placed in a 1-liter, 3-necked, round-bottomed flask equipped with a reflux condenser, dropping funnel, and electrically driven glass stirrer and brought to constant temperature in a thermostat maintained at 25 ± 0.5°. One-half mole of bromine dissolved in 50 cc. of aqueous acetic acid was added to the solution through the dropping funnel, with constant stirring, over a period of one hour. Stirring at constant temperature was continued for twenty-three hours after completion of the addition of bromine. The reaction mixture was then poured into cold water and stirred with bisulfite to remove the unreacted bromine. The diluted mixture was divided into two portions. Each portion was extracted with two 200-cc. portions of ether. The ethereal extract was washed with aqueous sodium carbonate until all evolution of carbon dioxide had ceased. The alkaline washings were combined and extracted with 100 cc. of ether. The combined ethereal extracts were dried over anhydrous sodium carbonate for distillation. The ether and unreacted benzene were removed and discarded. Separation of the residue was effected by means of a twenty-inch electrically heated column filled with glass helices. The first fraction, containing bromobenzene and *t*-butylbenzene, distilled at 150–170°, d^{25}_{25} 0.8678, amount 37.4 g. The column was allowed to drain and was replaced by a small distillation outfit through which the entire residue, consisting of *t*-butylbenzene and bromo-*t*-butylbenzene, was distilled. This second fraction contained 41.2 g. of material, d^{25}_{25} 1.2453.

The density of the first fraction corresponds to 0.88% bromobenzene (0.0021 mole). The density of the second fraction corresponds to 99.28% bromo-*t*-butylbenzene (0.1919 mole).

A 4.3390 g. (5 cc.) sample of fraction I was dissolved in 40 cc. of ether and allowed to stand in contact with 1 g. of sodium wire overnight at room temperature. The sodium which had not reacted in twelve hours was destroyed with ethanol. The sodium bromide formed was extracted with water. The aqueous solution was diluted to 50 cc., of which 10-cc. portions were treated with 5 cc. of 0.1 *N* silver nitrate solution. The excess silver nitrate was titrated with 8.65 cc. of 0.0522 *N* potassium thiocyanate. This value corresponds to 0.0021 mole of bromobenzene in fraction I.

A 1.2453 g. (1-cc.) sample of fraction II was dissolved in 40 cc. of benzene and refluxed with 2 g. of sodium, cut into small pieces, for five hours. The aqueous extract of the sodium bromide formed was diluted to 100 cc.; 10-cc. portions were treated with 10 cc. of 0.1 *N* silver nitrate. The excess silver nitrate was titrated with 8.05 cc. of 0.0522 *N* potassium thiocyanate. The titration value corresponds to 0.1918 mole of bromo-*t*-butylbenzene in fraction II.

Applying the equation of Ingold, *et al.*,[6,39] $k_x/k_y = (\log x/x_0)/(\log y/y_0)$, where x and y represent the final concentrations of *t*-butylbenzene and benzene and x_0 and y_0 the initial concentrations, the ratio of velocities is 114.9/1.

Acknowledgment.—We gratefully acknowledge the assistance afforded by a grant from the Penrose Fund of the American Philosophical Society.

Summary

1. *t*-Butylbenzene is brominated about 115 times faster than benzene at 25°. This is explained by hyperconjugation involving carbon–carbon bonds.

2. It is pointed out that the so-called inductive effect of alkyl groups may be explained by hyperconjugation, and it is suggested that this may explain the entire effect. The factors that influence the operation of the effect are discussed.

[39] Ingold and Smith, *J. Chem. Soc.*, 905 (1938).

BRYN MAWR, PA. RECEIVED AUGUST 8, 1947

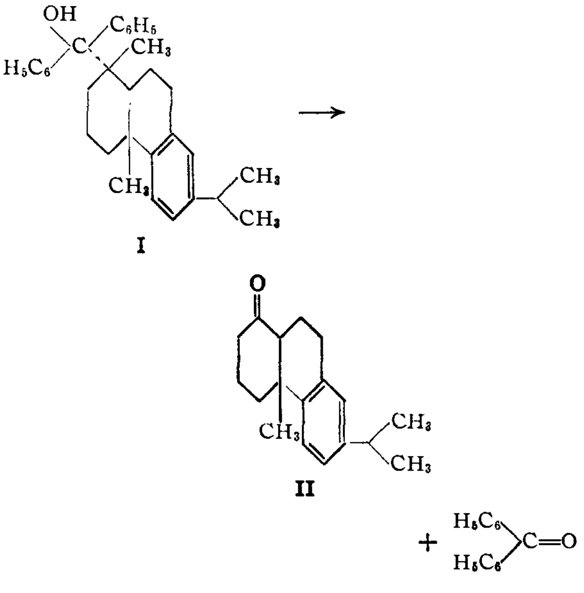
[CONTRIBUTION FROM RIDBO LABORATORIES, INC.]

Studies on Resin Acids.[1] II. The Oxidation of Diphenyl-*t*-dehydroabietinol. A Postulated Mechanism

BY HAROLD H. ZEISS

The oxidation of tertiary alcohols is not a reaction generally employed in the laboratory principally because of product complexity and low yields. In the course of our study of the resin acids the previously reported tertiary resin alcohol, diphenyl-*t*-dehydroabietinol (I),[1] has been subjected to chromic acid oxidation in glacial acetic acid from which the cyclic ketone, 1-keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (II), is obtained in yields as high as 67%, together with benzophenone. It is to be noted that this oxidation differs from the Barbier–Wieland type of oxidative degradation in that there cannot be a preceding dehydration of the carbinol to an olefin, since no hydrogen atoms are attached to the carbon atoms at which oxidation occurs.

Fifteen years ago Vocke[2] submitted the diphenyl carbinol of tetrahydroabietic acid to the



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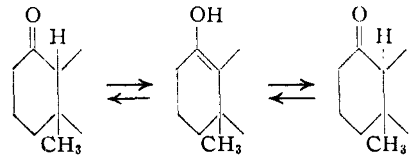
[1] Paper I, THIS JOURNAL, **69**, 302 (1947).

[2] Vocke, *Ann.*, **497**, 247 (1932).

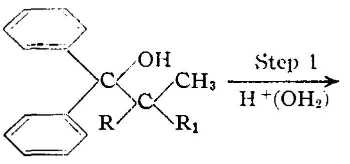
action of chromic acid at room temperature and with warming from which only benzophenone and benzoic acid were reported in the reaction mixture in addition to a considerable amount of unoxidized carbinol. At 50° diphenyl-*t*-dehydroabietinol is also largely unchanged by chromic acid and at 90° is oxidized to acidic material at the expense of the ketone (II). The optimum temperature for this oxidation has been found to be 80°, at which temperature the maximum yield of (II) is obtained with no unreacted carbinol (I) present and a minimum amount of acidic products, probably arising from ring cleavage.

The cyclic ketone (II) is isolated, presumably, as a stereoisomeric mixture resulting from keto-enol tautomeric equilibrium. The ease of this tautomerism is adequately supported by Hückel,[3] who reported the facile conversion of *cis*-α-decalone to *trans*-α-decalone by simple distillation at atmospheric pressure. After purification through the sodium bisulfite addition product and through the use of Girard reagent T, the ketone (II) was obtained analytically pure as a pale yellow, viscous liquid from which the crystalline 2,4-dinitrophenylhydrazone derivative has been prepared. The sodium bisulfite addition product, combustion analyses and molecular refraction data leave little doubt that the structure of the cyclic ketone is as represented by (II). The identity of the benzophenone was established by mixed melting point determination and the 2,4-dinitrophenylhydrazone derivative.

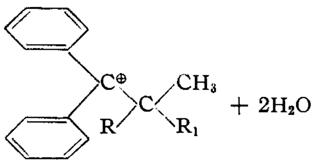


As a gross approximation this reaction may be described as a dealcoholation (loss of methyl alcohol) followed by cleavage of the resulting double bond to form (II) and benzophenone. This of course is a highly oversimplified explanation but one which stipulates that any reasonable mechanism must account for the loss of the elements of methyl alcohol. One such mechanism is postulated solely as the basis of a working hypothesis.

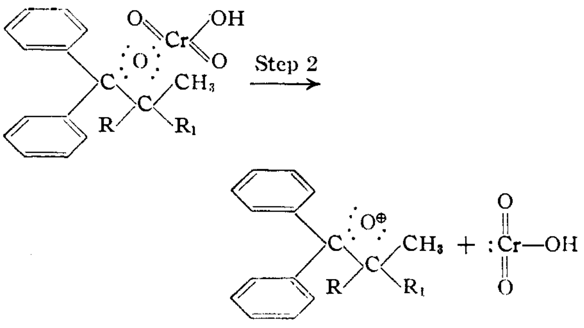
The first step is a proton transfer reaction to form a tertiary carbonium ion stabilized by resonance contributions from two phenyl groups (Step 1).



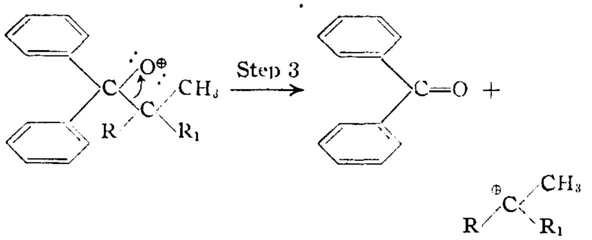
$R = —CH_2$
$R_1 = —CH$



The resultant center of low electron density is susceptible to nucleophilic attack by chromate ion to form a chromium complex which may then dissociate into two fragments (Step 2), the chromium atom now having a full share in the electron pair and the tertiary carbon fragment possessing a positively charged oxygen atom. The other alternative is a Wagner–Meerwein rearrangement leaving the electron deficient center on the carbon atom bearing the R and R₁ substituents. This latter possibility is unlikely to predominate because of the higher energy of the resulting carbonium ion.



In order to relieve the situation in which the oxygen atom is bearing a positive charge, the electron pair of the carbon–carbon bond must migrate (Step 3) since the phenyl-carbon bonds are unavailable.



This shift releases the diphenylmethyl structure as benzophenone and leaves the positive charge on the carbon atom carrying the methyl group.

Repetition of chromate ion attack on the new carbonium ion and subsequent formation of positive oxygen leaves three possibilities open for electron shift. By Steps 4a or 4b the acidic by-products are explained. Step 4c accounts for the formation of (II) but invites high speculation as to the formation of the very high energy methyl carbonium ion. Another explanation is one in which the carbonium ion rearranges to form the exocyclic double bond which immediately is

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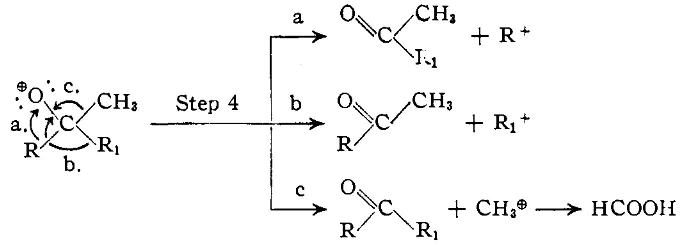
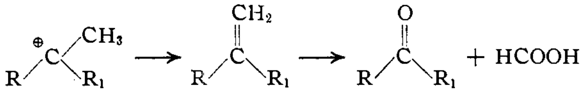
[3] Hückel, *Ann.*, **441**, 1 (1925).



cleaved by chromate ion to (II) and formaldehyde or formic acid. In this connection it is



interesting to note that Phillipov,[4] on oxidation of 1-methylcyclohexanol-1 with permanganate in aqueous solution, obtained cyclohexanone and formic acid on the one hand and acetic acid and glutaric acid on the other. The latter reaction was preponderant, however, under these conditions.

This oxidation is being further investigated as to the mechanism involved and its general application to tertiary alcohols as a class.

Experimental

1-Keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene (II): (a) Oxidation at 90°.—A solution of 42 g. of chromic trioxide in 30 ml. of water and 280 ml. of glacial acetic acid was added dropwise to a stirred solution of 33 g. of diphenyl-*l*-dehydroabietinol[5] in 300 ml. of glacial acetic acid at 90°. The addition extended over a period of one and one-half hours after which time heating and stirring were continued for three hours. The acetic acid was removed by distillation at the water pump and the remaining residue treated with sulfurous acid and dilute sulfuric acid on the steam-bath. The oily layer appearing on the surface of the cooled green solution was then extracted with ether. After washing the ethereal layer with water, the acidic material[6] was extracted with 1% sodium hydroxide. The ether layer was then washed free of alkali, dried over magnesium sulfate and the ether evaporated. The orange-red oil thus obtained gave two main fractions on fractional distillation: fraction 1, distilling at 140–150° (3 mm.) as a yellow fluid, and fraction 2, distilling at 220–230° (7 mm.) as an orange-red, viscous oil. Crystallization from methanol of fraction 1 gave large, transparent rods of benzophenone melting at 46.5–47.5°. Its 2,4-dinitrophenylhydrazone was prepared which gave a m. p. at 238–239°. A mixed m. p. of the crystals from fraction 1 with authentic benzophenone showed no depression. The yield of fraction 2, compound (II), was 9 g. (46%) and was identified as described under (b).

(b) Oxidation at 80°.—85 g. of diphenyl-*l*-dehydroabietinol was oxidized in exactly the same manner as in (a) with 103 g. of chromic trioxide with the one exception that the solution was maintained at 80 ± 0.5° during the oxidation. Fractional distillation of the neutral portion of the oxidation mixture gave 31.5 g. (63.5%) of crude ketone (II), boiling at 165–215° (1 mm.), and 16.2 g. (46%) of benzophenone.

The ketone was purified for analysis by the following methods: redistillation of the crude ketone, precipitation of the sodium bisulfite addition product in the cold (too unstable for characterization), regeneration and redistillation of (II), treatment with Girard reagent T, regeneration and final distillation of (II) as a pale yellow, viscous liquid at 208–212° (3 mm.[7]); $[\alpha]^{23}\text{D}$ 46° (4% in abs. alcohol); $[\eta]^{22}\text{D}$ 1.5572; d^{22} 1.0582.

Anal.[8] Calcd. for $C_{18}H_{24}O$: C, 84.38; H, 9.36. Found: C, 84.42, 84.54; H, 9.60, 9.41; M_R calcd., 77.65; found, 78.01.

The 2,4-dinitrophenylhydrazone of (II) was prepared in the usual manner which, after three recrystallizations from ethyl acetate, gave a sharp m. p. of 176.5–177°. A mixed m.p. with 2,4-dinitrophenylhydrazine showed a 12° depression.

Anal.[8] Calcd. for $C_{24}H_{28}N_4O_4$: N, 12.84. Found: N, 12.43, 12.32.

Acknowledgment.—The author is grateful to Dr. M. Frisch for experimental assistance in this work.

Summary

The oxidation of the tertiary alcohol, diphenyl-*l*-dehydroabietinol, to the cyclic ketone, 1-keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene, is described in which dehydration preliminary to oxidation cannot occur. A mechanism for the oxidation of this diphenyl carbinol has been postulated.

PATERSON, NEW JERSEY RECEIVED SEPTEMBER 3, 1947

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[4] Phillipov, *J. prakt. Chem.*, [2] **93,** 162 (1916).

[5] $[\alpha]^{23}\text{D}$ 91° (4% in absolute alcohol).

[6] These by-products were not investigated.

[7] All distillations for the purification of (II) were carried out in a short path still with a central take-off; see footnote (51), Woodward and Doering, THIS JOURNAL, **67**, 860 (1945).

[8] Combustion analysis by Dr. Carl Tiedcke Microlaboratories, New York.