to mix the perhydrol with the heavy water and subsequently separate by physical methods the bulk of the hydrogen peroxide from the water, so that a direct check of the extent of any exchange was not feasible. Instead, 1-ml. lots of the perhydrol were mixed at room temperature with 2-ml. portions of heavy oxygen water, and the solution left for 48 hours with addition of a trace of a catalyst active in promoting the decomposition of hydrogen peroxide. At the end of this time the liquid was raised just to the boiling point to complete the decomposition, and the residual water purified and its density determined. The complete disappearance of the peroxide was confirmed by chemical tests. In a further experiment the mixture of peroxide and heavy water was left for 24 hours at room temperature before addition of the catalyst. The results are shown in Table II, from which it is evident that the decrease in density observed is wholly accounted for by the water produced in the decomposition of the peroxide and that added with the perhydrol, and we conclude that the oxygen evolved did not suffer exchange with the enriched water. Clearly under these conditions there is little if any exchange of the hydrogen peroxide molecule with water: neither does the heterogeneous catalytic decomposition require the active participation of the water molecule.

TABLE II

Catalyst	Obs.	$\Delta\gamma d$ calcd. for 1.0 from H_2O_2	$\Delta\gamma d$ calcd. for 2.0 from H_2O_2
$MnO_2 + Mn_2O_3$	−51	−50	−56
Fe_2O_3	−51	−50	−56
Palladized asbestos	−52	−50	−56
Platinized asbestos	−52	−50	−56
Platinized asbestos added after 24 hr.	−52	−50	−56

The perhydrol was then used to oxidize sodium sulfite: 2 ml. of perhydrol was mixed with 4 ml. of enriched water, and 1.71 g. of finely powdered anhydrous sodium sulfite added slowly with stirring. The temperature of the mixture reached 40° during the oxidation. At the end of the oxidation the mixture was boiled, cooled and the density of the water determined as before. A parallel experiment showed that substances capable of decolorizing permanganate were equivalent to less than 1 ml. of 0.1 N $KMnO_4$ at the end of the reaction. With the quantities used above, the decrease in density to be expected due to the water added as perhydrol, including that which would remain after the reaction $H_2O_2 + Na_2SO_3 \rightarrow H_2O + Na_2SO_4$ was $\Delta\gamma d = -50$.

The total decrease to be expected if the second oxygen atom in the hydrogen peroxide molecule suffered exchange with the heavy water was $\Delta\gamma d = -56$, while the total decrease to be expected if the three oxygen atoms of the sodium sulfite also exchanged was $\Delta\gamma d = -65$: the observed decrease in water density was $\Delta\gamma d = -52$, demonstrating that, allowing for the normal error, the experimental technique, and by comparison with the results in Table II, direct transfer occurs of the oxygen atom from the hydrogen peroxide molecule to the sodium sulfite. The experimental error in the water density determinations recorded here is ±1 γd ($1\gamma d$ = 1 in 10^6 of density).

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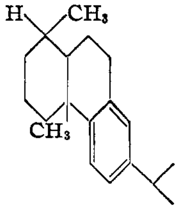
Diphenyl-*t*-dehydroabietinol and its Oxidation Product

BY HAROLD H. ZEISS

In the course of continued work with the resin acids it has become apparent to us that our earlier reported studies in this field are subject to correction. It has been found that the procedure described for the isolation of diphenyl-*t*-dehydroabietinol (I)[1] leads instead to a cleavage product, which, on treatment with hot chromic acid, is oxidized to ketonic material of different structure than that previously proposed.[2] In view of the recently published paper of Brossi, Gutman and Jeger[3] in which the same conclusions are reached, it is considered appropriate to report our results at this time.

Authentic I is obtained from the Grignard reaction between methyl dehydroabietate and phenylmagnesium bromide according to the original procedure, with the exception of subjecting the crude product to crystallization from glacial acetic acid instead of to distillation. The ultraviolet spectrum of the crystalline carbinol, m.p. 139°, is consistent with that of the dehydroabietic-type structure as exemplified by the spectrum of dehydroabietic acid (Fig. 1). If, however, the crude carbinol is vacuum distilled in a Claisen flask, a yellow oil is collected which analyzes correctly for I but which gives an ultraviolet spectrum similar to that of benzophenone. The explanation for this has been secured from the observation that crystalline I, when heated between 190–230° and then cooled to room temperature, is transformed into a yellow liquid which also gives a benzophenone-type spectrum (Fig. 2). The presence of benzophenone is confirmed by its isolation from the mixture.

The thermal cleavage of I is reminiscent of the type experienced by other workers with tertiary alcohols.[4] In this instance the expected products are benzophenone and nordehydroabietane (II, 12-methyl-1,2,3,4,9,10,11,12-octahydroretene).



II

Evaporative distillation and chromatography were

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(1) H. H. Zeiss, THIS JOURNAL, **69**, 302 (1947).

(2) H. H. Zeiss, *ibid.*, **70**, 858 (1948).

(3) A. Brossi, H. Gutmann and O. Jeger, *Helv. Chim. Acta*, **33**, 1730 (1950).

(4) P. Ramart-Lucas, *Ann. chim.*, [8] **30**, 349 (1913); V. Grignard and F. Chambret, *Compt. rend.*, **182**, 299 (1926).

employed to separate a hydrocarbon fraction (IIa) from the benzophenone.

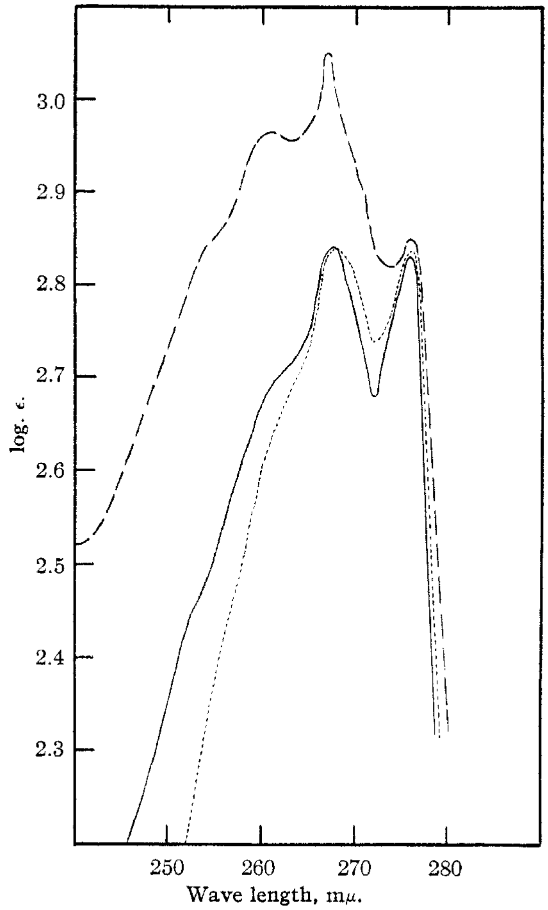


Fig. 1.—Dehydroabietic acid, 0.0004 *M*, (——); IIa, 0.0003 *M*, (- - - -); I, 0.00026 *M*, (— —), in 95% ethanol.

That the hydrocarbon structure is represented by II is suggested by the comparison of the ultraviolet spectrum of IIa with that of dehydroabietic acid (Fig. 1). The failure of IIa to decolorize a solution of potassium permanganate indicates the absence of olefinic linkage. When equimolecular amounts of benzophenone and IIa are combined, the spectrum of the synthetic mixture is similar to that obtained with the cleavage mixture.

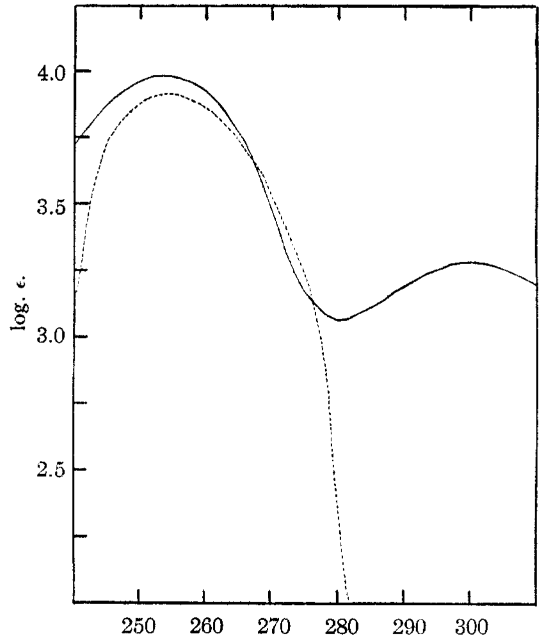
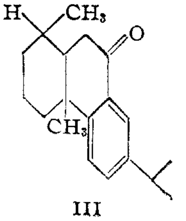


Fig. 2.—IIIa, 0.00006 *M*, (——); cleavage product, 0.00007 *M*, (- - - -), in 95% ethanol.

Oxidation of the cleavage products of I with chromic acid[2] cannot conceivably lead to 1-keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene as stated. The isolation of benzophenone from the original oxidation is accounted for by its initial presence. The ketone (IIIa) which was also isolated is believed to consist chiefly of 9-keto-12-methyl-1,2,3,4,9,10,11,12-octahydroretene (III). The spectrum of IIIa contains absorption bands (Fig. 2) characteristic of compounds having a keto group conjugated with a phenyl ring as in α-tetralone and 7-methyl-α-tetralone.[5] Combustion analyses of III and of its 2,4-dinitrophenylhydrazone would agree with those reported for IIIa. Oxidation of a hydrocarbon of structure II at the C-9 position is also consistent with the point of oxidative attack in dehydroabietic acid to give 9-ketodehydroabietic acid.[6] One attempt to dehydrogenate IIIa with palladium-charcoal in boiling *p*-cymene according to Linstead and Michaelis[7] failed to yield any isolable 9-retenol and/or retene. The oxidation thus encountered can no longer be regarded as a basis for the mechanism earlier hypothesized.[2] However, there is at present no evidence which contraindicates the intermediate formation of chromate esters in the oxidation of tertiary alcohols. This possibility, therefore, remains attractive but unconfirmed.



III

Experimental[8]

Diphenyl-*t*-dehydroabietinol (I).—Methyl dehydroabietate (3 g.) and phenylmagnesium bromide reacted in ether as previously described.[1] After removal of diphenyl by steam distillation, the residual gum was dissolved in glacial acetic acid, treated with Norit and then allowed to stand at room temperature for several weeks. The crystallizate which had formed was recrystallized from acetic acid to give 1.5 g. of large, transparent prisms: m.p. 138–139°; $[\alpha]^{27}_{D}$ +45° (α = +0.27°, c = 0.6%).

Anal. Calcd. for $C_{32}H_{38}O$: C, 87.61; H, 8.73. Found: C, 87.37; H, 8.55.

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(5) P. Ramart-Lucas and M. J. Hoch, *Bull. soc. chim.*, [5] **2**, 327 (1935), reported $\lambda_{max.}$ at 239 and 279 mμ with log ε = 4.03 and 3.17, respectively, for α-tetralone; for 7-methyl-α-tetralone (*cf.* reference (3)) $\lambda_{max.}$ has been found at 251 and 303 mμ with log ε = 4.22 and 3.48, respectively.

(6) A. E. Drake, U. S. Patent 2,434,643 (1948).

(7) R. P. Linstead and K. O. A. Michaelis, *J. Chem. Soc.*, 1134 (1940).

(8) All melting points are corrected. Optical rotations were determined in 95% ethanol.

Thermal Cleavage of I.—Crystalline I (0.20 g.) was placed in a small glass tube open to the atmosphere and heated in an oil-bath for one hour between 190–230°. On cooling a clear yellow liquid was obtained, which, on treatment in 40 ml. of ethanol with 2,4-dinitrophenylhydrazine, gave 0.06 g. of the corresponding hydrazone of benzophenone. Recrystallization from ethanol yielded pure material; m.p. 238–239°. Mixed m.p. with authentic 2,4-dinitrophenylhydrazone produced no depression.

The Grignard reaction was repeated with 38 g. of methyl dehydroabietate, and the crude product was freed of biphenyl by steam distillation. The impure carbinol was then subjected to *evaporative distillation* at 3 mm. in a modified Hickman still. At 90° a small amount of residual biphenyl, m.p. 67–69°, collected on the cold finger. Between 140–150° 2.5 g. of distillate was collected which slowly crystallized. Recrystallization from methanol yielded unreacted methyl dehydroabietate, m.p. 60.5–61.5°. Another cut (3 g.), distilling in the same range, was also crystalline ester. An increase in temperature to 180° produced 5 g. of a non-crystallizing oil. The main fraction was evaporatively distilled between 190–200° and consisted of 12 g. of a clear, colorless liquid. An additional amount (5 g.) was obtained in the same temperature range. A portion of the main fraction (1 g.) with 1.5 g. of 2,4-dinitrophenylhydrazine in 100 ml. of ethanol and 2 ml. of hydrochloric acid yielded 0.5 g. of benzophenone 2,4-dinitrophenylhydrazone.

Isolation of Hydrocarbon Fraction (IIa).—A portion of the main fraction (5 g.) from the above distillation was redistilled evaporatively at 3 mm. Between 60–90° two fractions were separated which deposited benzophenone on standing. The fraction collected between 90–100° (2.2 g.) was dissolved in 200 ml. of petroleum ether (b.p. 30–60°) and passed through a column of aluminum oxide ($h = 8''$, $d = 1''$). The column was washed with an additional 500 ml. of petroleum ether, and the solvent ether removed. The residual oil was again evaporatively distilled between 90–100° (3 mm.): 0.9 g.; $n^{25}\text{D}$ 1.5428; $d^{25}{}_4$ 0.961; $[\alpha]^{25}\text{D}$ + 102° ($\alpha = +1.04°$, $c = 1.02$).

Anal. Calcd. for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 89.46; H, 10.53.

The hydrocarbon did not decolorize potassium permanganate in acetone solution but reacted with bromine in carbon tetrachloride with the evolution of hydrogen bromide.

Oxidation of IIa.—Ten grams of the hydrocarbon (IIa) was oxidized at 80° with chromic acid as described.[2] From the oxidation mixture there was obtained 2.8 g. of ketone (IIIa), $n^{27}\text{D}$ 1.5560. Its 2,4-dinitrophenylhydrazone, after recrystallization from ethyl acetate, melted between 196–197.5°; mixed with 2,4-dinitrophenylhydrazine, the m.p. was depressed.

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Comment on Mechanism of Photolysis of Acetaldehyde

BY PAUL D. ZEMANY AND MILTON BURTON[1]

The banded absorption of acetaldehyde at longer wave lengths (3400 Å.) and the continuous absorption in the shorter ultraviolet (2800–2400 Å.) with gradual transition between suggest two different mechanisms of the photolytic process.[2] Gorin introduced iodine into samples photolyzed at 25°; assuming that iodine would react with any methyl radicals primarily formed and that all methane produced under such circumstances comes from a primary rearrangement, he concluded that the free radical split preponderates at 3130 Å. but that the rearrangement is the major reaction at 2537 Å.[3] Comparison of the high-temperature quantum yield data of Rollefson and Grahame[4] may also be used as evidence that the free radical split occurs more readily at the longer wave length. Blacet and his co-workers[5] used methods similar to those of Gorin but arrived at results quantitatively different. If we note the probabilities of radical split and molecular rearrangement as p_r and p_m, respectively, the data for p_r/p_m may be compared

λ, Å.	Gorin	Blacet, *et al.*
3130	2.6	20
2537	0.34	1.1

By a different method which is described in detail elsewhere[6] we have obtained data which permit an independent estimate of the probabilities of the competing photolytic mechanisms.

Equimolar mixtures of CH_3CHO and CD_3CDO at a total pressure of 37.8 cm. were photolyzed at a temperature of 25° to the extent of 3 or 4 per cent. In the first sample in a quartz bulb irradiated by a Germicidal lamp, photolysis was caused largely by the 2537 Å. mercury line. In a second sample in a Pyrex bulb, with GE H4 lamp as illuminant, photolysis was effected by radiation longer than 3000 Å.

Consider the competing reactions

$$CD_3CDO \xrightarrow{h\nu} CD_3 + CDO \qquad (1)$$

$$CD_3CDO \xrightarrow{h\nu} CD_4 + CO \qquad (2)$$

The succeeding reactions for the energetic radical primarily produced include two important reactions for our consideration

$$CD_3 + CD_3CDO \longrightarrow CD_4 + CD_3CO \qquad (3)$$

$$CD_3 + CH_3CHO \longrightarrow CD_3H + CH_3CO \qquad (4)$$

Reaction (2) can yield only CD_4 but reaction (1) can yield both CD_4 and CD_3H. If only rearrangement occurs in the photolysis of the mixture, the product methane should be exclusively CD_4 and CH_4. Using mass spectrographic methods of analysis the following results were obtained.

λ, Å.	3130	2537
CD_4/CD_3H	1.08	2.4

No CD_2H_2 was formed.

The interpretation of these results involves certain considerations of the nature of the reactions. The very existence of CD_3H in relatively large yield shows that reaction (3) can occur at 25°. However, the best data we have[3] indicate that the chain length can at most be unity at room temperature. A reasonable conclusion is that CD_3 as initially formed in reaction (1) has excess energy, even when produced with light of $\lambda > 3000$ Å., sufficient to provide activation energy for reaction (3) in a first collision. To complete our estimate we make assumptions regarding reactions (3) and (4): (a) They have approximately the same steric factors. (b) Their activation energies are not high.[7] (c)

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[1] Department of Chemistry, University of Notre Dame, Notre Dame, Ind.

[2] P. A. Leighton and F. E. Blacet, THIS JOURNAL, **55**, 1766 (1933).

[3] E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[4] G. K. Rollefson and D. C. Grahame, *ibid.*, **7**, 775 (1939).

[5] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942); F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

[6] P. D. Zemany and M. Burton, *J. Phys. Colloid Chem.*, forthcoming publication.

[7] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, gives 8–10 kcal./mole.