University, 1957.

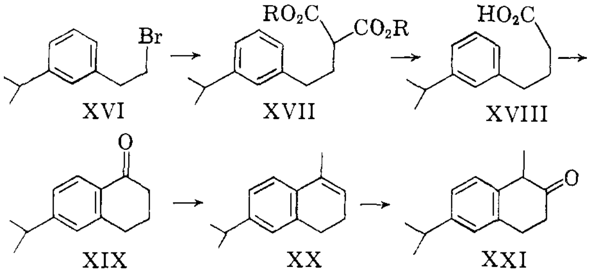
[16] *Cf.* G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960).

[17] J. A. Barltrop and A. C. Day, *Chemistry & Industry*, 1450 (1959).

[18] N. N. Saha, B. K. Ganguly and P. C. Dutta, *J. Am. Chem. Soc.*, **81**, 3670 (1959), have on the other hand found it possible to isolate only *cis* A/B fused acids on further transformations of our ketone (XI, R = H).

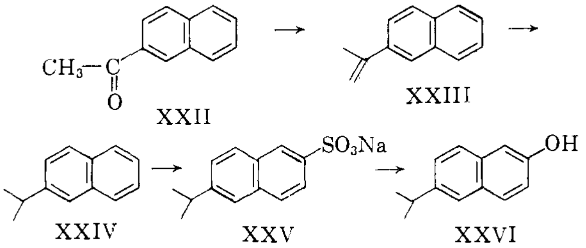
[19] M. E. Kuehne, *ibid.*, **83**, 1492 (1961).

[20] This synthesis of 1-methyl-7-isopropyltetralone-2 was carried out by Martin E. Kuehne (Ph.D. Dissertation, Columbia University, 1955).

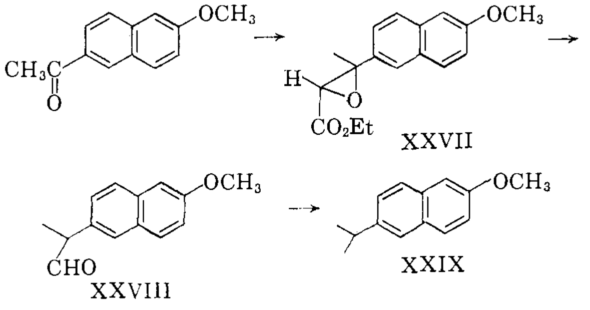


XVI XVII XVIII XIX XX XXI

monomethylating β-tetralones. With the subsequent development of such a method,[21] a shorter route to XXI became possible. Starting from 2-acetylnaphthalene (XXII) and using essentially the procedure of Bergmann and Weizmann,[22] 2-isopropylnaphthalene (XXIV) was prepared in an over-all yield of 80–85%. Sulfonation of XXIV then was carried out essentially by the procedure described by Fieser[23] for 2-methylnaphthalene. The crystalline sodium salt XXV thus obtained was not purified, but was directly fused with potassium hydroxide to give 6-isopropyl-2-naphthol (XXVI) in about 40–50% yield. It was felt at this point that an unambiguous proof of the relative position of the isopropyl and the hydroxyl groups was necessary. This was achieved by transforming the known 2-acetyl-6-methoxynaphthalene[24] into the propionaldehyde derivative XXVIII *via* the glycidic ester XXVII. Wolff–Kishner reduction of the aldehyde then gave authentic 2-methoxy-6-isopropylnaphthalene (XXIX). This crystalline substance, m.p. 63.5–64.5°, proved identical with the methyl ether prepared from the naphthol obtained by the sulfonation fusion sequence.

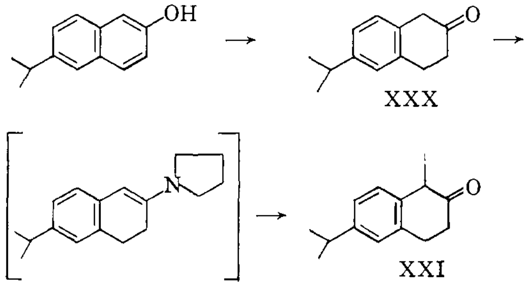


XXII XXIII XXIV XXV XXVI



XXVII XXVIII XXIX

Reduction of the naphthol XXVI by the method of Birch[25] gave 6-isopropyl-2-tetralone (XXX) as a liquid, isolated as its bisulfite addition product in 43–49% yield and characterized by its *p*-nitro- and 2,4-dinitrophenylhydrazones. The desired 1-methyl derivative of the 2-tetralone then was obtained by the use of the enamine alkylation reaction[21]: the ketone was converted into its pyrrolidine enamine which, without isolation, was alkylated by refluxing with methyl iodide in dry dioxane solution. Hydrolysis of the salt produced in the reaction gave 1-methyl-6-isopropyl-2-tetralone (XXI) in 80% yield. The product, a liquid boiling at 120–123° (0.7 mm.), was characterized by its 2,4-dinitrophenylhydrazone which melted at 142.5–144°. This was identical with the dinitrophenylhydrazone of the material made by the longer synthesis *via* 6-isopropyl-1-tetralone.



XXX XXI

Addition of ring A to the bicyclic ketone XXI was carried out by the addition of ethyl vinyl ketone in the presence of aqueous methanolic potassium hydroxide.[26] The tricyclic ketone XV was thus obtained in 74% yield as an oil boiling at 156–164° (0.15 mm.). It showed the expected spectral properties, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 6.05–6.19 μ and $\lambda_{\max}^{\mathrm{EtOH}}$ 245 mμ, ϵ 15,000, and was characterized as its red 2,4-dinitrophenylhydrazone which melted at 173.5–175°.

Up to this stage although nineteen of the twenty carbon atoms of dehydroabietic acid are now in their proper arrangement we have not had to face any stereochemical problems. The first of these now was met with the introduction at carbon atom 4 of a group which could be converted into a carboxyl function: such a group has to be introduced in the α-orientation, *trans* to the angular methyl group at carbon atom 10. We chose an acetic ester grouping as our potential carboxyl. This was introduced at C_4 by transforming the ketone XV into its anion by treatment with potassium *t*-butoxide, followed by removal of the *t*-butyl alcohol formed by co-distillation with benzene, and addition of ethyl bromoacetate. The alkylation product was largely the expected keto ester XXXI as shown by the strong new peak at 5.85 μ in the infrared and the almost complete disappearance of the α,β-unsaturated ketone absorption at 6.05 μ. We will now discuss the stereochemistry of this alkylated ester.

The presence of the axial angular methyl group at C_{10} in the rigid enolate ion XVa was expected to make the transition state for alkylation in which the bromo ester would approach from the β-side, *cis* to the angular methyl group, of higher energy than the alternative approach from the α-

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[21] G. Stork, R. Terrell and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954).

[22] F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

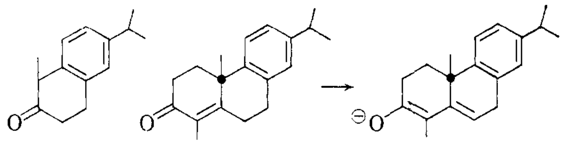
[23] L. F. Fieser, J. L. Hartwell and A. M. Seligman, *J. Am. Chem. Soc.*, **58**, 1223 (1936).

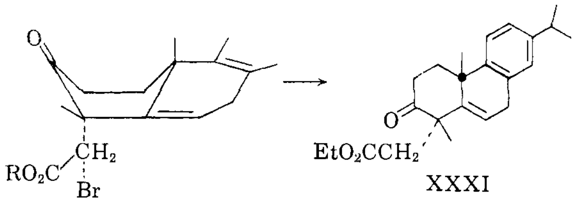
[24] R. Robinson and H. N. Rydon, *J. Chem. Soc.*, 1934 (1939).

[25] A. J. Birch, *ibid.*, 430 (1944); J. A. Barltrop and J. E. Saxton, *ibid.*, 1038 (1952).

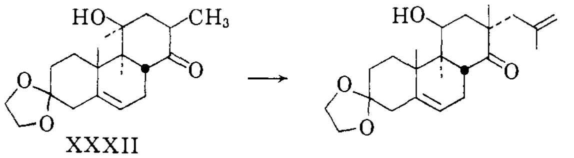
[26] *Cf.* J. W. Cornforth and R. Robinson, *ibid.*, 1855 (1949).

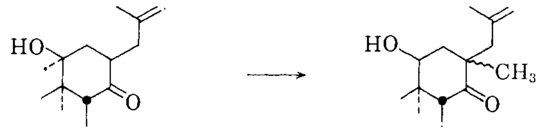
side (*cf.* XVb) thus leading to the proper stereochemistry of the potential carboxyl. The correctness of the stereochemistry shown in XXXI eventually was demonstrated by the conversion of the substance into *dl*-dehydroabietic acid. It should be noted that without such rigidity, or with a much smaller alkylating agent, one could not have had as much confidence in the stereochemical anticipation. For instance, while the alkylation of the tricyclic ketone XXXII with methallyl iodide leads to the introduction of the methallyl group *trans* to the axial hydroxyl substituent the related alkylation of the ketone XXXIII with methyl iodide produces an almost inseparable mixture of epimers.[27] Again methylation of the β-keto ester XXXIV with methyl iodide has been shown by Wenkert[28] to produce both possible epimers at C_4 the major product having, however, the podocarpic acid stereochemistry. Finally, we have already referred to the result of Kuehne[19] who has shown that the alkylation with methyl iodide of the β-ketonitrile XIV leads to entry of the methyl group *cis* to the axial methyl at C_{10}.[29]

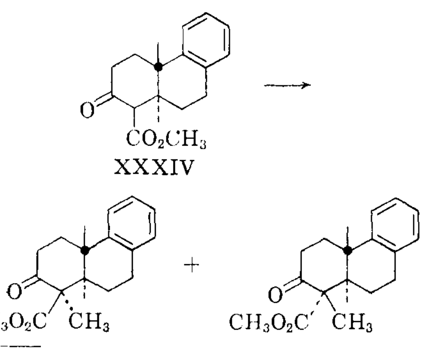

XV XVa



XVb XXXI


XXXII


XXXIII XXXIV

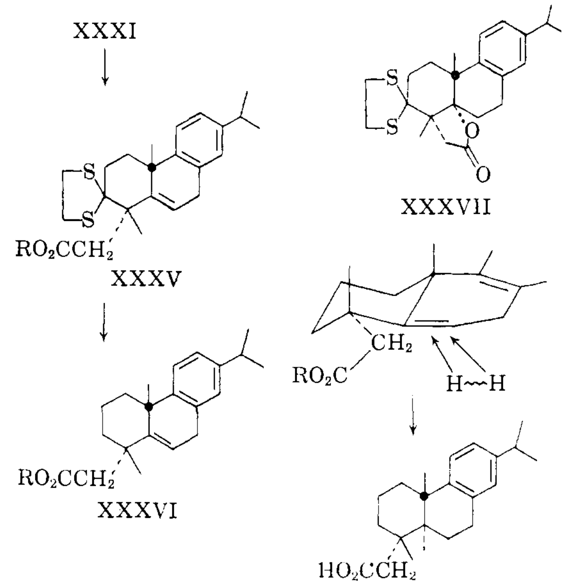


XXXIV

We now turn to the removal of the C_3-oxygen function and to the establishment of the proper configuration at C_5.

Conversion of XXXI into its thioketal was accomplished by treatment with ethanedithiol in the presence of anhydrous hydrogen chloride. Saponification then produced the crystalline thioketal acid XXXV, R = H, m.p. 183–186°. The spectral evidence obtained on the mother liquors from the crystallization of the acid gave strong indications that a major by-product in the formation of the thioketal is the lactone XXXVII.

Esterification of the thioketal acid with diazomethane, followed by desulfurization in the presence of Raney nickel and saponification, gave a crystalline acid which exhibited different melting points from run to run. This peculiarity was eventually traced to the presence of varying amounts of the product in which the double bond at 5–6 had been saturated during the Raney nickel treatment. Completion of the hydrogenation by treatment with hydrogen in the presence of palladium-on-charcoal gave the desired dihydro acid XXXVIII, m.p. 173–174°. In this acid a new asymmetric center has been introduced at C_5 during the catalytic hydrogenation. It was our expectation that this process would result in the introduction of a hydrogen from the α-side of the molecule because of the rigidity conferred upon the system by the combination of the Δ^5-double bond and the aromatic ring, thus greatly favoring approach of the catalyst from the side of the mole-



XXXV XXXVI XXXVII XXXVIII

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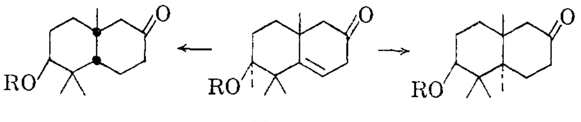
[27] L. H. Sarett, W. F. Jones, R. E. Beyler, R. M. Lukes, G. I. Poos and G. E. Arth, *J. Am. Chem. Soc.*, **75**, 2112 (1953).

[28] E. Wenkert and A. Tahara, *ibid.*, **82**, 3229 (1960).

[29] In this particular case alkylation *via* a transition state in which the developing *p*-orbital maintains overlap with the carbonyl group greatly favors the half-chair conformation. In the half-boat (*cf.* XVb) the carbonyl would no longer overlap properly with the C_1–C_2 double bond and the half-boat transition state, which would result in entry of the methyl group from the α-side, thus becomes of higher energy than usual.

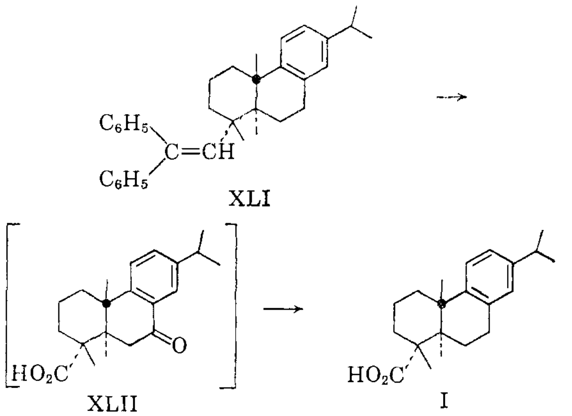
cule opposite the two axial methyl groups at C_{10} and C_4. It is important to note that without the degree of rigidity which is present here prediction of the course of the hydrogenation is on considerably shakier ground. For instance, it has been shown[30] that while the hydrogenation of the hydroxy enone XXXIX, R = H, produces a *trans*-decalone system, the similar hydrogenation of its acetate (XXXIX, R = Ac) leads to *cis* stereochemistry of the ring junction.



XXXIX

The structure and relative stereochemistry shown in the acid XXXVIII imply that it should be *dl*-homodehydroabietic acid. This was proved to be the case by comparison with the optically active substance prepared from natural dehydroabietic acid: Arndt–Eistert homologation of dehydroabietic acid gave (+)-homodehydroabietic acid (XXXVIII), m.p. 146–147.5°, $[\alpha]^{25}\text{D}$ +7°. The infrared spectrum of this substance was superimposable on that of our synthetic racemic acid, melting point 173–174°.

There remained now only to remove one carbon atom from the acetic acid chain at C_4 to complete the total synthesis of dehydroabietic acid itself. This was accomplished by the use of the Barbier–Wieland degradation. Treatment of the methyl ester of XXXVIII with phenylmagnesium bromide followed by dehydration of the resulting diphenylcarbinol gave the diphenylethylene XLI. It was anticipated that chromic acid oxidation of the diphenylethylene system would be attended by simultaneous oxidation of the benzylic position to produce the keto acid XLII. We first showed that, as expected, the keto acid obtained by chromic acid oxidation of dehydroabietic acid could be reconverted by palladium–charcoal reduction in acetic acid to dehydroabietic acid. We therefore oxidized the diphenylethylene XLI with a considerable excess of chromic acid and, without isolation, submitted the oxidation product to catalytic reduction with palladium. Crystallization of the acid product from methanol–water gave *dl*-dehydroabietic acid. The synthetic material melted at 179.5–180.5° and, in addition to the proper analytical figures, gave an infrared spectrum which was superposable with that of natural dehydroabietic acid, m.p. 172–173°. The methyl ester prepared from the synthetic acid with diazomethane melted at 71.5–73° and again gave an infrared spectrum which was completely superimposable on that of the natural ester, m.p. 62–63°. This completed the stereospecific total synthesis of *dl*-dehydroabietic acid.[31]



XLI

XLII

I

Experimental

3-Isopropylphenylethylmalonic Acid (XVII).—Sodium (1.72 g., 0.75 g. atom) was dissolved in 20 ml. of absolute ethanol and 16.0 g. of diethyl malonate (0.100 mole) was added. The solution was cooled to room temperature and 11.35 g. of the phenethyl bromide XVI[14] (0.0500 mole) dissolved in 10 ml. of absolute ethanol was added. The reaction was refluxed for 7 hours, cooled, 30 ml. of 45% aqueous potassium hydroxide added and again refluxed for 2 hours. After standing overnight at room temperature, a part of the ethanol was distilled out and water was added until the solution turned milky. Refluxing for 1 hour cleared the solution. More water was added (turning the solution cloudy), followed by 10 g. of potassium hydroxide. The total volume was now about 150 ml. and thus was about 11% in potassium hydroxide. After refluxing for 90 minutes, the solution was cooled, extracted twice with benzene and the aqueous portion was filtered into an excess of dilute hydrochloric acid. The acidic solution was extracted four times with ether and the extracts were dried over magnesium sulfate and evaporated; 11.0 g. of crude malonic acid remained (88% yield). This material was used directly for the decarboxylation.

4-(3-Isopropylphenyl)-butyric Acid (XVIII).—The crude diacid above (11.0 g.) was heated at 180° for 20 minutes, after which the evolution of carbon dioxide stopped. Distillation at 153° (0.4 mm.) gave 7.5 g. of the monoacid (yield from crude diacid, 83%; over-all yield from the propyl bromide, 73%). The product was used directly in the next step.

6-Isopropyltetralone-1 (XIX).—Powdered phosphorus pentachloride (72.5 g., 0.348 mole) was added to a cold solution of 60.0 g. of the phenylbutyric acid XVIII (0.291 mole) in 240 ml. of dry benzene. The reaction was permitted to stand for 2 hours at room temperature and then was added to 50 ml. of stannous chloride (0.428 mole) in 125 ml. of dry benzene, with cooling in an ice-bath. After 45 minutes, the reaction mixture was poured onto ice, about 50 ml. of concentrated hydrochloric acid was added and the tetralone was extracted with ether. The extracts were washed 3 times with cold 3% hydrochloric acid, once with water, twice with 10% aqueous sodium hydroxide and again twice with water. After drying over magnesium sulfate and evaporation of the solvent, the product was distilled at 143–146° (0.2 mm.) giving 49.0 g. of product (90% yield from the phenylbutyric acid). The 2,4-dinitrophenylhydrazone derivative melted at 196.0–196.3°.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47. Found: C, 61.49; H, 5.43.

1-Methyl-3,4-dihydro-6-isopropylnaphthalene (XX).—Methyl iodide (5.5 g., 0.039 mole) in 10 ml. of dry ether was added to a stirred suspension of 0.71 g. of magnesium (0.039 mole) in 50 ml. of dry ether. After the metal had reacted completely, 5.5 g. of the tetralone XIX (0.029 mole), dissolved in 25 ml. of dry ether, was introduced slowly and the reaction was stirred for 2 hours. A solution of 3.0 g. of ammonium chloride in about 100 ml. of water was then added, the layers were separated and the aqueous portion was extracted with ether. The combined ether extracts were dried over magnesium sulfate and evaporated. The crude residue of tertiary alcohol could be used directly for the dehydration which was carried out by dissolving in a small amount of chloroform and refluxing for 2.5 hours

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[30] T. G. Halsall, W. J. Rodewald and D. Willis, *J. Chem. Soc.*, 2798 (1959); see also N. B. Haynes and C. J. Timmons, *Proc. Chem. Soc.*, 345 (1958).

[31] The successful reduction of dehydroabietic acid to abietic acid has been reported recently by A. W. Burgstahler and L. R. Worden, *J. Am. Chem. Soc.*, **83**, 2587 (1961).

with 1.0 g. of potassium bisulfate. Removal of the solvent and distillation at 95–100° (0.3 mm.) gave 5.0 g. of product (93% over-all yield from the tetralone). This was used directly in the next step.

1-Methyl-7-isopropyl-tetralone-2 (XXI).[20]—To a solution of 40.0 g. of the dihydronaphthalene XX (0.215 mole) in 160 ml. of dry ether, 160 ml. of a 1.4 molar solution of monoperphthalic acid in ether (0.224 mole) was added at 0°. The reaction was left for 36 hours at −20°, at 5° for 4 hours, at room temperature for 4 hours and finally was stored at −20° for 36 hours. The precipitated phthalic acid was filtered off and the ether solution was shaken with 160 ml. of 3% hydrochloric acid, left at room temperature for 7 hours and again shaken with 160 ml. of 3% hydrochloric acid. Acid washing was repeated twice at intervals of 2 hours. The solution was then washed with aqueous sodium bicarbonate, dried over magnesium sulfate and evaporated. The filtered precipitate and all aqueous washings were combined, neutralized with sodium bicarbonate and extracted with ether. The extracts were combined for drying with the main ether portion, above. Distillation of the crude product at 122–124° (0.5 mm.) gave 34.2 g. of the tetralone XXXI (79% yield). This was characterized as its semicarbazone, m.p. 166.0–166.5°.

Anal. Calcd. for $C_{15}H_{21}ON_3$: C, 69.11; H, 8.11. Found: C, 68.88; H, 8.07.

2-Isopropenylnaphthalene (XXIII).—The procedure of Bergmann and Weizmann,[22] which involves the dehydration of dimethyl-2-naphthylcarbinol was essentially that used, but with potassium bisulfate as the dehydrating agent we could obtain only a 31% yield of product. The method was therefore somewhat modified, as follows.

To a solution of methylmagnesium iodide, from 86.4 g. (3.6 moles) of magnesium and 510 g. (3.6 moles) of methyl iodide, in 750 ml. of ether, was added as rapidly as practical 510 g. (3.0 moles) of 2-acetylnaphthalene (XXII) in 1800 ml. of ether. The mixture was refluxed for 45 minutes, cooled, and ice and dilute sulfuric acid were added. The aqueous layer was extracted with ether and the combined organic solutions were washed with aqueous sodium bisulfite and water. After drying, the solvent was removed and the residue was heated at 160° for a half-hour under water-pump vacuum. Water was formed rapidly and removed, following which the product was distilled at 102–110° (1.0 mm.) (reported[22] b.p. 155° (11 mm.)). It crystallized upon cooling, 454 g. (90%) being obtained. In small scale runs, the material was distilled directly, without prior heating to remove water. The yields, here, were somewhat lower. Although the product could be recrystallized from methanol to give material melting at 51–54° (reported[22] m.p. 56°) it generally was used directly without further purification.

The infrared spectrum had a large peak at 11.22 indicative of the terminal methylene group. No bands were present in the hydroxyl or carbonyl regions.

2-Isopropylnaphthalene (XXIV) was prepared from XXIII, above, by Raney nickel[32] hydrogenation in ethyl acetate, in a Parr shaker, according to the procedure of Bergmann and Weizmann.[22] The reaction was completed in 1.25–2 hours, giving yields of 90–94% of distilled product, b.p. 102–110° (1.0 mm.) (reported[22] b.p. 99–100° (0.2 XX.)), $n^{26}\text{D}$ 1.5830.

The infrared spectrum had a fairly large peak at 11.26 μ not due to a terminal methylene group, since the consistently reproducible hydrogenation data, as well as the details of the spectrum, showed that very little, if any, starting material remained in the product.

Sodium 2-Isopropyl-6-naphthalenesulfonate (XXV).—The procedure followed was essentially that of Fieser[23] for the preparation of the corresponding 2-methyl compound. To 375 ml. of concentrated sulfuric acid was added 414 g. (2.44 moles) of 2-isopropylnaphthalene. The mixture was stirred at 115° for 3.5 hours, during which the color became dark brown and homogeneity was achieved. The solution then was added carefully to 2000 ml. of water and neutralized with excess sodium hydroxide in 1000 ml. of water. Upon cooling, the sodium sulfonate crystallized as shiny, white plates, 430 g. (65%) being obtained. In other runs, yields of 50–80% resulted. The analytical sample was prepared by twice recrystallizing the sodium sulfonate from water.

Anal. Calcd. for $C_{13}H_{13}O_3SNa$: C, 57.37; H, 4.82; S, 11.76. Found: C, 57.26; H, 4.73; S, 11.53.

The sulfonamide, m.p. 190–190.5°, was prepared with phosphorus pentachloride, then ammonia, and recrystallized from 95% ethanol.

Anal. Calcd. for $C_{13}H_{15}O_2NS$: C, 62.64; H, 6.07; N, 5.62; S, 12.84. Found: C, 62.44; H, 5.87; N, 5.49; S, 12.83.

6-Isopropyl-2-naphthol (XXVI).—The crude sodium sulfonate (XXV) was used, without purification, 430 g. being fused, in five batches, with 1290 g. of potassium hydroxide pellets and 15 ml. of water, in a large iron crucible. The temperature of fusion was not determined, but the melt was heated for 5 to 10 minutes after it had quickly changed from a thick slurry to a thin liquid. After cooling, the material was dissolved in water, filtered, and the light brown filtrate was acidified with hydrochloric acid. The naphthol precipitated and was air-dried to yield 229 g., 78% based on the sulfonate and 51% based on 2-isopropylnaphthalene. In several preceding runs, the yields were 55–86% and 39–44%, respectively. The crude naphthol melted at 102–107°. The infrared spectrum had bands at 2.78 μ due to the hydroxyl, and at 7.26 and 7.33 μ due to the isopropyl group. The analytical sample was prepared by several recrystallizations from ligroin (b.p. 70–90°) and melted at 111.5–112.5°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.78; H, 7.84.

Ethyl 2,3-Epoxy-3-(6-methoxy-2-naphthyl)-butyrate (XXVII).—A solution of 10 g. (0.05 mole) of 6-methoxy-2-acetylnaphthalene and 9.81 g. (0.08 mole) of ethyl chloroacetate in 35 ml. of tetrahydrofuran was cooled to 5°. A solution made by the reaction of 2.73 g. (0.07 g. atom) of potassium and 60 ml. of pure *t*-butyl alcohol was then added, under nitrogen at 5°, over a 1.5-hour period.[33] The color changed from green to orange-red to orange-brown, and potassium chloride began to precipitate toward the end of the addition, after which the mixture was stirred overnight at room temperature. Water and tetrahydrofuran were added and the organic layer was washed with aqueous sodium chloride and dried. Removal of solvent gave solid material, which was recrystallized from 95% ethanol, yielding 5.8 g. (40%) of almost white glycidic ester, m.p. 103–108°. Repeating the reaction on 30 g. of ketone gave 15.7 g. (37%) of product. The infrared spectrum showed the expected carbonyl peak at 5.82 μ. The analytical sample had m.p. 107–108.5°.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.37; H, 6.38.

2-(6-Methoxy-2-naphthyl)-propionaldehyde (XXVIII).—The procedure followed was similar to that used for the synthesis of 2-phenylpropionaldehyde.[34] To a solution from 3 g. (0.13 g. atom) of sodium, 25 ml. of absolute ethanol and 3 ml. of water was added, at room temperature, a solution of 17.5 g. (0.061 mole) of the glycidic ester XXVII in the minimum volume of tetrahydrofuran. After 1 hour, the resulting salt of the glycidic acid was separated, washed with ether and air-dried to give 16.3 g. (95%). In a prior, small scale run, a 100% yield had resulted.

The corresponding acid could be obtained as a white solid, which decomposed to a brown gum upon standing. Therefore, the procedure followed was to suspend the salt in water, add excess hydrochloric acid, and heat for 0.5 hour on the steam-bath, carbon dioxide being evolved. Filtration then gave the aldehyde XXVIII as a yellow solid, m.p. 46–56°, in 93% yield. Purification *via* the bisulfite addition product gave the substance as a colorless compound melting at 52–57°, but no solvent suitable for recrystallization could be found. Peaks in the infrared spectrum were present at 3.65 and 5.82 μ.

The semicarbazone, from benzene, had m.p. 174–175°.

Anal. Calcd. for $C_{15}H_{17}O_2N_3$: C, 66.40; H, 6.32; N, 15.49. Found: C, 66.28; H, 6.24; N, 15.55.

2-Methoxy-6-isopropylnaphthalene (XXIX).–1.—This was prepared by the Huang-Minlon modification[35] of the Wolff–

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[32] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[33] *Cf.* C. F. H. Allen and J. V. Allan, *Org. Syntheses*, **24**, 87 (1944).

[34] *Cf.* W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, *J. Am. Chem. Soc.*, **75**, 4995 (1953).

[35] Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

Kishner reduction on 2.0 g. of the above aldehyde XXVIII. The product precipitated when the reaction mixture was poured into water, 0.7 g. (38%) being obtained after one recrystallization from 95% ethanol. Undoubtedly, much higher yields could have resulted had the reaction been repeated on a large scale. Several recrystallizations from 95% ethanol gave the analytical sample, m.p. 63.5–64.5°.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.98; H, 8.13.

2.—Compound XXIX was also prepared from the 6-isopropyl-2-naphthol (XXVI) obtained by the fusion reaction described earlier by treatment with methanol and sulfuric acid, according to the procedure of Davis.[36] The yield was not determined. Boiling the crude product with Norite, followed by several recrystallizations from 95% ethanol, gave white scales, m.p. 64–65.5°.

The products from these two reactions were shown to be the same by mixed m.p., 64–64.5°, and by the identity of their infrared spectra.

6-Isopropyl-2-tetralone (XXX).—The conditions used for the Birch reduction were those found to give optimum results with 2-naphthol, the procedure being essentially that of Barltrop and Saxton. Once-recrystallized 6-isopropyl-2-naphthol (XXVI, 18.6 g., 0.1 mole) was suspended in 14.5 ml. of absolute ethanol and 300 ml. of liquid ammonia was added. With stirring, 6.9 g. (0.3 g. atom) of sodium, in small pieces, was added and the solution was then stirred for 2 hours. Ammonium chloride, 18 g., was then added, the ammonia was evaporated, water was added, and the mixture was acidified with hydrochloric acid, with cooling. The resulting red oil was extracted into ether, and the ethereal solution was shaken overnight with a saturated, aqueous solution containing 0.6 mole of sodium bisulfite. The addition product was then washed with ether and air-dried, 26.0 g. of white material thus being obtained. This was decomposed by mild heating with aqueous sodium carbonate, the resulting oil then being extracted into ether. The organic solution was washed with water, dried and the solvent was removed. Distillation of the residue gave 8.6 g. (46%) of colorless tetralone, b.p. 107–112° (0.3 mm.), n^{31}_{D} 1.5355, which solidified at about 10°. The product gave the blue color in base, characteristic of 2-tetralones unsubstituted in the 1-position. The infrared carbonyl band was at 5.90 μ. Another similar run gave a 49% yield; when the reaction was run on 229 g. of unrecrystallized naphthol a 43% yield of tetralone resulted.

The *p*-nitrophenylhydrazone was recrystallized from methanol to give fine yellow needles, m.p. 172.5–174.5°.

Anal. Calcd. for $C_{19}H_{21}O_2N_3$: C, 70.56; H, 6.55; N, 13.00. Found: C, 70.87; H, 6.69; N, 13.00.

The orange **2,4-dinitrophenylhydrazone**, from methanol, melted at 115.5–118.5°.

Anal. Calcd. for $C_{19}H_{20}O_4N_4$: C, 61.94; H, 5.47; N, 15.21. Found: C, 62.13; H, 5.16; N, 15.13.

1-Methyl-6-isopropyl-2-tetralone (XXI) was made by the eneamine alkylation reaction: 65 g. (0.346 mole) of 6-isopropyl-2-tetralone (XXX) in 500 ml. of anhydrous, thiophene-free benzene was heated to reflux under nitrogen and treated, dropwise, with 48 g. (0.67 mole) of pyrrolidine in 60 ml. of dry benzene. The solution was then refluxed for 1 hour, during which somewhat more than the theoretical amount of water was removed with a water separator. Next, 550 ml. of solvent was distilled off and the remaining light red solution was cooled. A solution of 190 g. (1.33 moles) of methyl iodide in 165 ml. of dry dioxane was added, followed by refluxing for 40 hours. Water, 165 ml. containing 1 ml. of hydrochloric acid, was added and the system was refluxed for 2 hours. About two thirds of the total solvent was distilled off, water and ether were added, and the aqueous layer was extracted with ether. The combined organic solutions were washed with aqueous bisulfite and water, dried, the solvent was removed *in vacuo*, and the product was distilled. An 83% yield (58 g.) resulted, b.p. 120–123° (0.7 mm.) and 170–174° (18 mm.), n^{31}_{D} 1.5320. A very slight blue color was given with base. The infrared spectrum was similar, but not identical, to that of the starting material (XXX), the carbonyl peak remaining at 5.90 μ. In other runs, yields of about 80% always resulted.

The orange **2,4-dinitrophenylhydrazone**, recrystallized from methanol, melted at 142.5–144°.

Anal. Calcd. for $C_{20}H_{22}O_4N_4$: C, 62.81; H, 5.80; N, 14.65. Found: C, 63.06; H, 5.78; N, 14.47.

2-Keto-1,4a-dimethyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene (XV). 1.—The procedure of Cornforth and Robinson[26] was used, 6.06 g. (0.03 mole) of 1-methyl-6-isopropyl-2-tetralone (XXI) in 30 ml. of dry benzene being added to 0.03 mole of freshly prepared 1-diethylamino-3-pentanone methiodide. At 5°, under nitrogen, sodium ethoxide, from 1.15 g. (0.05 g. atom) of sodium and 30 ml. of absolute ethanol, was added over 5 minutes, with stirring, the color becoming blue, then yellow. After stirring at 5° for 1.5 hours, the solution was refluxed 1 hour, cooled, acidified with hydrochloric acid, water was added and the aqueous layer was extracted with ether. The combined organic solutions were washed with water, dried, the solvent was removed, and a thick, yellow oil (6.0 g., 75%) distilled at 165–175° (0.4 mm.). In a later run, the distillation was done under nitrogen, but the product was still yellow. The product could not be induced to crystallize. Attempts at purification, *via* the semicarbazone or methydrazone[37] each of which was chromatographed on alumina, failed to yield crystalline ketone. The infrared spectrum had peaks at 6.05 and 6.19μ, a small shoulder at 5.90μ being due to unreacted tetralone. The ultraviolet spectrum showed λ^{EtOH}_{max} 245 mμ, ε 15,000.

The red 2,4-dinitrophenylhydrazone was recrystallized from methanol. It melted at 173.5–175° and had ultraviolet maxima, in absolute ethanol, at 258 and 385 mμ, the extinctions being 19,400 and 30,300, respectively.

Anal. Calcd. for $C_{25}H_{28}N_4O_4$: C, 66.94; H, 6.29; N, 12.49. Found: C, 66.97; H, 6.26; N, 12.57.

2.—The ketone XV was also prepared by a modification of a method originated by Wilds.[38] To a solution of 2.24 g. (0.04 mole) of potassium hydroxide in 4.5 ml. of water and 45 ml. of methanol was added, at 0° under nitrogen, 6.06 g. (0.03 mole) of the tetralone XXI in 10 ml. of methanol. The solution was cooled to −20° and 2.52 g. (0.03 mole) of ethyl vinyl ketone was added slowly, with nitrogen flushing, the temperature being kept below −15°. Then, during 1 hour, the temperature was allowed to rise to 0°, the solution next standing overnight at room temperature. It was then refluxed for 3 hours under nitrogen, cooled and treated with the theoretical amount of hydrochloric acid. Ether and water were added, the organic layer was washed with water, dried and the solvent was removed. The product was then distilled at 156–164° (0.15 mm.), 5.95 g. (74%) of material, identical, by infrared comparison, with that obtained *via* the Mannich base, resulting. In a large scale run, a 70% yield was obtained. Chromatography on alumina failed to give crystalline ketone.

Ethyl 2-Keto-1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9-hexahydro-1-phenanthreneacetate (XXXI).—*t*-Butyl alcohol, 300 ml., was dried by refluxing with sodium and distilling from calcium hydride directly into the reaction flask. This was allowed to react with 8.6 g. (0.22 g. atom) of potassium, almost all of the *t*-butyl alcohol being distilled off after the potassium had dissolved. The ketone XV (53.5 g., 0.2 mole) in 250 ml. of dry benzene was then added under nitrogen and, with frequent additions of benzene, solvent was continuously removed until the refractive index of the distillate was constant at that of benzene, the resulting solution of the anion XVa being dark red. Benzene was added to bring the volume of 400 ml., and 66.8 g. (0.4 mole) of ethyl bromoacetate in 150 ml. of dry benzene was added dropwise, at 0°, under nitrogen, with stirring. The color lightened considerably, the mixture then being allowed to warm slowly to room temperature and to stand overnight. A few drops of hydrochloric acid was added, then water. The aqueous layer was extracted with ether, the combined organic solutions were washed with aqueous sodium chloride, then dried, and the solvent was removed. Distillation from an oil-jacketed flask at 1 mm. pressure and a bath temperature of 200–240° gave 62.0 g. (88%) of product, soluble in all the common organic solvents, as a yellow glass. This could not be induced to crystallize. The distillation was performed rapidly, since some decomposition occurred, a gas apparently being evolved. In previous, smaller

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[36] W. A. Davis, *J. Chem. Soc.*, **77**, 33 (1900).

[37] R. B. Woodward, T. P. Kohman and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).

[38] A. L. Wilds and R. G. Werth, *J. Org. Chem.*, **17**, 1149 (1952).

runs, yields of 80–84% resulted. The infrared spectrum had a large peak at 5.85 and a very small one at 6.05μ.

1,4a-Dimethyl-2-ethylenedithio-7-isopropyl-1,2,3,4,4a,9-hexahydro-1-phenanthreneacetic Acid (XXXV, R = H).—The crude keto ester XXXI (62.0 g., 0.175 mole) was dissolved in 50 g. (0.53 mole) of ethanedithiol, and dry hydrogen chloride was passed through the solution overnight. Water was formed shortly after the gas was introduced. The mixture became dark red, but most of the color was removed by bubbling nitrogen through for 10 minutes. Ether was then added and the organic layer was washed with aqueous carbonate and water; the very small amount of acidic material from the basic extracts was discarded. The solution was then dried, the ether was removed and the remaining oil was heated at 100° on the water-pump to remove ethanedithiol. This left behind an orange, glassy mixture (70 g.) containing the thioketal-ester.

This crude material was saponified directly with 160 g. of potassium hydroxide in 100 ml. of pure dioxane, 120 ml. of water and 1,200 ml. of 95% ethanol. After refluxing for 2 hours, most of the solvent was distilled off, water and ether were added, and the aqueous layer was extracted with ether. The combined organic solutions were washed with water, dried and the solvent was removed to leave 17.2 g. of dark orange gum, having no infrared carbonyl peak. This neutral material was undoubtedly the thioketal of the unalkylated ketone.

The basic layer was then acidified with hydrochloric acid and the resulting acid was extracted into ether. The ethereal solution was washed with water, dried and the solvent was removed to yield an orange solid, neutralization equivalent 413, calcd. for XXXV, R = H, 402. The solid was boiled with cyclohexane, a large volume being required to effect even partial solution. Since the color all went into solution, leaving white, crystalline material behind, only a portion of the acid was actually recrystallized from cyclohexane, the rest being simply digested with it. Here, a total of 24.1 g. of white acid was obtained which showed $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.92μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 267 mμ, ϵ 900.

Additional recrystallizations from cyclohexane gave the analytical sample, m.p. 183–186°. Considerable difficulty was encountered in getting consistent microanalytical data.

Anal. Calcd. for $C_{23}H_{30}O_2S_2$: C, 68.63; H, 7.51; S, 15.90. Found: C, 69.26, 68.27; H, 7.67, 7.52; S, 15.30, 16.75.

Desulfurization of the Thioketal Acid XXXV, R = H.—A solution of diazomethane, from 18 g. of N-methyl-N-nitrosourea,[39] was added slowly to 24.1 g. (0.06 mole) of acid XXXV, R = H, in 500 ml. of ether. After 0.5 hour at room temperature, excess acetic acid was added and the organic solution was washed with aqueous bicarbonate and water. Drying and solvent removal then gave, quantitatively, the crude, solid ester XXXV, R = CH_3; it was not further purified, but was dissolved directly in 150 ml. of dry dioxane, about 450 g. of Raney nickel and 1,800 ml. of absolute ethanol then being added. The mixture was refluxed overnight on the steam-bath, after which the nickel was removed by filtration and washed several times with hot ethanol. After removal of the solvent the product was distilled at 1 mm. pressure, bath temperature 200–230°. A 78% yield (15.2 g.) of thick, colorless oil was obtained. This material (3.54 g.) was saponified by refluxing with a solution of 22 g. of potassium hydroxide in 22 ml. of water and 200 ml. of 95% ethanol for 6 hours. About two thirds of the solvent was distilled off, water and ether were added, and the acidic fraction was isolated in the usual way. One recrystallization from methanol–water gave 2.98 g. (88%) of white acid, m.p. 167–169.5°, later shown to be a mixture of XXXVI and XXXVIII. Additional recrystallizations from methanol–water and from hexane did not alter the melting point. The product gave a positive test with permanganate in acetone, manganese dioxide being evident within 3 minutes.

Anal. Calcd. for XXXVI ($C_{21}H_{28}O_2$): C, 80.73; H, 9.03. Found: C, 80.27, 80.21; H, 9.70, 9.51.

Saponification of ester from earlier desulfurizations had given samples melting at 150–152° and 155–158°. The first of these gave analytical values more closely approximating those for the olefinic compound XXXVI. The infrared spectrum had a carbonyl band at 5.91μ. Ultraviolet maxima, in absolute ethanol, at 267 and 275.5 mμ had extinctions of 998 and 942, respectively.

Anal. Found: C, 80.49; H, 8.92.

1,4a-Dimethyl-7-isopropyl-1,2,3,4,4a,9,10a-octahydro-1-phenanthreneacetic acid (XXXVIII) was prepared by stirring under hydrogen, at room temperature and normal pressure, a solution of 5.292 g. of acid m.p. 167–169° (partially hydrogenated) from the desulfurization and 1.5 ml. of sulfuric acid in 250 ml. of acetic acid. Palladium-on-charcoal (10%, 1.8 g.) was the catalyst used. About 30% of the theoretical amount of hydrogen was absorbed, at which point the uptake ceased. The catalyst was removed, most of the acetic acid was distilled off under mild heating *in vacuo*, methanol and then water were added to the hot solution. Cooling, followed by filtration of the precipitated product and air-drying, gave 4.456 g. (84%) of white acid, m.p. 168–171°. In other hydrogenations of acid from the same desulfurization, 27–50% of the theoretical amount of hydrogen was apparently absorbed. The product was soluble in all the common organic solvents except aliphatic hydrocarbons.

In prior hydrogenations, using material with m.p. 155–158°, approximately the amount of hydrogen calculated for one double bond was absorbed. Analytical samples recrystallized several times from hexane and/or methanol–water melted at 172–173.5° and 173–174°.

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.25; H, 9.49.

The product showed no reaction with neutral permanganate in acetone after 1 hour and had $\lambda_{\max}^{\mathrm{EtOH}}$ ϵ 268, 276 mμ, ϵ 797, 885. The infrared spectrum of the acid in chloroform solution was found to be identical with that of material prepared by homologation of dehydroabietic acid.

Homologation of Natural Dehydroabietic Acid.—Saponification of methyl dehydroabietate (from Hercules Powder Co.), by the method of Fleck and Palkin,[40] gave the natural product. The Arndt–Eistert synthesis was then carried out essentially by the procedure described by Herr and Miescher,[41] who also homologated a tertiary carboxyl group. The acid chloride was prepared from 1 g. of acid and 3 ml. of oxalyl chloride in 5 ml. of chloroform. It was a thick yellow oil which was not purified, but converted directly into the diazoketone with excess diazomethane. The reaction mixture was allowed to stand at room temperature for 40 hours, solvent removal then giving the diazoketone as a yellow oil absorbing at 4.80 and 6.20 μ in the infrared. This, in 30 ml. of methanol at 60°, was treated with two 0.5-g. portions of freshly-prepared silver oxide and the mixture was then refluxed for 20 hours. Most of the silver oxide was thus reduced, the yellow solution containing a white precipitate which was filtered off. Solvent removal, on the water-pump, left the homoester as a yellow oil which was saponified by refluxing for 6 hours with a solution of 7 g. of potassium hydroxide in 7 ml. of water and 63 ml. of 95% ethanol. Most of the solvent was distilled off, ether and water were added, and the neutral and acidic fractions were isolated in the usual manner. The neutral material had an infrared peak at 5.75μ, but was not further investigated.

The acidic product was recrystallized twice from methanol–water to give 166 mg. of (+)-homodehydroabietic acid (XXXVIII), m.p. 142–145°. Additional recrystallizations gave the analytical sample, m.p. 146–147.5°. The acid had $[\alpha]^{25}\mathrm{D}$ +7° (*c* 2.50 in absolute ethanol).

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.43; H, 9.75.

The infrared spectrum in chloroform solution was identical with that of the synthetic, racemic homoacid XXXVIII, m.p. 172–173.5°, described above. The spectra were taken on the same paper and were superimposable.

The **1,4a-Dimethyl-7-isopropyl-1-(2,2-diphenylethenyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XLI).**—The synthetic, racemic, homoacid XXXVIII (3.40 g., 0.0108 mole), was esterified with excess diazomethane, as previously described for the methylation of the thioketal acid. The resulting methyl ester (3.29 g.) was dissolved in 25 ml. of anhydrous ether and added fairly rapidly to a large excess of phenylmagnesium bromide, from 4.21 g. of magnesium and

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(39) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, J. Wiley and Sons, Inc., New York, N. Y., 1942, p. 50.

(40) E. E. Fleck and S. Palkin, *J. Am. Chem. Soc.*, **60**, 921 (1938).

(41) J. Herr and K. Miescher, *Helv. Chim. Acta*, **31**, 229 (1948).

27.5 g. of bromobenzene, in 50 ml. of ether. The mixture was refluxed 2 hours, cooled and ice and dilute sulfuric acid were added. The aqueous layer was extracted with ether, the combined organic solutions were washed with water, the ether was evaporated and volatile impurities were removed by steam distillation. The remaining yellow oil was taken up in ether, the solution was washed with water, dried, and the solvent was removed to give 4.5 g. of carbinol as a yellow glass. This had an infrared hydroxyl band at 2.78μ; no carbonyl peak was present, showing that the reaction had gone to completion. That extensive dehydration had not occurred was proved by the absence of a strong peak at 249 mμ.

Dehydration of the crude carbinol was then accomplished by refluxing, for 2 hours, its solution in 200 ml. of acetic acid and 100 ml. of redistilled acetic anhydride. Most of the solvent was removed, with mild heating, on the water-pump, the residue then being heated at 100° and 1 mm. until, as shown by infrared, all the acetic anhydride was gone. The 4.4 g. of remaining crude material was shown by infrared and ultraviolet spectra to be chiefly the diphenylethylene XLI. The ultraviolet peak at 249 mμ, ϵ 12,300, proved the presence of a conjugated system, while the absence of the hydroxyl band in the infrared proved that dehydration had occurred. A small peak at 5.88μ suggested that the acetate of the carbinol was present, as an impurity, in the reaction product. This material was used directly in the oxidation step.

Synthetic *dl*-Dehydroabietic Acid (I).—The best conditions found for the chromium trioxide oxidation are those described below; all other conditions gave lower yields. In all cases, the spectra of the resulting neutral fraction showed that organic material, other than benzophenone, was present. Reoxidation of this neutral material, however, never gave more than a minute amount of dehydroabietic acid.

The crude diphenylethylene above (2.053 g., 4.73 mmoles) was dissolved in 35 ml. of chloroform and 140 ml. of acetic acid was added. Addition of 5.0 g. (0.05 mole) of chromium trioxide in 20 ml. of water, over a 5-minute period, caused the solution to turn very dark. After 1 hour at room temperature, the solution was warmed for 2 hours at 60–70°, cooled, and water and ether were added. The aqueous layer was extracted with ether and the combined organic solutions were washed several times with water. The acidic material was then extracted with 5% aqueous sodium hydroxide, the ether solution then being washed with water until the washings, which were added to the basic extracts, were neutral. The neutral fraction, largely benzophenone, was then obtained from the ethereal solution. The basic extracts were acidified with hydrochloric acid and the resulting oily acid extracted into ether. This ethereal solution was washed with water, dried, and the solvent removed to yield a yellow gum which was dissolved in acetic acid and treated with hydrogen in the presence of 10% palladium-on-charcoal. The mixture was stirred, under hydrogen, for 20 hours, two additions of fresh catalyst being made in the process. The catalyst was then removed, ethereal washings of it being added to the solution which was next evaporated to dryness *in vacuo*. About 600 mg. of yellow gum resulted which was crystallized from methanol–water to give only 255 mg. (18%) of almost white *dl*-dehydroabietic acid, m.p. 172–175°. The analytical sample, m.p. 179.5–180.5°, was obtained by several recrystallizations from methanol–water. (Natural, optically active, dehydroabietic acid melts at 172–173°.) The infrared spectrum of this synthetic acid was taken on the same paper as that of the natural product. The two spectra were completely identical, peaks occurring at 5.98, 6.73, 6.89, 7.29, 7.38, 7.87, 12.12μ and elsewhere.

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 80.30; H, 9.41.

Synthetic Methyl *dl*-Dehydroabietate.—*dl*-Dehydroabietic acid (50 mg.) was treated with excess diazomethane, as described above for the methylation of the thioketal acid, except that the reaction mixture was allowed to stand for 2 hours prior to the work-up. The resulting yellow oil was crystallized from methanol–water to give 22 mg. of racemic ester. Additional recrystallizations from this solvent pair gave the analytical sample, m.p. 71.5–73°, as fine, white needles, similar in appearance to the natural ester, m.p. 62–63°. The infrared spectra in chloroform of the racemic compound and of authentic methyl dehydroabietate were superimposable, the carbonyl band appearing at 5.86 μ.

Anal. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62. Found: C, 80.09; H, 9.44.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

Alumina: Catalyst and Support. XIV. Dehydrogenation, Dehydrocyclization and Isomerization of C_5- and C_6-Hydrocarbons over Chromia–Alumina Catalysts[1,2]

BY HERMAN PINES AND SIGMUND M. CSICSERY[3]

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Alumina *per se* has intrinsic acidic properties which influences the reactions of hydrocarbons over chromia–alumina catalysts. Catalysts containing alumina made from aluminum isopropoxide have relatively strong acidic sites. Extensive cationic isomerization and polymerization of the dehydrogenation products of *n*-pentane, *n*-hexane, methylpentanes and methylcyclopentane were observed over this catalyst. Dehydrogenation and dehydrocyclization proceed without appreciable isomerization and polymerization over chromia–alumina where the alumina was obtained from potassium aluminate. The reaction product of *n*-hexane dehydrogenation over this non-acidic catalyst contained 52 mole % benzene *vs.* 13 mole % over the acidic chromia–alumina catalyst. In case of 2- and 3-methylpentane and methylcyclopentane the results were reversed: the yields of benzene obtained from the acidic catalyst were higher.

The dehydrogenation of paraffins over chromia–alumina catalysts had been a subject of extensive studies for almost three decades.[4] No attention has been paid however to the role of alumina in this reaction.

Recent investigations in our laboratory have revealed that the catalytic properties of aluminas depend upon their methods of preparation. Alumina obtained from aluminum isopropoxide by

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[1] Paper VII of the series "Aromatization of Hydrocarbons." For previous papers of these series see S. M. Csicsery and H. Pines, *Chemistry & Industry*, 1398 (1961).

[2] Presented in part at the Princeton University Conference on "Active Centers in Heterogeneous Catalysis," May 11–12, 1961, Princeton, N. J.

[3] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Fund.

[4] For review of the literature see: (a) A. H. Steiner, in "Catalysis," Vol. IV, edited by P. H. Emmett, Reinhold Publ. Corp., New York, N. Y., 1956, pp. 529–560. (b) G. F. Ciapetta, R. M. Dobres and R. W. Baker, Vol. VI, pp. 492–692. (c) C. Hansch, *Chem. Revs.*, **53**, 353 (1953).