by placing strong electron-withdrawing substituents on the double-bonded carbon atoms, susceptibility to attack by nucleophilic species can be enhanced.[23] The same goal may also be reached by increasing the nucleophilicity of the attacking reagent.[24] Carbanions of the type studied must be strongly nucleophilic, and the double bond appears sufficiently polarizable to permit rather rapid attack by such species. Substituted ethylenes should react more slowly than ethylene, because of electron release by the alkyl groups. On the other hand, since when a choice is available the most branched side-chain (with an α-hydrogen) is alkylated,[4] the nucleophilicity of the α-carbanion, and not the acidity of the α-hydrogen, is the dominating factor. In keeping with this, secondary and especially tertiary, but not primary, alkyl lithiums add rapidly to ethylene at −60°.[5]

Acknowledgments.—I owe a special debt to Seymour Meyerson, without whose ingenuity in mass spectrometry the major portion of this work would not have been possible. I acknowledge, also, helpful discussions of this work with Professor Fausto Ramirez of Columbia University, and with members of the research staff of the Standard Oil Company (Indiana).

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(23) Examples are the addition of Grignard reagents or cyanide ion to α,β-unsaturated ketones or esters and the base-catalyzed addition of alcohols to perfluoro-olefins.

(24) Reference 22, p. 667.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Terpenes. IV.[1] The Acid-induced Cyclization of Dihydro-α-ionone

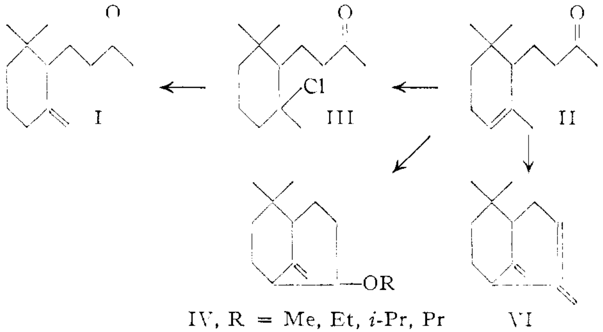
BY G. BÜCHI, K. BIEMANN, B. VITTIMBERGA AND M. STOLL[1a]

RECEIVED DECEMBER 17, 1955

Dihydro-α-ionone (II) undergoes cyclization in the presence of phosphoric acid. Three bicyclic hydrocarbons were isolated and the structures of two of them were elucidated by hydrogenation, dehydrogenation and oxidative degradation and shown to be 1,1,6-trimethyl-1,2,3,7,8,8a-hexahydronaphthalene (VII) and 2,2,6-trimethyl-9-methylene-bicyclo[3,3,1]-6-nonene (XII). A possible mechanism for the formation of the bicyclic hydrocarbons is discussed.

Dihydro-γ-ionone (I), a constituent of the steam-volatile fraction of ambergris[2] has been synthesized from dihydro-α-ionone (II) *via* the tertiary chloride III.[3] The addition of hydrochloric acid to II in ether solution, however, is not quantitative and a considerable amount of non-ketonic material is formed.

The study of this reaction, using hydroxylic solvents, has been continued in the laboratory of Firmenich and Cie.[4] It has been shown that dihydro-α-ionone (II) when treated with anhydrous hydrochloric acid in the presence of lower aliphatic alcohols is converted to bicyclic ethers IV, whereas the corresponding tertiary alcohol V is formed when the reaction is carried out in 2-butanol. In all cases studied small quantities of hydrocarbons were formed for which structure VI had been suggested.



IV, R = Me, Et, *i*-Pr, Pr
V, R = H

VI

In the present communication we wish to report work on the acid-induced cyclization of dihydro-α-ionone (II) in the absence of solvents.

Upon treatment of dihydro-α-ionone (II) with 85% phosphoric acid at 25°, a mixture of isomeric hydrocarbons $C_{13}H_{20}$ was obtained from which the individual components were isolated by chromatography and fractional distillation. Hydrogenation experiments showed that all three hydrocarbons $C_{13}H_{20}$ contain two double bonds and are therefore bicyclic. In the compound formed in largest quantity (VII) the double bonds are conjugated (ultraviolet: λ_{max} 240 mμ, log ε 4.36) and catalytic reduction in the presence of Adams platinum catalyst gave VIII, identical in all respects with authentic 1,1,6-trimethyldecalin.[5] Confirmatory evidence for the carbon skeleton of VII was obtained by catalytic dehydrogenation over palladium–charcoal[6] at 323°; ionene (IX), identical with an authentic sample was obtained.[7] In order to differentiate between structures VII and X, both of which are compatible with the ultraviolet absorption spectrum, the hydrocarbon was oxidized by osmium tetroxide and the resulting tetrol $C_{13}H_{24}O_4$ (XI) cleaved with potassium periodate. No formaldehyde was formed and the hydrocarbon must therefore have structure VII (1,1,6-trimethyl-1,2,3,7,8,8a-hexahydronaphthalene) rather than X.

The infrared spectrum of the second hydrocarbon (XII), formed in the cyclization of dihydro-α-ionone (II), shows bands at 6.07 and 11.35 μ typical for terminal methylene groups. The ultraviolet absorption spectrum indicates the absence of con-

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(1) Paper III, G. Büchi, W. S. Saari and A. Eschenmoser, *Experientia*, in press.

(1a) Firmenich and Cie., Geneva.

(2) L. Ruzicka, C. F. Seidel and M. Pfeiffer, *Helv. Chim. Acta*, **31**, 827 (1948).

(3) L. Ruzicka, G. Büchi and O. Jeger, *ibid.*, **31**, 293 (1948).

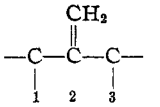
(4) M. Stoll, B. Willhalm and G. Büchi, *ibid.*, **38**, 1573 (1955).

(5) V. Prelog and B. Vaterlaus, *ibid.*, **32**, 2082 (1949).

(6) A. G. Anderson, Jr., and J. A. Nelson, THIS JOURNAL, **73**, 232 (1951).

(7) M. T. Bogert and V. G. Fourman, *ibid.*, **55**, 4670 (1933).

jugation; catalytic hydrogenation of XII did not lead to VIII. Therefore XII must have a carbon skeleton differing from the one of VII. The boiling point, index of refraction and infrared spectrum of XII are identical with the corresponding data reported for a hydrocarbon (VI) obtained previously by dehydration of V.[4] Chemical degradation of V indicated the presence of a tertiary hydroxyl and a grouping



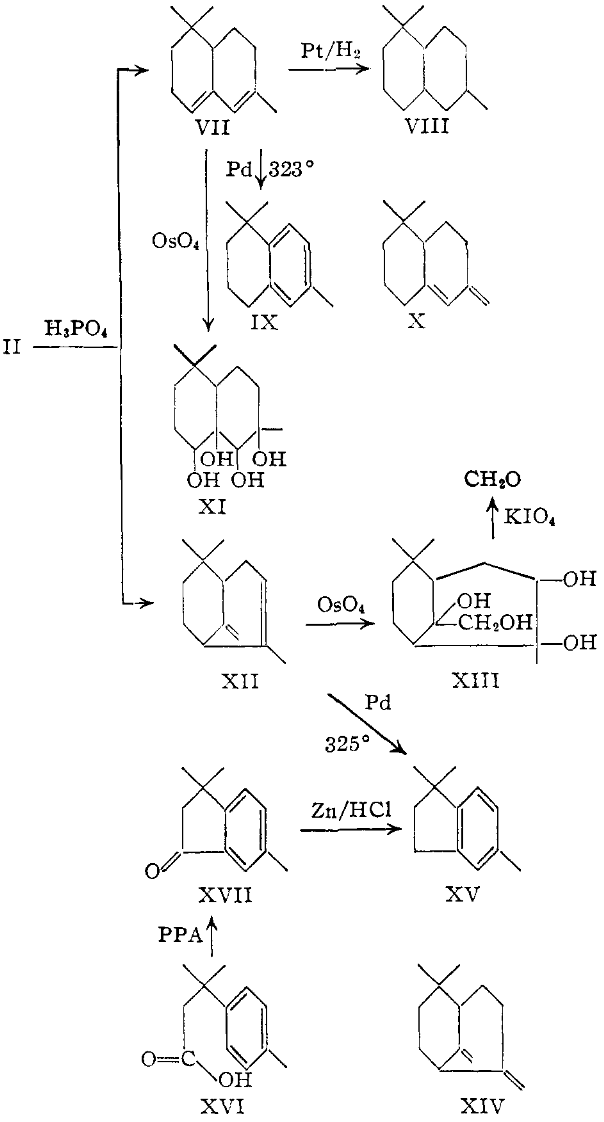
$$\underset{1}{-\mathrm{C}}-\overset{\mathrm{CH_2}}{\overset{\|}{\underset{2}{\mathrm{C}}}}-\underset{3}{\mathrm{C}-}$$

The reported[4] abnormal behavior of IV on ozonization indicated that carbon atoms 1 and 3 are located at bridgeheads. These facts suggest structure V for the cyclization product. The change from II to V can be rationalized easily by the carbonium ion theory of acid-catalyzed cyclizations. The dehydration of V to VI was realized under very mild conditions, and the diene should therefore be represented by either XII or XIV.

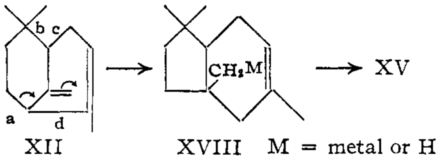
In order to distinguish between these two alternate structures the hydrocarbon was oxidized with osmium tetroxide to the crystalline tetrol $C_{13}H_{24}O_4$ (XIII) which on cleavage with potassium periodate gave 84% of one equivalent of formaldehyde (mannitol under identical conditions produced 86.5% of the calculated amount of formaldehyde). The diene therefore contains only one $>C=CH_2$ group and must be 2,2,6-trimethyl-9-methylene-bicyclo[3,3,1]-6-nonene (XII).

Further evidence for the difference between the carbon skeletons in VII and XII was obtained through dehydrogenation of hydrocarbon XII over palladium at 325°[6]; a product was obtained in good yield whose infrared and ultraviolet absorption spectra pointed to a substituted indan structure containing a geminal dimethyl group. Analysis of the corresponding dinitro derivative agreed better with a trimethylindan (C_{12}) than with a tetramethylindan (C_{13}). Analysis of the hydrocarbon did not allow a distinction between these two possibilities. 1,1,5-Trimethylindan (XV) was therefore synthesized by an unambiguous method and the indan as well as its dinitro derivative were identical with the products obtained by dehydrogenation of XII. Slight differences in the extinction coefficients (but not in the wave length) in the ultraviolet spectrum of the hydrocarbons are probably due to an impurity in the product of dehydrogenation.

For the synthesis of the indan XV, β-(*p*-tolyl)-isovaleric acid (XVI)[8] was cyclized to 1,1,5-trimethylindanone-3 (XVII), m.p. 42–42.8°, by means of polyphosphoric acid[9] in 98% yield. This compound had previously been prepared by the action of aluminum chloride on the acid chloride and described as a liquid (b.p. 131–132° (10 mm.)).[10] Clemmensen reduction of XVII yielded the hydrocarbon XV in 80% yield.



It is, however, impossible to accommodate the terminal and the trisubstituted non-conjugated double bonds present in XII in a 1,1,3a,5-tetramethylhexahydroindan system.[10a] Consequently the hydrocarbon is best represented by a substituted bicyclo[3,3,1]nonene structure (XII) and its conversion to XV can be rationalized by the sequence



High temperature and/or catalyst-induced polarization of the terminal methylene group followed by migration of bond a would lead to a resonance-stabilized allylic carbonium ion, XVIII (or radical) which upon aromatization with concomitant loss of the angular methyl group would lead to XV.

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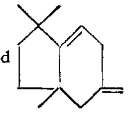
[8] J. Colonge and L. Pichat, *Bull. soc. chim. France*, 177 (1949).

[9] J. Koo, THIS JOURNAL, **75**, 1891 (1953).

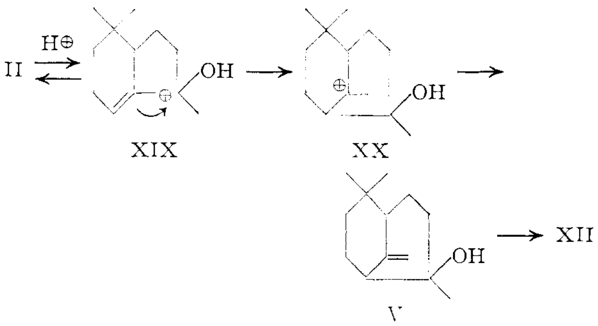
[10] J. Colonge and G. Weinstein, *Bull. soc. chim. France*, 961 (1951).

[10a] The only compound  which does meet these requirements would be expected to isomerize to a conjugated diene in the presence of acid.

Migration of any of the remaining bonds b, c or d, however, would lead to non-allylic carbonium ions (or radicals) and is therefore energetically less favored. It might be pointed out that Cook[11] was unable to dehydrogenate 2,3-benzbicyclo[3,3,1]-2-nonene to an aromatic system, a fact which points out the importance of a functional group on the one-carbon bridge.

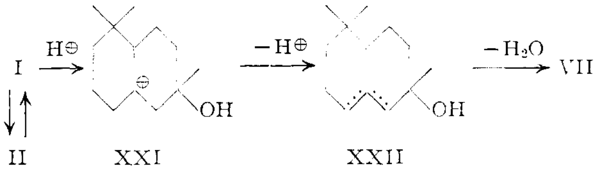
The structure of the third hydrocarbon formed in the cyclization of dihydro-α-ionone (II) could not be determined because it is formed in small quantity only and is exceedingly sensitive to air.

The formation of XII by acid-induced cyclization of II is easily explainable in the terms

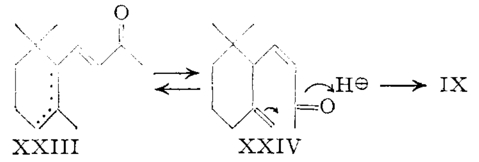


Addition of a proton to the carbonyl function of II produces the ion XIX which cyclizes irreversibly to XX by forming a new six-membered ring. This bicyclic carbonium ion can lose a proton from one position only (Bredt's rule), and the change thus leads to V by introduction of a semicyclic double bond. Subsequently the tertiary alcohol V is converted to the cyclohexene XII which in the absence of other complications is usually more stable than the corresponding methylenecyclohexane.[12]

The change from II to VII is only formulable in the terms of the sequence[12a]



Dihydro-α-ionone (II) and dihydro-γ-ionone (I) are readily interconvertible in the presence of acidic catalysts.[3] Although the concentration of I at equilibrium is very small, its cyclization to the decalin ring system XXI must be much faster than the cyclization of II to the bicyclo[3,3,1]nonane system (XX). Strong support for this sequence has been adduced by the conversion of I to XXII by acid catalyzed cyclization under very mild conditions.[13] The proposed scheme furthermore offers a reasonable explanation of the well known conversion of α- and β-ionone (XXIII) to ionene (IX)[7] which should proceed *via* the unstable but highly reactive *cis*-γ-ionone (XXIV).



Acknowledgments.—We thank the Massachusetts Institute of Technology (FSSP) and the Research Corporation of New York for fellowships to K. B., and Dr. Max Tishler, Merck and Co., Inc., for a generous gift of osmium tetroxide.

Experimental[14]

Cyclization of Dihydro-α-ionone (II).—Seventy-five grams of dihydro-α-ionone (b.p. 81–83° at 1.1 mm., n^{25}D 1.4753) was added under stirring to 380 g. of 85% phosphoric acid at 9 to 12° during 30 min. The resulting solution was warmed up to 25° and stirring was continued for two additional hours. A slow flow of nitrogen was passed through the flask during the whole operation. The pink emulsion was poured into 1.5 l. of water and extracted with 800 ml. of ether in four portions. The ether solution was washed with bicarbonate and water. After evaporation of the solvent, the remaining yellow oil (66 g.) was chromatographed on 800 g. of alumina (act. I) using petroleum ether as a solvent. The first fractions yielded 53.8 g. (79%) of an oil which was fractionated through a 3-ft. spinning-band column at 3.8 mm. Fraction 1, 58.3–60.5°, 2.1 g., n^{25}D 1.4839; (2) 60.5–63.5°, 1.56 g., n^{25}D 1.4860; (3) 63.5–67°, 1.56 g., n^{25}D 1.4892; (4) 67–70°, 2.80 g., n^{25}D 1.4925; (5) 70–72.8°, 4.05 g., n^{25}D 1.4905; (6) 72.8–80°, 2.66 g., n^{25}D 1.4901; (7) 80–87°, 3.50 g., n^{25}D 1.5051; (8) 87–90.2°, 5.03 g., n^{25}D 1.5142; (9) 90.2–91.5°, 25.71 g., n^{25}D 1.5186; residue: yellow resin. Redistillation of the combined fractions 4 and 5 through a 1-ft. spinning-band column yielded 1.56 g. (2.3%) of XII (b.p. 68° at 3.3 mm., n^{25}D 1.4938); principal infrared bands: 3.5, 6.07, 6.9, 7.22, 7.37, 8.28, 8.78, 8.86, 11.35, 12.08 and 12.75 μ; ultraviolet (in cyclohexane) λ_{max} 240 mμ, ε 550.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.08; H, 11.48.

Redistillation of fraction 6 combined with the tail cut of fractions 4 + 5 (4 g. altogether) through a 1-ft. spinning-band column yielded 1.06 g. (1.6%) of a compound of b.p. 77–79° at 4 mm., n^{25}D 1.4850; principal infrared bands: 3.5, 6.0, 6.9, 7.25, 7.37, 8.41, 10.28, 10.63, 10.95, 11.39, 12.15 and 14.0 μ; ultraviolet (in cyclohexane) λ_{max} 240 mμ, ε 2000.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 84.65; H, 11.28.

Redistillation of fraction 9 through a 3-ft. spinning-band column yielded 20.64 g. (30%) of VII (b.p. 90.2–90.6° at 3.6 mm., n^{25}D 1.5192); principal infrared bands: 3.5, 6.18, 6.9, 7.25, 7.37, 9.85, 10.52, 11.38 and 12.1 μ; ultraviolet (in cyclohexane) λ_{max} 240 mμ, ε 21,300.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44. Found: C, 88.81; H, 10.90.

Hydrogenation of the Hydrocarbon VII to 1,1,6-Trimethyldecalin (VIII).—One gram of VII was hydrogenated in 23 ml. of glacial acetic acid on Pt (from 50 mg. of PtO_2) at atmospheric pressure. Hydrogen (263 ml.) was absorbed at 25° and 770 mm. (calcd. for two double bonds: 271 ml.). The solution was poured into 100 ml. of water and extracted with petroleum ether. After washing with bicarbonate and water, and evaporation of the solvent, 1.01 g. of an oil remained, which was fractionated at 3.6 mm. The middle-fraction (0.42 g.) was collected at 84°, n^{25}D 1.4780 (lit.[5] n^{24}D 1.4779); principal infrared bands: 3.5, 6.9, 7.22 and 7.37 μ.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 87.05; H, 13.24.

Dehydrogenation of VII to Ionene.—Two grams of VII was passed by means of a stream of dry nitrogen through a column of 3 g. of palladium (5%)-on-charcoal and 3 g. of asbestos at the temperature of boiling benzyl benzoate

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[11] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 62 (1936).

[12] H. C. Brown, J. H. Brewster and H. Shechter, This Journal, **76**, 467 (1954).

[12a] Note added in proof.—An analogous mechanism has recently been proposed for the cyclization of β-methylheptenone by J. Meinwald and R. F. Grossmann, This Journal, **78**, 992 (1956).

[13] M. Stoll and M. Hinder, *Helv. Chim. Acta*, **38**, 1593 (1955).

[14] Melting points and boiling points are uncorrected. Analyses by Mmes. Alvord and Kula and Dr. S. M. Nagy, Massachusetts Institute of Technology, Microanalytical Department.

(b.p. 323°) during 4 hours.[6] The reaction product was condensed at −80° and the nitrogen was bubbled through petroleum ether at Dry Ice temperature. The product (1.69 g.) was fractionated twice and the fraction of b.p. 110–111° (10 mm.) was collected (0.36 g.), $n^{24}\text{D}$ 1.5174 (lit.[7] $n^{20}\text{D}$ 1.5225, b.p. 107° (10 mm.)); principal infrared bands (in carbon disulfide): 3.5, 6.2, 7.23, 7.38 and 12.21 μ; ultraviolet (in cyclohexane): strong absorption below 230 mμ, maxima at 269 mμ (ϵ 660), 277 mμ (ϵ 710), minimum at 275 mμ (ϵ 440).

Oxidation of VII by Osmium Tetroxide.—A mixture of 4.93 g. (0.02 mole) of osmium tetroxide and 1.70 g. (0.0096 mole) of VII in 30 ml. of pyridine was allowed to stand 12 days at 26–30°. During this time dark crystals separated. The pyridine was evaporated at reduced pressure, the residue dissolved in 400 ml. of ethanol–benzene (1:1) and a mixture of 25 g. of mannitol, 25 g. of potassium hydroxide, 100 ml. of water and 200 ml. of ethanol was added (two phases). After refluxing (8 hours) and concentrating to 250 ml., 100 ml. of water was added and the solution extracted with 300 ml. of ether in 6 portions. A dark brown residue, 1.97 g., crystallized partially. After recrystallization from benzene and chromatography of the mother liquors 1.16 g. of tetrol XI was obtained (m.p. 164–165°). Further recrystallization raised the m.p. to 165.5–166.5°.

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.74; H, 9.79.

Cleavage of the Tetrol XI.—A mixture of 37.8 mg. (0.148 mmole) of tetrol XI (in 3 ml. of water), 18 ml. of 0.04 *M* potassium periodate (in 1 *N* sulfuric acid) and 0.5 ml. of concd. sulfuric acid was allowed to stand for one hour at room temperature. Ten ml. of water was added, the mixture distilled and 15 ml. collected; 150 mg. of dimedon in 6 ml. of 50% ethanol was added to the distillate. No precipitate of formaldimedon was formed after standing for several days.

Hydrogenation of XII.—Seven tenths of a gram of XII was hydrogenated as described above. Hydrogen (186 ml.) was absorbed at 25° and 750 mm. (calcd. for two double bonds, 197 ml.). Fractionation at 1 mm. yielded 0.42 g. (middle cut), b.p. 67°, $n^{25}\text{D}$ 1.4787; principal infrared bands: 3.5, 6.9, 7.3, 9.2, 10.2 and 11.5 μ.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.42; H, 13.31.

Oxidation of XII by Osmium Tetroxide.—A mixture of 1.04 g. of XII, 3.0 g. of osmium tetroxide and 15 ml. of pyridine was treated as described above. The oxidation product was recrystallized from water and 0.79 g. (58%) of tetrol XIII was obtained, m.p. 104–106°, after recrystallization m.p. 106–107°.

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 63.79; H, 9.75.

Cleavage of Tetrol XIII.—A solution of 31.5 mg. of tetrol XIII was treated with potassium periodate as described above. Soon after adding the dimedon, needles began to precipitate. After 30 hr. the precipitate was filtered off, washed with water and dried over potassium hydroxide in a vacuum desiccator; 31.5 mg. of the formaldimedon was obtained (84% calcd. for one $-CHOH-CH_2OH$ group per molecule), m.p. 189.5–190.5°. No depression occurred after mixing with an authentic sample. (Mannitol (29.8 mg.) was oxidized with 27 ml. of 0.04 *M* potassium periodate in exactly the same manner, yielding 82.9 mg. of formaldimedon, *i.e.*, 86.5% of the calcd. amount.)

Dehydrogenation of XII to 1,1,5-Trimethylindan (XV).—One gram of the hydrocarbon XII was dehydrogenated as described above, using 2 g. of palladium–charcoal and 2 g. of asbestos. The catalyst was heated to 325° (by refluxing mineral oil). The product (0.772 g.) was fractionated at 4.1 mm.: (1) 73–75.5°, 0.103 g., $n^{22.5}\text{D}$ 1.5040; (2) 75.5–79°, 0.104 g., $n^{22.5}\text{D}$ 1.5072; (3) 79–85°, 0.168 g., $n^{22.5}\text{D}$ 1.5120. All fractions showed principal infrared bands at 3.5, 6.2, 6.9, 7.24, 7.37, 7.65, 8.94, 11.42 and 12.25 μ; ultraviolet (in cyclohexane): maxima (in mμ) at 215 (ϵ 8500), 264 (ϵ 1220), 269 (ϵ 1330), 272 (ϵ 1290) and 278 (ϵ 1300); minima at 237 (ϵ 370), 266 (ϵ 1160), 271 (ϵ 1220) and 275.5 (ϵ 775).

Anal. of fraction 2: Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06; for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.71; H, 10.44.

Nitration.—A mixture of all three fractions (74 mg.) was treated with 0.4 ml. of concd. sulfuric acid and 0.25 ml. of concd. nitric acid for 2 hr. at 0° and shaken for 9 hr. at 25°. The emulsion was then poured into water and extracted with ether. After washing, drying and evaporation in the usual manner, 84 mg. of a yellow oil was obtained, which was purified by chromatography over alumina and vacuum distillation; ultraviolet (in ethanol): strong end absorption (ϵ 17,000 at 210 mμ), min. at 238 mμ (ϵ 6,040), max. at 249.5 mμ (ϵ 6,600), infl. at 300 mμ (ϵ 2,340).

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20; for $C_{13}H_{16}N_2O_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 57.99; H, 6.01; N, 11.41.

After a few days the sample crystallized; recrystallized from methanol, m.p. 78–80°; no depression after mixing with a synthetic sample of the dinitro-compound described below.

1,1,5-Trimethylindanone-3 (XVII).—Polyphosphoric acid (350 g.) was heated to 80° in a flask protected from moisture. Thirty grams of β-(*p*-tolyl)-isovaleric acid (XVI)[8] was added and the mixture stirred for 90 min. at 70–80°. Then it was poured into 600 ml. of ice-water and extracted with ether. After washing with bicarbonate and water, the ethereal solution was dried and evaporated. The residue (26.80 g. or 98%) crystallized, m.p. 40–42.5, b.p. 110° at 3.8 mm. (lit.[10] 131–132° at 10 mm.). It was recrystallized twice from methanol, raising the m.p. to 42–42.8°.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.13; H, 8.22; principal infrared bands (in carbon tetrachloride): 3.42, 5.85, 6.2, 6.7, 7.24, 7.36, 7.8, 8.0, 8.63, 9.1 and 12.15 μ; ultraviolet (in ethanol): max. at 247 mμ (ϵ 12,200) and 301 mμ (ϵ 3,100); min. at 224.5 mμ (ϵ 2,860) and 270 mμ (ϵ 500).

1,1,5-Trimethylindan (XV).—A solution of 12.5 g. of the trimethylindanone (XVII) in 50 ml. of ethanol was added in three portions during 2 hr. to a refluxing mixture of 50 ml. of concd. hydrochloric acid, 20 ml. of water and 25 g. of amalgamated zinc. Concentrated hydrochloric acid, 35 ml., was added during the same time. After boiling under reflux 17 additional hours, 150 ml. of water was added and the product extracted with ether in the usual manner. The residue of the ethereal solution was distilled through a Holzman column at 87–87.5° (11 mm.) yielding 9.19 g. (80%). For analysis it was redistilled, $n^{24}\text{D}$ 1.5111. Infrared bands identical with the ones of the dehydrogenation product; ultraviolet abs. spectrum in cyclohexane: maxima (in mμ) at 215 (ϵ 8900), 264 (ϵ 975), 269 (ϵ 1330) 272 (ϵ 1420) and 278 (ϵ 1840); minima at 237 (ϵ 100), 266 (ϵ 890), 271 (ϵ 1250) and 275.5 (ϵ 660).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.15; H, 9.83.

1,1,5-Trimethyl-4,6-dinitroindan.—One gram of the trimethylindan was nitrated as described above, using 6.0 ml. of concd. sulfuric acid and 4.0 ml. of concd. nitric acid. The crystalline residue of the ether extract (1.403 g.) was recrystallized twice from methanol, m.p. 80–81°; ultraviolet (in ethanol) strong end absorption, min. at 237 mμ (ϵ 7000), max. at 249.5 (ϵ 7550), infl. at 300 mμ (ϵ 2,500).

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.33; H, 5.72; N, 11.07.

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