Experimental[10]

9-(3-Dimethylamino-1-oxopropyl)-anthracene (Ib) Picrate.—The hydrochloride of Ib was reported by Fry.[11] It was converted to the picrate with alcoholic picric acid. The picrate crystallized from acetone-water in red crusts, m.p. 194-196°, or yellow short needles, m.p. 158-159°. The latter modification was analyzed.

Anal. Calcd. for $C_{25}H_{22}N_4O_8$: C, 59.3; H, 4.4. Found: C, 59.1; H, 4.5.

9-(3-Dimethylamino-1-hydroxypropyl)-anthracene (IIb).—The hydrochloride of Ib[11] (2.6 g.) was shaken with aqueous sodium carbonate and ether. Drying and evaporation of the ether left an oil which was dried in the vacuum desiccator overnight, stirred in 30 ml. of dry ether and treated during 10 minutes with 3.5 ml. (three equivalents)[6] of 1.8 *M* ethereal lithium aluminum hydride diluted with 7 ml. of dry ether. The mixture was decomposed by slow addition of 5 ml. of water. The clear ethereal solution was decanted, dried, evaporated to *ca.* 10 ml. and diluted with 3-4 ml. of ligroin (30-60°) to give 1.0 g. (45%) of IIb, m.p. 118-119°; prisms from ethanol.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.7; H, 7.6. Found: C, 81.7; H, 7.7.

The hydrochloride (NIH 4126) was prepared by addition of alcoholic hydrogen chloride (to congo red acidity) to an acetone solution of IIb and dilution with ether; yellowish prisms from ethanol-ether, m.p. 194-196° (dec.), $\lambda_{\max.}^{\text{absol. EtOH}}$ 256 mμ (log ε 5.213).

Anal. Calcd. for $C_{19}H_{22}ClNO$: C, 72.3; H, 7.0. Found: C, 71.9; H, 7.2.

9-(3-Morpholino-1-hydroxypropyl)-anthracene (IIa) Hydrochloride (NIH 4127).—To a stirred suspension of 1.6 g. of Ia[1] and 30 ml. of dry ether was added 1.5 ml. of 1.8 *M* ethereal lithium aluminum hydride in 20 ml. of dry ether during 15 minutes. The mixture was stirred for an additional one-half hour, then 3 ml. of water was added slowly. Decantation, drying and acidification of the ether with alcoholic hydrogen chloride gave 1.6 g. (90%) of hydrochloride, m.p. 204-205° (dec.). It crystallized from ethanol in yellow-tinged needles, m.p. 209-210° (dec.), $\lambda_{\max.}^{\text{absol. EtOH}}$ 256 mμ (log ε 5.206).

Anal. Calcd. for $C_{21}H_{24}ClNO_2$: C, 70.5; H, 6.8. Found: C, 70.7; H, 7.0.

The base, prepared from the hydrochloride with dilute, aqueous ammonia, crystallized from ethanol-water in rods of m.p. 124.5-126°.

Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.5; H, 7.2. Found: C, 78.6; H, 7.2.

9-(1-Hydroxyethyl)-anthracene (IIc).—One gram of 9-acetylanthracene[1] was reduced as described for Ia. The decomposed mixture was shaken with 10% hydrochloric acid. Drying and evaporation of the ether left a solid which crystallized from methanol in needles, m.p. 117-121°; yield 0.8 g. (80%). Recrystallized from ether-ligroin (30-60°) the IIc melted at 124-125° alone or in mixture with material prepared from 9-anthracenecarboxaldehyde.[5]

9-(3-Morpholino-1-acetoxypropyl)-anthracene Hydrochloride.—A mixture of 0.15 g. of IIa hydrochloride, 0.1 ml. of acetic anhydride and 2 ml. of dry pyridine was shaken for 7 hours and evaporated to dryness *in vacuo.* The residue was washed with acetone and recrystallized from ethanol; yield 80%, oblong plates, m.p. 214-215° (dec.). Analysis indicated one mole of solvate ethanol which was indeterminate by weight loss.

Anal. Calcd. for $C_{23}H_{26}ClNO_3 \cdot C_2H_5OH$: C, 67.3; H, 7.2; Cl, 8.0. Found: C, 67.5; H, 7.3; Cl, 8.2.

Crystallization of the product from methanol gave a solvate-free hydrochloride; prisms.

Anal. Calcd. for $C_{23}H_{26}ClNO_3$: C, 69.1; H, 6.6. Found: C, 68.6; H, 6.7.

9-(3-Dimethylamino-1-acetoxypropyl)-anthracene Hydrochloride.—The hydrochloride of IIb was acetylated as described for that of IIa; dense, yellow-tinged prisms,[12] m.p. 211-212° (dec.), from acetone.

Anal. Calcd. for $C_{21}H_{24}ClNO_2 \cdot H_2O$: C, 67.0; H, 7.0. Found: C, 66.9; H, 7.0.

On refluxing this hydrated hydrochloride with methanolic alkali IIb was regenerated.

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(10) Melting points, observed in a capillary, are uncorrected. The absorption measurements and microanalyses are from the Institutes service analytical laboratory under the direction of Mr. William C. Alford.

(11) E. M. Fry, *J. Org. Chem.*, **10**, 259 (1945).

(12) The compound first crystallized as white, thin prisms which gradually changed to the more dense, tinged ones.

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

The Oxidation of Isoborneol with Chromic Acid[1]

BY WILLIAM A. MOSHER AND ESLEY O. LANGERAK[2]

Isoborneol on oxidation with chromic anhydride in aqueous acetic acid yields 96% camphor, 2% α-campholenic acid and 2% 1,2,2-trimethylcyclopentanol-3-acetic acid. These two acids have not been previously isolated from isoborneol oxidation and the latter is a new terpene-derived hydroxy-acid.

These products are accounted for through the deficient oxygen intermediate. The results with isoborneol are significant because the alcohol and acid functions are obtained in the same molecule as a result of the splitting reaction.

Mosher and Langerak[3] have previously shown that cleavage of secondary aliphatic alcohols to aldehydes and alcohols of lower molecular weight is a general reaction, although only trace yields of the cleavage products are obtained unless one group attached to the carbinol carbon is tertiary such as is the case with methyl-*t*-amylcarbinol (I). A 7% yield of *t*-amyl alcohol is formed when this secondary alcohol is oxidized with chromic anhydride in aqueous acetic acid.[4] The similarity in group relationships between this aliphatic alcohol (I) and isoborneol (II) is at once apparent, and suggests this terpene alcohol for oxidative study.

Because of its relation to camphor synthesis, the oxidation of isoborneol has received considerable study. This literature is well reviewed by Simonsen[5] but special attention should be called to the work of Acharya and co-workers[6] who reported yields of camphor as high as 96% using nitric acid in sulfuric acid solution; the highest yield reported by those workers with chromic acid is 70%.

Our oxidation of isoborneol with chromic anhy-

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(1) Presented before the Division of Organic Chemistry, American Chemical Society, Philadelphia, April, 1950.

(2) F. G. Cottrell Research Fellow in Chemistry 1946-1949. From a thesis presented in partial fulfillment of the requirements for the Ph.D. degree, 1949.

(3) Mosher and Langerak, THIS JOURNAL, **71**, 286 (1949).

(4) Mosher and Whitmore, *ibid.*, **70**, 2544 (1948).

(5) Simonsen, "The Terpenes," 2nd Edition, Vol. II, Cambridge University Press, 1949.

(6) Acharya and co-workers, *J. Univ. Bombay*, **11A**, pt. 5, 113 (1943); *C. A.*, **37**, 5952 (1943).

dride in acetic acid solution proceeded smoothly to yield 96% camphor, 2% α-campholenic acid (III) and 2% 1,2,2-trimethylcyclopentanol-3-acetic acid (IV) (an hydroxydihydro-α-campholenic acid). These last two compounds have not previously been isolated from isoborneol oxidation; compound (IV) is a new terpene-derived hydroxy-acid.

Figure 2 sets forth the proposed mechanism for the formation of camphor and the other products observed in this study. The essential step is the removal of hydride ion, presumably through an initial chelation of the oxidizing agent with the hydroxyl group. The electronically deficient oxygen-containing intermediate may then expel a proton to form camphor or it may appropriate a pair of electrons from the ring to give a monocyclic carbonium ion (VII). This ion would give α-campholenic acid on loss of a proton or the new acid (IV) by displacing a proton from the water in the solvent. Presumably aldehydes would be first formed by the ring opening process; however, these would be readily oxidized to the observed acids in the medium present.

That the two acids, α-campholenic acid (III) and the new acid (IV), are formed from the original isoborneol rather than from further oxidation of camphor appears probable from the work of Bredt,[7] who demonstrated that the oxidation of camphor by chromic acid in aqueous acetic acid yields *p*-diketocamphane. None of this compound was found in the present investigation. Temperatures in this work were always below 30° while Bredt employed reaction temperatures as high as 80°.

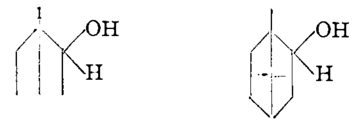
The new acid (IV) is resistant to oxidation but is readily dehydrated to α-campholenic acid.

Although the splitting reaction observed here appears to be identical in nature with that previously reported, the results obtained are significant in that the alcohol function and the acid function are in the same molecule after the reaction has taken place. In the oxidation of such alcohols as isopropyl-*t*-butylcarbinol both *t*-butyl alcohol and isobutyraldehyde were isolated but there is no direct evidence that the aldehyde and the alcohol come from the same molecule. The present investigation provides such evidence.

Experimental

Oxidation of Isoborneol.—Isoborneol [(*dl*), m.p. 211–212°, phenylurethan, m.p. 139°, obtained from the Organic Chemicals Department of E. I. du Pont de Nemours and Co.], 154 g. (1.0 mole), was dissolved in 110 ml. of glacial acetic acid and placed in a 1-l. three-necked flask equipped with stirrer, thermometer, reflux condenser and addition funnel. A solution of 65 g. (0.65 mole) of chromium trioxide dissolved in 40 ml. of water and 65 ml. of glacial acetic acid was added dropwise over a period of 5.75 hours. Temperature was held below 30° by means of a cold water-bath whenever necessary.

The green solution was diluted with 600 ml. of water and extracted three times with ether. The aqueous solution was put aside and the combined ether extracts were repeatedly extracted with a saturated sodium bicarbonate solution, and then treated with solid anhydrous sodium carbonate until the green chromium color had been completely removed. After slow evaporation under a current of air 139.0 g. of a white crystalline solid, m.p. 176–178°, identified as camphor, remained. Its 2,4-dinitrophenylhydrazone, m.p. 168°, and semicarbazone, m.p. 242°, showed no depression in melting points on admixture with authentic samples.



Methyl-*t*-amylcarbinol Isoborneol

Fig. 1.

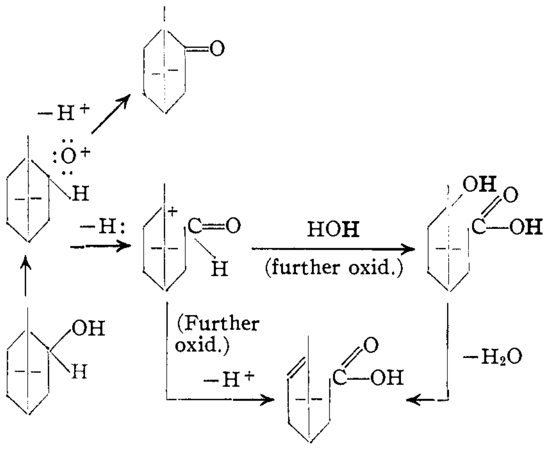


Fig. 2.

The solid sodium carbonate was combined with the sodium bicarbonate extracts and acidified with dilute sulfuric acid. The precipitate was taken into ether, and the ethereal solution, on evaporation, yielded 7.6 g. of a slightly pink viscous liquid which deposited a colorless crystalline solid after standing overnight. The solid acid melted at 117–118°, and after recrystallization from chloroform and from anhydrous ether melted sharply at 122°. It is difficultly soluble in cold water, but soluble in hot water and alcohol and slightly soluble in petroleum ether (b.p. 65–110°).

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.48; H, 9.74; neut. equiv., 186.2. Found: C, 64.00, 63.82; H, 9.49, 9.68; neut. equiv., 185.9.

The acid gave a positive test for hydroxyl with ceric nitrate. A small portion was heated with an aqueous solution of oxalic acid.[8] After several minutes an oily layer formed which on cooling was removed by extraction with ether. Anhydrous ammonia bubbled into the ethereal solution gave a colorless ammonium salt, m.p. 126°; Tiemann[9] gives the melting point of the ammonium salt of α-campholenic acid as 126°. The ammonium salt of the original hydroxy acid was also prepared by this method and found to melt at 142–144° with decomposition. It appeared to be stable at ordinary temperatures.

The 5.0 g. of liquid acid from the filtrate was purified by distillation to yield 3.7 g. of α-campholenic acid as a slightly yellow liquid with a sharp acid odor, b.p. 170–176° (30 mm.), n^{25}D 1.4744. It decolorized bromine in carbon tetrachloride immediately; no hydrogen bromine was given off. Its ammonium salt, prepared as above, melted at 125–126°. It decomposes quite rapidly on standing; the following analysis was made within 24 hours after the preparation.

Anal. Calcd. for $C_{10}H_{19}O_2N$: N, 7.56. Found: N, 7.12, 6.96, 6.91, in the order listed.

About 0.2 g. of this ammonium salt was heated in a sealed tube for 4 hours at 200°. The resulting amide was crystallized from petroleum ether, blades, m.p. 121–122°, reported[9] 124°. The quantity was too small to permit recrystallization.

The residue from the distillation of the α-campholenic acid solidified on standing, and after recrystallization from chloroform and from anhydrous ether yielded 1.3 g. of hydroxydihydro-α-campholenic acid. A total of 3.9 g. of the acid was obtained.

Material balance on this run was 95.7%, consisting of

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(7) J. Bredt, *J. prakt. Chem.*, [II] **106**, 336 (1923).

(8) *Cf.* O. Wallach, *Ann.*, **239**, 18 (1887).

(9) F. W. Tiemann, *Ber.*, **30**, 246 (1897).

TABLE I

OXIDATION OF ISOBORNEOL WITH CHROMIC ACID

Temperature was held below 30° for all oxidations

Run	Isoborneol, g.	CrO_3, g.	H_2O, ml.	gl. AcOH, ml.	Addn. time, hr.	Yield, % camphor	Yield, % OH-acid	Yield, % α-campholenic acid	Material balance, %
1	77.12	30	18	80	3.5	96.0	0.28	0.3	96.6
2	154.24	60	160	160	4.6	96.3	1.7	1.7	99.7
3	154.24	65	175	175	5.75	91.4	2.1	2.2	95.7
4	154.24	65	175	175	7.0	88.1	0.8	0.9	89.7

91.4% (139 g.) of camphor, 2.1% (3.9 g.) of hydroxydihydro-α-campholenic acid, and 2.2% (3.7 g.) of α-campholenic acid.

Check runs 2, 3 and 4 were made and the results are given in Table I

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

A Polarographic Study of the Oxalato Complexes of Titanium

BY ROBERT L. PECSOK

Titanium(III) and -(IV) yield reversible polarographic waves in oxalic acid solutions with pH less than 3. The half-wave potential is independent of the concentration of titanium, and is expressible as $E_{1/2} = -0.25 - 0.080\ pH + 0.020 \log [H_2C_2O_4]$ in volts *vs.* the saturated calomel electrode. Data are given from which this equation is derived and its form explained by a treatment of the equilibria involved. The yellow oxalato-titanium(III) ion has been investigated spectrophotometrically.

The polarographic reduction of titanium(IV) in oxalate solutions has been used by Adams[1] in the analysis of clays and clay products. He reported that the half-wave potential was a function of the concentrations of sulfuric acid, titanium, and iron. Lingane and Vandenbosch[2] questioned the dependence of the half-wave potential on the concentrations of titanium and iron, and gave data showing that it was independent of both.

The titanium waves have been studied in tartaric acid[3,4,5] and citric acid[4,5] solutions. This paper presents the results of a systematic study of the polarography of the titanium(III) and -(IV) oxalate complexes. An electrode reaction is proposed to account for the behavior of the half-wave potential of the system.

Experimental

All polarograms were taken with a Sargent Model XXI Polarograph utilizing an H-cell with an external saturated calomel electrode. No damping was employed for any polarograms. The cell was maintained at 25.0 ± 0.1° in a grounded water-bath. The internal resistance of the several cells used was assumed to be negligible since the half-wave potential of lead ion was found to be independent of its concentration.

Purified nitrogen was used to remove dissolved oxygen from the test solutions and from the supporting electrolyte before adding the titanous chloride reagent. Residual currents were measured and the proper corrections applied where necessary. In most cases, since the waves were so well defined with horizontal plateaus, residual current corrections were made by extrapolation.

The pH of the solutions was measured with a Beckman model G pH meter, in most cases, after the polarogram had been taken.

Solutions of titanous and titanic chloride made up from the commercially available 20% titanous chloride reagent were found to contain an approximately equivalent amount of zinc and thus were not suitable for this work. A stock solution of titanous chloride was prepared by distilling titanic chloride reagent in the presence of sodium, collecting only the water-white fraction, dissolving in redistilled hydrochloric acid, and reducing electrolytically between carbon electrodes under nitrogen. This stock solution was approximately 0.1 *M* in hydrochloric acid. The titanic chloride stock solution was prepared by oxidation of the titanous solution after increasing its hydrochloric acid content to 3 *M*. The titanous solution was standardized by pipeting an aliquot into an excess of ferric sulfate and subsequent titration with standard dichromate solution. The titanic solution was standardized by passage of an aliquot through a Jones reductor into an excess of ferric sulfate, followed by titration as above.

Supporting electrolytes were made up from reagent grade chemicals as required. No maxima were observed in any of the polarograms and therefore no suppressor was added.

Results and Discussion

Titanium(IV) forms complexes with many organic hydroxy acids. In preliminary work, re-

TABLE I

HALF-WAVE POTENTIALS OF TITANIUM(IV) IN ORGANIC ACIDS

Supporting electrolyte	$E_{1/2}$, v. *vs.* S.C.E.	Type of wave
0.2 *M* tartaric acid	−0.38	Reversible
Satd. tartaric acid	− .42	Reversible
0.2 *M* citric acid	− .37	Reversible
Satd. citric acid	− .49	Irreversible
Satd. salicylic acid	− .35	Reversible
0.2 *M* succinic acid	− .85	Poorly defined
0.2 *M* formic acid	− .79	Poorly defined
3.5 *M* lactic acid	− .40	Reversible
0.2 *M* acetic acid	− .85	Poorly defined
0.1 *M* hydrochloric acid	− .81	Irreversible
Satd. phthalic acid	− .93	Irreversible

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[1] D. F. Adams, *Anal. Chem.*, **20**, 891 (1948).

[2] J. J. Lingane and V. Vandenbosch, *ibid.*, **21**, 649 (1949).

[3] V. Caglioti and G. Sartori, *Gazz. chim. ital.*, **66**, 741 (1936).

[4] R. Strubl, *Collection Czech. Chem. Commun.*, **10**, 475 (1938).

[5] M. Kalousek, *ibid.*, **11**, 592 (1939).