cinic acid complexes, do not exhibit enhanced reaction rates. An "adsorption" mechanism is ruled out, for the rate of reduction of aquopentamminocobaltic perchlorate is not affected by the mere presence of cobalt-free polymer. We lean to the hypothesis that the rapid reaction corresponds to those cobalt-bearing sidechains of which the carboxyl groups overlap an extended system of hydrogen-bonded amide groups; and that electron transfer from chromium occurs *through* this system.

The products of the reduction of the polymeric complexes have been isolated by dialysis and lyophilization of the reaction mixture They contain chromium equivalent to the initial cobalt, but the sites of this bound chromium are not known. These products are not entirely soluble in water and dissolve sluggishly in formic acid. A film of the polymer has $\nu_{C=O}$ 1650 cm.$^{-1}$, but treatment with water at 100° does not produce any β-form (1625 cm.$^{-1}$). It is conceivable that the rapid reduction process produces a change in the conformation of the polymer which constrains the remainder of reaction to occur by a process involving direct chromium attack at the carboxyl bearing the oxidant.

We are grateful to Professor Henry Taube for his interest in this work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO KENNETH D. KOPPLE
CHICAGO 37, ILLINOIS GEORGE F. SVATOS

RECEIVED APRIL 25, 1960

THE ISOMERIZATION OF TRIALKYLACETIC ACIDS IN SULFURIC ACID[1]

Sir:

Trialkylacetic acids have been found to isomerize in concentrated sulfuric acid under conditions which do not result in significant decarbonylation. The same mixture consisting chiefly of 2,2-dimethylvaleric acid (I)[2] and 2-methyl-2-ethylbutyric acid (II)[2] resulted from the isomerization of either I or II in concentrated sulfuric acid. Solutions of either I or II (0.27 molar) in 94.9% sulfuric acid approached the equilibrium ratio (I/II) of 2.84 with first order kinetics and a half life of 51 minutes at 26.3°. The appearance of a third component 2,2,3-trimethylbutyric acid (III),[3] proceeded much slower. This acid accounted for *ca.* 3% of the mixture after three hours and became about equal to II after 48 hours. The isomerization of III under these conditions slowly yielded I and II in the ratio of 2.84.

Acid II was isomerized in sulfuric acid, the mixture of carboxylic acids separated and converted to the amides. From this mixture the pure amide of I[2] (identified by infrared, m.p. and mixed m.p. 94-95°) was isolated by fractional crystallization. The acid mixtures were analyzed by gas chromatography of the corresponding alcohols (obtained by $LiAlH_4$ reduction) using a 12′ column of Resoflex[4] R-726 on fire brick. Infrared spectrograms of isomerized mixtures were identical with appropriate mixtures of I, II, and III.

The four nine carbon tri-*n*-alkylacetic acids were interconverted rapidly under the same conditions to yield 2,2-dimethylheptanoic acid as the major component. This emphasizes the general nature of this isomerization. The disappearance of 2,2-diethylvaleric acid, which represented *ca.* 1% of the isomerized mixture, proceeded by initially first order kinetics with a half life of less than five minutes. Slower changes occurred to yield products which are presumably analogous to III. The thermodynamically most stable species appear to predominate in isomerized mixtures of both the seven and nine carbon trialkylacetic acids.[5]

That this isomerization occurred at least in part by a decarbonylation-carbonylation process was demonstrated by the exchange of radioactive II (labeled with C^{14} in the carboxyl carbon) in concentrated sulfuric acid with unlabeled carbon monoxide.[6] Also, slow introduction of 2-methyl-2-butene into a sulfuric acid solution of II resulted in the formation of 2,2-dimethylbutyric acid.

The author thanks Messrs. P. L. Gant and R. D. Gallagher for assistance in the tracer experiment and Dr. M. G. Ettlinger for a helpful discussion.

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[1] Presented at the 6th Tetrasectional Meeting of the Oklahoma Sections of the American Chemical Society, March 26, 1960.

[2] Compound I was prepared by oxidation of 2,2-dimethyl-1-pentanol obtained from the Carbide Chemical Corporation, and II was prepared from the Grignard. The melting points of the amides (94–95 and 74–75°) and the physical properties of the acids agree with values previously reported; D. V. N. Hardy, *J. Chem. Soc.*, 464 (1938).

[3] F. C. Whitmore and K. C. Laughlin, THIS JOURNAL, **55**, 3735 (1933).

[4] Cambridge Industries Co., Inc., Cambridge, Mass.

[5] Similar reactions in which the more stable isomer predominated have been reported by R. E. Pincock, E. Grigat and P. D. Bartlett, THIS JOURNAL, **81**, 6332 (1959); G. Stork and M. Bersohn, *ibid.*, **82**, 1261 (1960).

[6] A carbonylation–decarbonylation mechanism has been demonstrated to occur in the isomerization of cinenic acid to geronic acid by J. Meinwald, H. C. Hwang, D. Christman and A. P. Wolf, *ibid.*, **82**, 483 (1960).

RESEARCH AND DEVELOPMENT DEPARTMENT
CONTINENTAL OIL COMPANY ALLAN LUNDEEN
PONCA CITY, OKLAHOMA

RECEIVED APRIL 16, 1960

THE ISOLATION OF THE ICOSAHEDRAL $B_{12}H_{12}^{-2}$ ION

Sir:

In 1955 Longuet-Higgins and Roberts[1] predicted that the $B_{12}H_{12}$ icosahedron would be stable only as the $B_{12}H_{12}^{-2}$ ion. We now wish to report the isolation of such an ion, in very low yield, from the reaction of 2-iododecaborane with triethylamine.

Sixteen grams of pure 2-iododecaborane and 35 g. of triethylamine were dissolved in 500 ml. of dry benzene and maintained at the reflux temperature for 5 hours. The yellow semi-solid which separated was treated with 150 ml. of acetone, the resulting solid separated by filtration and washed with water to remove the triethylammonium salt[2] of $B_{10}H_{10}^{-2}$ formed as a by-product. The residual solid was recrystallized twice from acetonitrile and ethanol to yield 1.4 g. (3.8%) of the triethylammonium salt of $B_{12}H_{12}^{-2}$ (I). Calcd.: B, 37.54; C, 41.63; H, 12.72; N, 8.09. Found: B, 37.48; C, 40.86; H, 12.97; N, 8.08.

Treatment of I with two equivalents of potassium hydroxide in boiling water displaced triethylamine

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[1] H. C. Longuet-Higgins and M. Roberts, *Proc. Royal Soc.* (*London*), **A230**, 110 (1955).

[2] M. F. Hawthorne and A. R. Pitochelli, THIS JOURNAL, **81**, 5519 (1959).

to produce the di-potassium salt, $K_2B_{12}H_{12}$ (II). Similarly, treatment of I with aqueous triphenylmethylphosphonium chloride solution precipitated the corresponding triphenylmethylphosphonium salt (III). Ebullioscopic molecular weight determinations of III in acetonitrile indicated an apparent molecular weight of 241 at infinite dilution (calcd. 231.9).

The infrared spectrum of II contained a terminal B-H stretching band at 3.97 μ and five additional bands between 4 and 25 μ (8.95 μ (w), 9.30 μ (s), 13.25 μ (w), 13.40 μ (w) and 14.0 μ (s). The simplicity of this infrared spectrum suggests a highly symmetrical anion.

Examination of the B^{11} nuclear magnetic resonance spectra of I in acetonitrile and II in water revealed a single strong doublet. In the case of I the doublet was centered at 419 cycles higher field than methyl borate and separated by 115 cycles. This result is in agreement with an icosahedral arrangement of boron atoms.

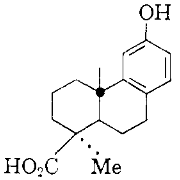
ROHM & HAAS COMPANY ANTHONY R. PITOCHELLI
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA M. FREDERICK HAWTHORNE

RECEIVED MAY 4, 1960

TOTAL SYNTHESIS OF *d*-PODOCARPIC ACID[1]

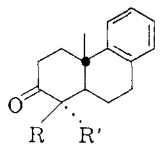
Sir:

We wish to report the total synthesis of *d*-podocarpic acid (*d*-I).[2] This completes the first phase of our studies of the synthesis of diterpenic natural products.[3]

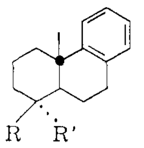


I

Methylation of the ketoester IIa[3d] with methyl iodide and potassium *t*-butoxide in *t*-butyl alcohol gave two alkylation products in 2.4:1 ratio, ketoesters IIb, m.p. 103-104° (found: C, 75.44; H, 7.93), and IIc, m.p. 111.5-113° (found: C, 75.72; H, 7.93), respectively.[4] Clemmensen reduction of the former yielded methyl *d,l*-deisopropyldehydroabietate (IIIb),[2d,5] m.p. 110-112° (found: C, 79.51; H, 8.81), whose infrared spectrum was identical with that of the *d*-antipode of IIIb.[6] Similar reduction of IIc led to methyl *d,l*-deoxypodocarpate (IIIc),[2d,7] m.p. 130-131° (found: C, 79.62; H, 9.13), whose infrared spectrum was the same as that of the *d*-enantiomer of IIIc.[8]



II



III

a, R = H, R' = CO_2Me
b, R = Me, R' = CO_2Me
c, R = CO_2Me, R' = Me
d, R = CN, R' = Me
e, R = CHO, R' = Me
f, R = CO_2H, R' = Me

Further proof of the structure of IIIc and a further supply of the compound were obtained by mixing *d*-IIIc, m.p. 141-142°, $[\alpha]_D$ +138.2° (ethanol)[3c] and *l*-IIIc, m.p. 141-142°, $[\alpha]_D$ −149.4° (ethanol) (found: C, 79.46; H, 8.93). The latter could be produced by the lithium aluminum hydride reduction of *l*-desoxypodocarponitrile (IIId)[8] to *l*-desoxypodocarpinal (IIIe), m.p. 90-93°, $[\alpha]_D$ −86.1° (ethanol) (Found: C, 84.18; H, 8.59), permanganate oxidation to *l*-desoxypodocarpic acid (IIIf), m.p. 194-195.5°, $[\alpha]_D$ −141.0° (ethanol) (Found: C, 79.33; H, 8.62), and diazomethane treatment. Basic hydrolysis of *d,l*-IIIc, as well as a synthetic 1:1 mixture of the aforementioned *l*-acid IIIf and its *d*-enantiomer, m.p. 197-198°, $[\alpha]_D$ +140.8° (ethanol),[3c] yielded *d,l*-desoxypodocarpic acid (IIIf), m.p. 232-233° (Found: C, 79.06; H, 8.53).[2d,7] Exposure of the latter to cinchonine and crystallization of the mixture from aqueous methanol yielded an insoluble salt, m.p. 197-201°, 210-215° (found: C, 78.49; H, 8.15; N, 5.10), identical with the salt formed from the *d*-acid IIIf. Mild hydrochloric acid metathesis liberated *d*-desoxypodocarpic acid (IIIf). Since this compound has been converted already to *d*-podocarpic acid (I),[3c] this completes the total synthesis of the natural product.

In view of the recent transformation of podocarpic acid to nimbiol[9] the present work represents a total synthesis of this compound also. Furthermore, it constitutes a formal total synthesis of ferruginol[10] and sugiol.[11]

DEPARTMENT OF CHEMISTRY ERNEST WENKERT
IOWA STATE UNIVERSITY AKIRA TAHARA
AMES, IOWA

RECEIVED MAY 7, 1960

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[1] The authors are indebted to the National Science Foundation for support of this research.

[2] For previous methods of synthesis of the racemic compound *cf.* (a) B. K. Bhattacharyya, *J. Ind. Chem. Soc.*, **22**, 165 (1945); (b) R. D. Haworth and B. P. Moore, *J. Chem. Soc.*, 633 (1946); (c) F. E. King, T. J. King and J. G. Topliss, *Chemistry and Industry*, 113 (1956); (d) U. R. Ghatak, THIS JOURNAL, **82**, 1728 (1960).

[3] (a), (b) E. Wenkert and T. E. Stevens, *ibid.*, **78**, 2318, 5627 (1956); (c) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 217 (1958); (d) *ibid.*, **81**, 5601 (1959).

[4] The reason for the amazing lack of stereospecificity in this case and the general problem of the stereochemistry of alkylation of rigidly held β-ketoesters is under present study.

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

[6] (a) M. Ohta and L. Ohmori, *Pharm. Bull.* (*Japan*), **5**, 91 (1957); (b) E. Wenkert and J. W. Chamberlin, THIS JOURNAL, **81**, 688 (1959).

[7] *Cf.* R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, 1299 (1939).

[8] E. Wenkert and B. G. Jackson, THIS JOURNAL, **80**, 211 (1958).

[9] E. Wenkert and V. I. Stenberg, Abstracts of the 137th Meeting of the American Chemical Society, April 5–14, 1960, p. 36-O.

[10] W. P. Campbell and D. Todd, THIS JOURNAL, **64**, 928 (1942).

[11] C. W. Brandt and B. R. Thomas, *J. Chem. Soc.*, 2442 (1952).