[Contribution from the George Herbert Jones Laboratory of the
University of Chicago]

THE PREPARATION AND OXIDATION OF *tert*-DIPHENYLDEHYDROABIETINOL

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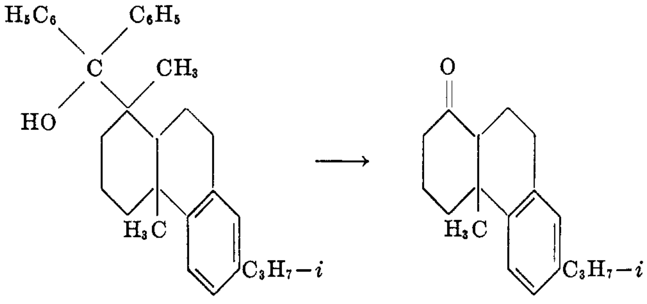
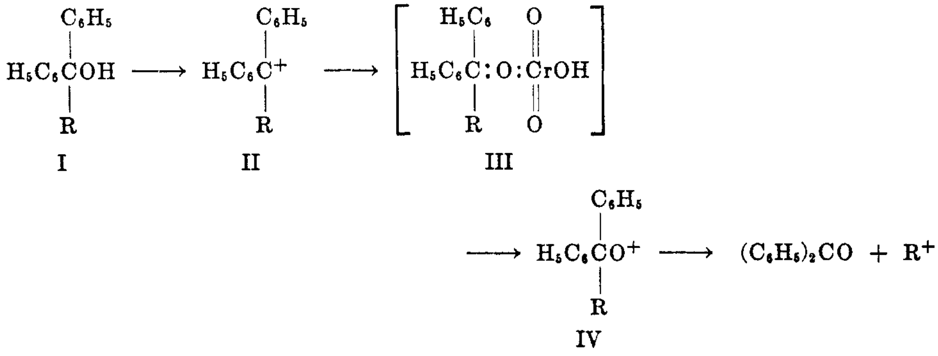
The attention of the present authors was attracted to the reported chromic acid oxidation of *tert*-diphenyldehydroabietinol (I) to "1-keto-12-methyl-7-isopropyl-1,2,3,4,9,10,11,12-octahydrophenanthrene" (*i.e.*, 1-oxo-4a-methyl-7-isopropyl-1,2,3,4,4a,9,10-10a-octahydrophenanthrene)[1] (V) because of the unusual reaction mechanism proposed "as the basis of a working hypothesis" to account for the reaction.



I V

It is suggested that the carbinol (I) is first dehydroxylated to form a carbonium ion (II), which then forms a complex (III) with a dichromate ion, from which it acquires an oxygen atom to form a positively charged alkoxy ion (IV). Decomposition of the positive alkoxy ion is presumed to liberate benzophenone and a carbonium ion (R^+), which is eventually converted to the cyclic ketone (V) (2).



$$\underset{\text{I}}{H_5C_6\overset{C_6H_5}{\underset{R}{C}}OH} \longrightarrow \underset{\text{II}}{H_5C_6\overset{C_6H_5}{\underset{R}{C^+}}} \longrightarrow \underset{\text{III}}{\left[H_5C_6\overset{H_5C_6}{\underset{R}{C}}{:}O{:}\overset{O}{\underset{O}{Cr}}OH\right]}$$

$$\longrightarrow \underset{\text{IV}}{H_5C_6\overset{C_6H_5}{\underset{R}{C}}O^+} \longrightarrow (C_6H_5)_2CO + R^+$$

Observations in this laboratory (3) cast serious doubt on the probability of the suggested behavior of the alkoxy ion (IV). Several tertiary aralkyl hydro-

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[1] Zeiss uses the abietic acid numbering of Fieser in naming the ketone said to be the oxidation product. The conventional phenanthrene numbering of the "Ring Index" is employed in the name inserted parenthetically.

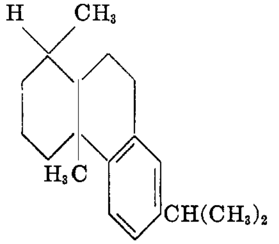
peroxides studied have been shown to react with Lewis acids to form intermediate alkoxy ions analogous to IV, which immediately rearrange by migration of an aryl group, to form carbonium ions. Under ordinary conditions the ultimate products are a ketone and a phenol. For example the acid-catalyzed decomposition of α-cumyl hydroperoxide may be outlined as follows:

$$C_6H_5(CH_3)_2COOH \longrightarrow C_6H_5(CH_3)_2CO^+ \longrightarrow$$

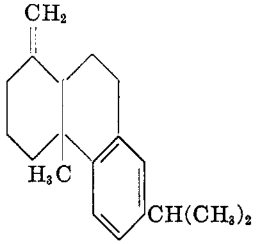
$$C_6H_5O(CH_3)_2C^+ \longrightarrow (CH_3)_2CO + C_6H_5OH$$

Similar behavior of the alkoxy ion (IV) would preclude the formation of benzophenone; the desirability of a reinvestigation of the reported oxidation of *tert*-diphenyldehydroabietinol seemed indicated.

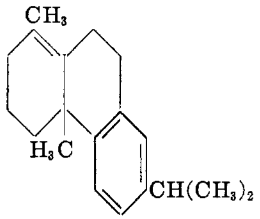
The preparation and thermal decomposition of tert-diphenyldehydroabietinol (I). Methyl dehydroabietate (m.p. 63°) reacted with phenylmagnesium bromide to give a hard glass from which *tert*-diphenyldehydroabietinol was obtained (by purification through an alumina chromatogram) as a white crystalline solid (m.p. 140–141°; $[\alpha]_D^{22}$ +57.6°). The material prepared by Zeiss (1, 2) (by distillation of the Grignard reagent reaction product), and assumed by him to have this constitution, was a pale yellow oil ($[\alpha]_D^{23}$ +91°).[2] There is no difficulty in duplicating Zeiss's results nor of demonstrating that Zeiss's experiments were not performed with *tert*-diphenyldehydroabietinol, since that carbinol undergoes extensive thermal decomposition when isolated in the manner described by him. Thus, when *tert*-diphenyldehydroabietinol (m.p. 140–141°) was distilled at reduced pressure the distillate was a colorless oil ($[\alpha]_D^{23}$ +53.7°) which could not be crystallized. On passage through an alumina column, followed by distillation, this oil was resolved into a mixture of hydrocarbons, benzophenone (51%), benzhydrol (19%), and unchanged carbinol (8%). The latter compound was isolated as its dehydration product (described hereafter). The hydrocarbon fraction was therefore (note formation of benzophenone and benzyhydrol) a mixture of the non-olefinic compound VI and, probably, olefins VII and VIII.



VI



VII



VIII

Ozonolysis of the hydrocarbon fraction confirmed this view. Most of the material was unattacked by ozone, and, after distillation, gave the correct carbon and hydrogen values for the hydrocarbon VI. The formaldehyde formed in the ozonolysis (isolated as the dimethone derivative) indicates the presence of the hydrocarbon

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[2] The sign of rotation is not specifically indicated by Zeiss, and is therefore presumably positive.

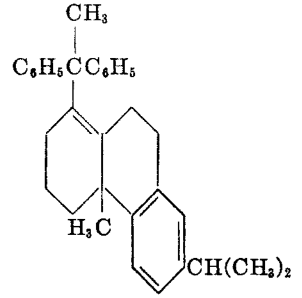
VII. The ketonic reaction product (no reaction with Schiff's reagent) when treated with 2,4-dinitrophenylhydrazine gave a deep-red precipitate. The color would suggest that the hydrazone must be one of an α,β-unsaturated ketone. The formation of such an unsaturated ketone from the ozonolysis product of VIII would not be unexpected, for the strong acid used in the preparation of the hydrazone would be sufficient to promote cyclization of the diketone formed from VIII.

It would appear therefore that the oxidation described by Zeiss (2) was not performed upon the supposed carbinol, and that any conclusions based upon that supposition should be discarded.

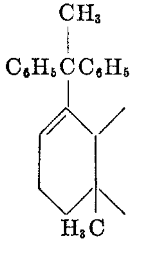
Oxidation of tert-diphenyldehydroabietinol with chromic acid. The authors also failed to isolate any of Zeiss's supposed ketone (V) from the oxidation products of the pure carbinol, although Zeiss (2) claims a yield of 67% for this substance. The products isolated by us were benzophenone and unidentified ketonic substances. Repeated attempts to separate a homogeneous material (Girard reagent T, chromotograms) were of little avail. In this respect our experience is similar to that of Vocke (4) with the oxidation products of the analogous *tert*-diphenyltetrahydroabietinol. We are therefore forced to the conclusion that the ketone sought (V) was not obtained by Zeiss in any high degree of purity (if at all).

Reaction of tert-diphenyldehydroabietinol with acid. When *tert*-diphenyldehydroabietinol (I) ($C_{32}H_{38}O$) dissolved (or suspended) in glacial acetic acid or methanol, is treated with a small amount of perchloric or sulphuric acid, a quantitative yield of a hydrocarbon, $C_{32}H_{36}$, is obtained. This formula corresponds to the loss of a molecule of water from *tert*-diphenyldehydroabietinol. The ultraviolet absorption spectrum of this hydrocarbon is almost identical with that of the carbinol (I), indicating that the hydrocarbon has no additional conjugation.

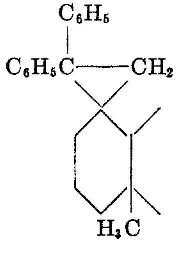
Structures assignable to the hydrocarbon, $C_{32}H_{36}$, produced by the dehydration of the carbinol (I), might include IX, X, and XI, as well as one containing a seven-membered ring (enlargement of the cyclohexane ring). However, a preponderance of the evidence seems to favor structure IX for the hydrocarbon. A similar rearrangement was observed (and proved conclusively) by Bateman and Marvel (5) in the acid dehydration of *tert*-butyldiphenylcarbinol.



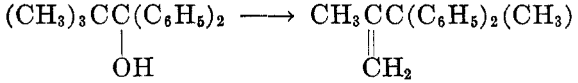
IX



X



XI



$$(CH_3)_3C\underset{\substack{|\\ OH}}{C}(C_6H_5)_2 \longrightarrow CH_3\underset{\substack{\|\\ CH_2}}{C}C(C_6H_5)_2(CH_3)$$

Hydrogenation of the hydrocarbon $C_{32}H_{36}$ was difficult, and when it was effected under drastic conditions the product was an octahydro derivative of the parent substance, namely, $C_{32}H_{44}$. Bromine (in carbon tetrachloride) reacted with this hydrocarbon only in the presence of light, and hydrogen bromide was evolved. The oily reaction product, which could not be induced to crystallize, was chromatographed on alumina, and gave a crystalline solid which contained no bromine and which gave an elementary analysis corresponding to the empirical formula $C_{32}H_{34}$. The ultraviolet absorption spectrum of this compound was similar to that of α- and β-methylstyrene, indicating that the double bond was in the expected position in the isopropenyl group.

Ozonization of the hydrocarbon was effected with difficulty. The crude product did not react with Schiff's reagent, though it did react with 2,4-dinitrophenylhydrazine. No crystalline ketone could be isolated from a series of ozonolysis experiments.

The unreactivity of the double bond towards hydrogenation and bromination, as well as the absence of aldehydic materials in the ozonolysis product excludes structure X for the hydrocarbon.

It is of interest to consider the optical rotations of the carbinol (I) and of the hydrocarbon $C_{32}H_{36}$ in connection with the possible structures IX, X, or XI and the rotation of the carbon atom C_{12} (C_{4a}) in dehydroabietic acid and the derivatives thereof here described. Obviously, the structure XI can be eliminated, because the change in configuration at C_1 is trivial, yet there is a tremendous difference in rotation between the hydrocarbon ($[\alpha]^{22}_{D}$ $-44.3°$) and the *tert*-diphenyldehydrabietinol ($[\alpha]^{22}_{D}$ $+57.6°$). However, if the "tentative suggestion" of Fieser (6) is correct, namely, that the carbon atom C_{12} has a positive rotation in dehydroabietic acid, then structures IX and X are also unsatisfactory. Although complete proof of correctness of structure IX for the hydrocarbon $C_{32}H_{36}$ is not available, it seems to be the most likely possibility. Under the circumstances, it would seem that the rotary contribution of the carbon atom C_{12} in dehydroabietic acid is negative.

EXPERIMENTAL

tert-Diphenyldehydroabietinol (I). One mole (47.1 g.) of methyl dehydroabietate (m.p. 63°; $[\alpha]^{22}_{D}$ $+57.7°$, 3% ethanolic solution), dissolved in 150 ml. of ether, was added gradually, over a period of 30 minutes, to a filtered solution of 3 moles of phenylmagnesium bromide in 300 ml. of ether, while the reaction mixture was maintained at reflux temperature. After six hours of continued reflux, ether was removed, and the residual material was heated on the steam-bath for about three hours. Benzene was added, and the hydrolysis of the Grignard complex was effected with iced 10% aqueous sulfuric acid. The yellow benzene extract was separated and was washed successively with dilute sulfuric acid, aqueous sodium bicarbonate solution, and water. Benzene and biphenyl were removed by steam-distillation, and the residual yellow glass was taken up in low-boiling (30–38°) ligroin solution, which was filtered, dried over magnesium sulfate, and seeded with a few crystals of *tert*-diphenyldehydroabietinol from a previous preparation. After two days the crystalline precipitate (18.3 g.) was washed with ligroin. Partial evaporation of the mother liquor yielded an additional 5.1 g. of crystalline product, bringing the total yield to 35.7% of purified carbinol.

Crystals of the carbinol were originally obtained by chromatographing a ligroin solution like that just described on an alumina column (Alcoa activated alumina, grade F20).

Benzene eluted first a yellow gum, which was discarded, and then a colorless glass, which crystallized upon trituration with methanol.

Anal. Calc'd for $C_{32}H_{38}O$: C, 87.7; H, 8.7.
Found: C, 87.6; H, 8.5.

Crystallization from methanol yields large colorless prisms that melt at 140–141°. The compound is more soluble in ethanol and in isopropanol than in methanol, and crystals obtained from solutions of the higher alcohols are solvated. The optical rotation of a 1% absolute ethanolic solution is $[\alpha]_D^{22}$ +57.6°, and that of a 2.3% solution in chloroform is $[\alpha]_D^{24}$ +60.5°. The value reported by Zeiss (2) for a 4% ethanolic solution of his product is $[\alpha]_D^{23}$ 91°.

Thermal decomposition of tert-diphenyldehydroabietinol (I). Low-pressure distillation of the crystalline carbinol (13 g.) was attempted with the aid of a short-necked flask heated by an oil-bath. Decomposition with passage of distillate began at an oil-bath temperature of about 180°. A total of 10.5 g. of pale-yellow oil was collected over a distillation range of 105–120°/0.4 mm. In 2% absolute ethanolic solution the optical activity of a sample of the distillate was $[\alpha]_D^{23}$ +53.7°. A portion of the distillate reacted with dinitrophenylhydrazine, but a pure hydrazone could not be isolated. Steam-distillation of the distillate did not effect the separation of a pure ketonic fraction.

A 10.3-g. sample of the oily distillate, dissolved in 50 ml. of ligroin (b.p. 60–68°) was chromatographed on a column packed with 50 g. of alumina. Successive elutions with the indicated solvents yielded three fractions as follows: 250 ml. ligroin, 8.0 g. *A* (colorless oil); 200 ml. benzene, 0.8 g. *B* (pale-yellow oil); 200 ml. methanol, 1.0 g. *C* (colorless oil).

By distillation at reduced pressure, fraction *A* was divided into three sub-fractions: (*a*) b.p. 96–100°/0.2 mm., 2.3 g.; (*b*) b.p. 100–118°/0.2 mm.; and (*c*) b.p. 118–125°/0.2 mm.

Sub-fraction (*a*) was nearly pure benzophenone, as witness its elementary analysis and the melting point and mixture melting point of its 2,4-dinitrophenylhydrazone (238°).

Anal. Calc'd for $C_{13}H_{10}O$: C, 85.7; H, 5.5.
Found: C, 85.9; H, 6.0.

Sub-fraction (*b*) was a mixture including a considerable proportion of benzophenone from which 1.8 g. of the 2,4-dinitrophenylhydrazone was obtained.

Sub-fraction (*c*) (a colorless oil) did not react with any of the reagents that usually form ketonic derivatives, and appeared to be essentially a mixture of hydrocarbons; n_D^{20} 1.5404; $[\alpha]_D^{23}$ +95.7° (1% in ethanol); $[\alpha]_D^{23}$ +89.6° (1% in chloroform). The material reacted slowly with bromine in carbon tetrachloride solution, and absorbed hydrogen slowly in the presence of platinum, but the products of these reactions were not investigated. Ozonization of a 0.78-g. portion in carbon tetrachloride at 0°, a three-hour reflux of the reaction mixture with water, and treatment of the aqueous layer with dimedone yielded 15 mg. (1.8%) of the formaldehyde derivative (m.p. and mixture m.p., 189°). The residual yellow oil obtained upon evaporation of the carbon tetrachloride reacted in part with 2,4-dinitrophenylhydrazine to give a deep-red oily precipitate. A ligroin (b.p. 60–68°) solution of a 0.67-g. portion of the inhomogeneous oil was chromatographed on a column packed with 30 g. of alumina. Washing with more ligroin removed from the column 0.45 g. of a colorless non-ketonic oil which distilled under 0.2 mm. pressure at an oil-bath temperature of 135–140°; n_D^{20} 1.5319; $[\alpha]_D^{23}$ +83.5° (0.5% in chloroform). This material was very sparingly soluble in methanol; it did not react rapidly with bromine in carbon tetrachloride solution. It was probably 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VI).

Anal. Calc'd for $C_{19}H_{18}$: C, 89.1; H, 10.9.
Found: C, 89.0; H, 11.1.

Further elution with benzene removed 0.17 g. of an oil which did not decolorize Schiff's reagent, but which reacted with 2,4-dinitrophenylhydrazine to yield a deep-red derivative that crystallized from chloroform-methanol solution in prisms melting at 188–189°. The elementary analysis of the hydrazone was consistent with its formulation as 3-acetyl-7-isopropyl-9b-methyl-1,2,3,3a,4,5-hexahydro-9b-benz[*e*]indene.

Anal. Calc'd for $C_{25}H_{28}N_4O_4$: C, 67.0; H, 6.3.
Found: C, 66.7; H, 6.6.

Fraction *B* from the original chromatographic separation of the thermal decomposition products of *tert*-diphenyldehydroabietinol resisted efforts to effect its crystallization, but yielded 1 g. of the 2,4-dinitrophenylhydrazone of benzophenone (m.p. and mixture m.p., 238–239°).

Anal. Calc'd for $C_{19}H_{13}N_4O_4$: N, 15.5. Found: N, 15.3

On standing, the filtrate from the 2,4-dinitrophenylhydrazone preparation slowly deposited 0.1 g. of crystalline material which, upon recrystallization from methanol-ethyl acetate solution, melted at 174°, and which, upon admixture, did not depress the melting point (175°) of a sample of the acid dehydration-rearrangement product of *tert*-diphenyldehydroabietinol described hereafter [1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,-4,4a,9,10-hexahydrophenanthrene, (IX)]. The yield of this product reported is equivalent to the recovery of 8% of *tert*-diphenyldehydroabietinol undecomposed by distillation.

Fraction *C* from the original chromatographic separation of the thermal decomposition products of *tert*-diphenyldehydroabietinol crystallized upon trituration with ligroin (b.p. 60–68°), yielding colorless platelets of benzhydrol (m.p. and mixture m.p., 68°). The identification of the product was further confirmed by preparation of its thioglycolic acid derivative by the method of Holmberg (7) (m.p. and mixture m.p., 130°). The yield reported (1.0 g.) is equivalent to 18.6% of the carbinol subjected to distillation.

Chromic acid oxidation of tert-diphenyldehydroabietinol. I. A solution of 12.7 g. of chromium trioxide in 10 ml. of water and 100 ml. of glacial acetic was added gradually, over a period of 90 minutes, to a stirred solution of 10 g. of the crystalline carbinol in 100 ml. of acetic acid. Throughout the addition and for three hours thereafter the temperature of the reaction mixture was maintained at 80 ± 2°. Solvents were removed under reduced pressure, and the residue was treated with cold 1 *N* aqueous sulfuric acid and extracted with ether. The ethereal extract was washed with 1% aqueous sodium hydroxide and three times with water. Evaporation of the dried ethereal extract yielded 5.9 g. of a mobile yellow oil which was subjected to distillation under reduced pressure. The first fraction of distillate collected (b.p. 97–102°/0.2 mm.) solidified upon cooling and was found to consist of 2.4 g. (57.0%) of benzophenone (m.p. and mixture m.p., 49–50°). The second fraction of distillate collected (b.p. 169–185°/0.15 mm.) amounted to 2.1 g. of viscous reddish-yellow liquid which, upon treatment with 2,4-dinitrophenylhydrazine, yielded a deep-red mixture of hydrazones, (m.p., 120–160°), which resisted attempts to separate it into pure components. Another portion of this liquid was treated with Girard Reagent T, and the ketonic material was regenerated as a yellow gum; $[\alpha]^{21}_{D}$ +74.7° in 1% ethanolic solution. Repetition of this procedure did not markedly alter the properties of the material; $[\alpha]^{21}_{D}$ +76.5° in 1% ethanolic solution. Low-pressure distillation of the gum yielded a viscous yellow oil; b.p. 165–170°/ 0.2 mm.; n^{20}_{D} 1.5637. Treatment with 2,4-dinitrophenylhydrazine gave a non-homogeneous product from which no single pure derivative could be isolated. The elementary analysis of this oil did not agree well with that calculated for Zeiss's ketone (V).

Anal. Calc'd for $C_{18}H_{24}O$: C, 84.4; H, 9.4.
Found: C, 80.4; H, 8.4.

II. A second (21-g.) portion of crystalline carbinol was oxidized as previously described. The resultant ethereal extract was twice extracted with 5% aqueous sodium carbonate solution and then repeatedly washed with water until neutral.

Acidification of the sodium carbonate solution and extraction with ether yielded 4.5 g. of an oil containing a considerable proportion of acetic acid.

The sodium carbonate-extracted and water-washed ethereal solution was evaporated, and the residual gum was subjected to steam-distillation until the distillate no longer gave a perceptible reaction with 2,4-dinitrophenylhydrazine. The ketonic material extracted from the steam-distillate with ether proved to be benzophenone (4.6 g., 66.4%) as before.

The dark gum remaining in the distilling flask (6.1 g.) was dissolved in a mixture of ligroin (b.p. 30–38°) and 16% of benzene, and was chromatographed on a column packed with 200 g. of alumina. The solvent that passed through the column carried with it a small amount of waxy material which, upon crystallization from methanol, yielded 50 mg. (0.3%)

of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene (IX); m.p. and mixture m.p., 174°; $[\alpha]^{21}_{D}$—42.3° in *ca.* 1.5% chloroform solution.

Elution with a 1:1 ligroin-benzene mixture removed only a negligible amount of material. Benzene elution removed first a yellow gum which yielded a red non-homogeneous derivative upon treatment with 2,4-dinitrophenylhydrazone.

Further benzene elution removed a colorless gum which, upon trituration with ligroin, yielded 4–5 mg. of a colorless ketone identical with one of those (*A*) obtained from the chromic acid oxidation of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene (m.p. and mixture m.p. 105°).

Final elution with a 1:1 ether-acetone mixture removed a viscous yellow oil which distilled at 10^{-4} mm. over the temperature range 160–180°; $[\alpha]^{19}_{D}$ +33.4° in *ca.* 1.5% chloroform solution. This oil was redissolved in ligroin and rechromatographed. Elution with a mixture of 10% methanol in ether yielded 1.02 g. of a gum ($[\alpha]^{18}_{D}$ +34.0° in *ca.* 1.5% chloroform solution) from which only a deep-red non-homogeneous derivative could be obtained with 2,4-dinitrophenylhydrazine.

Anal. Found: C, 78.8; H, 6.9.

III. The oxidation of the carbinol with chromic acid was also carried out in acetic acid solution at room temperature, with and without the addition of water; all oxidations were complete in 15–20 hours. Again only benzophenone and a non-resolvable mixture of miscellaneous ketonic materials were obtained.

Hydrogen peroxide oxidation of tert-diphenyldehydroabietinol (I). To a stirred solution of 4.38 g. of the crystalline carbinol in 35 ml. of propionic acid was added 3.4 ml. of 30% hydrogen peroxide solution, followed by 4.2 ml. of 70% perchloric acid solution. The mixture was warmed at 50° for two hours and then cooled. The resultant white precipitate was washed with propionic acid; it proved to be 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene (IX) (2.0 g., 47.6%); m.p. and mixture m.p., 174°; $[\alpha]^{23}_{D}$ —42.8° in *ca.* 2% chloroform solution.

The yellow oxidation filtrate was highly diluted with water, and the precipitated oil was separated, dissolved in benzene, and chromatographed on an alumina column. The ether eluate did not crystallize, but, upon treatment with 2,4-dinitrophenylhydrazine, yielded 0.28 g. of the hydrazone of benzophenone (m.p. mixture and m.p., 237–238°). No other homogeneous material could be isolated from the column.

The aqueous solution from which the benzophenone-bearing oil had been separated was made alkaline and extracted with ether. From the ether extract an additional 0.2 g. of the 2,4-dinitrophenylhydrazone of benzophenone was obtained. (Total yield equivalent to 13% of benzophenone.)

The alkaline aqueous solution was adjusted to *p*H 7.4 and again extracted with ether. The oily ether extract was extracted with 2 *N* sulfuric acid and then treated with bromine water, yielding 0.08 g. (2.9%) of tribromophenol (m.p. and mixture m.p., 94°).

Acid-catalyzed dehydration-rearrangement of tert-diphenyldehydroabietinol (I): *1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene* (IX). To a boiling solution of 15 g. of the crystalline carbinol in 300 ml. of methanol was added a solution of 5 ml. of concentrated sulfuric acid in 25 ml. of methanol. Within a few minutes separation of a white solid began; refluxing was continued for two hours. After overnight standing of the reaction mixture, the white precipitate was washed with methanol. It was then redissolved in the minimum of boiling ethyl acetate, and boiling methanol was added to the solution to the point of incipient crystallization. From the cooled system the hydrocarbon (IX) was obtained in the form of colorless prisms melting at 175° (11.8 g., 82.0%). The optical activity in 2% chloroform solution is $[\alpha]^{22}_{D}$ —44.3°.

Anal. Calc'd for $C_{32}H_{36}$: C, 91.4; H, 8.6; Mol. wt., 420.

Found: C, 91.3; H, 8.4; Mol. wt. (cryosocopic, benzene), 399.

The ultraviolet absorption spectrum of a cyclohexane solution of the hydrocarbon includes three maxima: 2605 Å, log ϵ_{max} 2.96; 2668 Å, log ϵ_{max} 3.00; 2755 Å, log ϵ_{max} 2.87. The absorption graph is almost identical with that for *tert*-diphenyldehydroabietinol

(I); it may be inferred, therefore, that neither the dehydration nor the attendant rearrangement effects the conjugation of newly-introduced with previously-existent unsaturation.

Bromination of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenanthrene (IX): *1-(1,1-diphenylethyl)-4a-methyl-7-isopropenyl-1,2,3,4,-4a,9,10-hexahydrophenanthrene.* One gram of the acid dehydration-rearrangement product (IX) was dissolved in a solution comprising 0.13 ml. of bromine and 10 ml. of carbon tetrachloride. No perceptible decolorization occurred in diffused light, but complete decolorization (with hydrogen bromide evolution) took place in 20 seconds under intense visible illumination. The gummy residue remaining upon evaporation of the carbon tetrachloride was dissolved in ligroin (b.p. 60–68°) and chromatographed on a column packed with 20 g. of alumina. Elution with a ligroin-benzene mixture containing 10% of benzene removed 0.4 g. (40%) of a solid which, after crystallization from aqueous acetone and recrystallization from methanol, melted at 133–134°; $[\alpha]_D^{23}$ —118.1° in 0.5% chloroform solution.

Anal. Calc'd for $C_{32}H_{34}$: C, 91.9; H, 8.1.
Found: C, 91.6; H, 7.9.

The product isolated absorbs bromine rapidly from carbon tetrachloride solution without evolution of hydrogen bromide. The ultraviolet absorption spectrum includes a maximum at 2445 Å, log ϵ_{max} 4.04, and a point of inflection at 2625–2660 Å, log ϵ_{infl} 3.86. The ultraviolet absorption pattern of the hydrocarbon is consistent with its formulation as an β-methylstyrene analog, but not as a phenylbutadiene analog; *cf.*, *e.g.*,

α-methylstyrene, max. 2430 Å, log ϵ_{max} 4.05;
β-methylstyrene, max. 2460, Å log ϵ_{max} 4.05; (8)
phenylbutadiene, max. 2880 Å, log ϵ_{max} 4.75. (9)

Hydrogenation of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-2,3,4,4a,9,10-hexahydrophenenanthrene (IX): *1-(1,1-diphenylethyl)-4a-methyl-7-isopropylperhydrophenanthrene.* A 0.15-g. portion of the hydrocarbon IX was dissolved in 30 ml. of warm (70°) acetic acid, 0.07 g. of Adams' catalyst was added, and the mixture was shaken in an atmosphere of hydrogen at atmospheric pressure for five hours. The colorless glass that remained upon solvent removal was dissolved in ligroin, and the resultant solution was passed through a column packed with 10 g. of alumina. Very little material was adsorbed by the column. The colorless glass obtained by evaporation of the ligroin yielded, from an acetone-methanol mixture, irregular colorless crystals that sintered at 68° and melted at 72–75°. The indefinite melting point is probably attributable to the presence of a mixture of geometrical isomers.

Anal. Calc'd for $C_{32}H_{44}$: C, 89.7; H, 10.3.
Found: C, 89.7; H, 10.0.

Ozonolysis of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-1,2,3,4,4a,9,10-hexahydrophenanthrene (IX). An ethyl acetate solution of the hydrocarbon did not react with ozone at −80°. A 2-g. portion, dissolved in 300 ml. of carbon tetrachloride, was then treated with a calculated fivefold excess of ozone at 0°. The resultant clear solution became turbid on overnight standing. Removal of solvent under reduced pressure left a friable solid soluble in ethyl acetate. Hydrogenation of the ethyl acetate solution in the presence of palladium on calcium carbonate left a non-crystalline material that did not react visibly with Schiff's reagent, but that did appear to react with reagents that ordinarily form ketonic derivatives. A 1.5-g. portion was taken up in a 1:1 benzene-ligroin (b.p. 60–68°) mixture, and the resultant solution was filtered and chromatographed on a column packed with 50 g. of alumina. The material not adsorbed by the column consisted of 80 mg. (3.9%) of a glass that crystallized upon trituration with ligroin. Recrystallization from ethyl acetate yielded colorless prisms that melted at 175.5°. A mixture of these with some of the crystalline starting material (m.p. 175°) melted at 145°. Because this material did not react with 2,4-dinitrophenylhydrazine in boiling methanol acidified with sulfuric acid it was presumed to be an epoxide.

Anal. Calc'd for $C_{32}H_{36}O$: C, 88.1; H, 8.3.
Found: C, 87.5; H, 8.3.

The optical activity of this material is $[\alpha]_D^{19}$ +94.4° (0.5% in chloroform). No other homogeneous fraction could be isolated from the chromatogram.

Chromic acid oxidation of 1-(1,1-diphenylethyl)-4a-methyl-7-isopropyl-1,2,3,4,-4a,9,10-hexahydrophenanthrene (IX). *I.* To a vigorously stirred solution of 2.0 g. of the hydrocarbon in 15 ml. of acetic acid were added 1.5 g. of chromic oxide and 0.35 ml. of 70% perchloric acid. (Preliminary experiments had shown that the addition of perchloric acid increases the reaction rate and enhances the yield of the principal isolable product.) The temperature rose rapidly to about 70° and was maintained at that level for about a half-hour. After overnight stirring of the reaction mixture the deep-green, substantially inorganic precipitate was removed and washed with a little acetic acid. The combined filtrate and washings were highly diluted with water, and the resultant precipitate was washed with water. The precipitate was then suspended in water and subjected to steam-distillation. When the aqueous distillate aggregated *ca.* 300 ml. it included nothing from which a derivative could be obtained with the aid of 2,4-dinitrophenylhydrazine in 2 *N* aqueous sulfuric acid. The non-volatile residue (*ca.* 1.5 g.) was then dried and taken up in a 4:1 benzene-ligroin mixture, and the resultant extract was filtered and then chromatographed on a column packed with 50 g. of alumina. Unchanged hydrocarbon (54 mg.) was not adsorbed. Two ketonic materials were obtained by benzene elution. The first fraction removed (monoketone *A*, 0.29 g.) was an almost colorless glass that crystallized upon trituration with methanol. Recrystallization from ligroin yielded colorless prisms melting at 106–107°; $[\alpha]_D^{19}$ —107.8° in *ca.* 2% chloroform solution.

Anal. Calc'd for $C_{32}H_{34}O$: C, 88.5; H, 7.8.

Found: C, 88.1; H, 8.1.

The 2,4-dinitrophenylhydrazone of this ketone crystallized from a methanol-ethyl acetate mixture in yellow needles melting at 213°.

Anal. Calc'd for $C_{38}H_{38}N_4O_4$: C, 74.2; H, 6.2; N, 9.1.

Found: C, 74.4; H, 6.5; N, 9.1.

The second fraction of the benzene eluate was an intractable gum which was eventually discarded. The third and final fraction was a small quantity (*ca.* 30 mg.) of a glass that crystallized upon trituration with ligroin. It melted at *ca.* 230° and formed a derivative with 2,4-dinitrophenylhydrazine. This product was obtained in larger quantities in the experiment next described. No other homogeneous materials were eluted from the column.

II. To a boiling solution of 2.0 g. of the hydrocarbon in 35 ml. of glacial acetic acid was added, over a period of ten minutes, a solution of 3.0 g. of chromium trioxide in 1 ml. of water and 15 ml. of acetic acid; the mixture was stirred under gentle reflux for an additional hour. After overnight standing the acetic acid was removed under reduced pressure, and the residual gum was extracted with water. The white precipitate then remaining was dissolved in ether. Extraction of the ethereal solution with 5% aqueous sodium carbonate solution removed 0.15 g. of oily acidic material which was not further investigated. The yellow gum (0.78 g.) recovered from the extracted, washed, and dried ethereal solution was dissolved in ligroin (b.p. 60–68°) and chromatographed on a column packed with 50 g. of alumina; there was no unadsorbed material. The first fraction of benzene eluate consisted of 4–5 mg. of monoketone *A* (m.p. and mixture m.p., 105–106°). Further benzene elution yielded 0.1 g. of pale-yellow gum which crystallized on standing; two recrystallizations from ethyl acetate yielded colorless prisms melting at 239° (monoketone *B*).

Anal. Found: C, 87.8; H, 7.8.

The 2,4-dinitrophenylhydrazone of this ketone crystallized from a methanol-ethyl acetate mixture in orange prisms melting at 257–258°.

Anal. Found: N, 10.0.

No other homogeneous materials were isolated from the chromatogram.

SUMMARY

Pure *tert*-diphenyldehydroabietinol has been prepared in crystalline form, and has been found to have properties significantly different from those of the material to which this constitution has been previously assigned.

Upon oxidation with chromic acid neither *tert*-diphenyldehydroabietinol itself,

nor its major thermal decomposition product, nor its acid dehydration-rearrangement product, yield isolable quantities of 1-oxo-4a-methyl-7-isopropyl-1,2,3,4,-4a,9,10,10a-octahydrophananthrene (Zeiss's ketone).

It is concluded that the oxidation described by Zeiss was not performed, as supposed, on *tert*-diphenyldehydroabietinol, and that the ketone sought was not obtained by him in any high degree of purity (if at all).

Some light has been shed upon the probable individual contribution of asymmetric carbon atom 12 to the optical activity of abietic acid.

CHICAGO 37, ILLINOIS

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