ethyl ether at room temperature using Adams catalyst gave 8.8 g. of 3-ethyl-1-pentanol, b.p. 90–91.5° (30 mm.), $n^{20}D$ 1.4287, d^{20}_4 0.8398.

Anal. Calcd. for $C_7H_{16}O$: C, 72.35; H, 13.88; MR_D, 36.1. Found: C, 72.03, 72.37; H, 14.10, 14.20; MR_D, 35.6.

Oxidation of 2.8 g. of 3-ethyl-1-pentanol by the method of Fournier[25] gave 1.04 g. of 3-ethyl-1-pentanoic acid, b.p. 207–208.5° (reported[26] for 3-ethyl-1-pentanoic acid, b.p. 212°. The amide was obtained as flaky plates from ethanol; m.p. 128.5–129.5° (reported[27] m.p. 127.5°). The piperazonium salt prepared by the method of Pollard[28] showed m.p. 133–134° (reported[29] m.p. 133–134°).

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[25] Fournier, *Bull. soc. chim. France*, [4] **5**, 920 (1909).

[26] F. Fichter, A. Kiefer and W. Bernoulli, *Ber.*, **42**, 4713 (1909).

[27] F. Bayer and Co., German Patent 222,809; *Chem. Zentr.*, **81**, II, 254 (1910).

[28] C. B. Pollard, D. E. Adelson and J. P. Bain, THIS JOURNAL, **56**, 1759 (1934).

[29] S. G. Powell and M. M. Baldwin, *ibid.*, **58**, 1872 (1936).

ITHACA, N. Y.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Condensation of Cyclic Olefins with Formaldehyde[1,2]

BY A. T. BLOMQUIST, JOSEPH VERDOL,[3] CLAIRE L. ADAMI, JOSEPH WOLINSKY[3] AND DONALD D. PHILLIPS

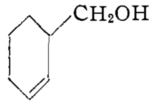
RECEIVED MARCH 30, 1957

Thermal condensation of formaldehyde with cyclohexene, *pure* α-pinene, *d*-limonene and 1-methylcyclohexene either in the presence of solvent acetic acid–acetic anhydride or in the absence of solvent affords, respectively, as principal products 2-cyclohexenemethanol acetate, 2-methylene-6,6-dimethylbicyclo[3.3.1]heptane-3-methanol, "homolimonenol," and an approximately equal mixture of 2-acetoxymethylmethylenecyclohexane and 3-acetoxymethyl-2-methylcyclohexene. The formation of these products is in accord with a postulation that suggests a planar six-membered ring for the transition state of the reaction.

A recent article presented our observations on the behavior of representative acyclic olefins in their thermal condensation with formaldehyde.[2] It seemed desirable to extend this study by examining also the thermal condensation of some typical cyclic olefins with formaldehyde. There was special interest in the behavior of α-pinene, *d*-limonene and cyclohexene as these olefins have been reported to be essentially unreactive in the condensation.[4–6] On the basis of our earlier work with the acyclic olefins[2] such cyclic olefins would be expected to be reactive albeit to perhaps a lesser extent. We have found, in fact, that the olefins cyclohexene, 1-methylcyclohexene, α-pinene and *d*-limonene do react with formaldehyde to afford monocondensation products to the extent of 10–54%.

The condensations with paraformaldehyde were carried out either in the presence or absence of solvent acetic acid–acetic anhydride at temperatures varying from 160–180°. The principal products obtained were primary unsaturated alcohols or their acetates in which the double bond occupied a position adjacent to that in the starting cyclic olefin.

The condensation of cyclohexene at 180° in solvent acetic acid–acetic anhydride gave the crude acetate of 2-cyclohexenemethanol (I) in *ca.* 10% yield together with a small amount of higher boiling material.[7] Although I has not been described previously all of its pertinent isomers have been reported. The properties of I and three of its crystalline derivatives did not correspond to those reported for 1-cyclohexenemethanol,[8] 4-cyclohexenemethanol,[9,10] 2-methylenecyclohexanol[8,11,12] and 2-methyl-1-cyclohexene-3-ol.[13,14] A tetrahydrobenzyl alcohol whose phenylurethan derivative showed m.p. 63°, was reported by Pommereau.[15] This may have been I as the phenylurethan derivative of our I showed m.p. 61–63°. The infrared absorption spectrum of I showed maxima at 13.83, 14.40 and 14.80 μ which are observed for 3-methyl and 4-methyl-1-cyclohexene, etc.,[16] and appear to be characteristic of an unsubstituted carbocyclic



I; Ia, the acetate

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Co.

[2] For a closely related preceding paper see A. T. Blomquist, M. Passer, C. S. Schollenberger and Joseph Wolinsky, THIS JOURNAL, **79**, 4972 (1957).

[3] Abstracted from part of the dissertations presented by J. Verdol in February, 1955, and J. Wolinsky in June, 1956, to the Graduate School of Cornell University in partial fulfillment of the requirements for the Degree Doctor of Philosophy. Part of the work reported here was done by Miss Claire Adami in conjunction with the Honors Program in Chemistry.

[4] J. P. Bain, THIS JOURNAL, **68**, 638 (1946).

[5] R. Pummerer, F. Aldebert, F. Büttner, F. Graser, E. Pierson, H. Rick and H. Sperber, *Ann.*, **583**, 161 (1953).

[6] N. O. Brace reported that cyclohexene and α-pinene do react with paraformaldehyde at 200–225° but gave no information about yield or structure of the products (THIS JOURNAL, **77**, 4666 (1955)).

[7] The mixture contained *trans*-2-hydroxymethyl-1-cyclohexanol diacetate (II) and possibly the diacetates of 1,3-bis-(hydroxymethyl)-cyclohexene (III) and 3,4-bis-(hydroxymethyl)-cyclohexene (IV). Evidence for II was the isolation of its bisphenylurethan derivative. The possible presence of III and/or IV was suggested by the observation that the mixture absorbed 75% of one equivalent of hydrogen upon catalytic reduction.

[8] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953).

[9] H. Fieselman, *Ber.*, **75**, 881 (1942).

[10] E. G. E. Hawkins, D. J. G. Long and F. W. Major, *J. Chem. Soc.*, 1462 (1955).

[11] M. Mousseron, J. Julien and F. Winternitz, *Bull. soc. chim. France*, [5] **15**, 883 (1948); **14**, 80 (1947).

[12] M. Mousseron and R. Jacquier, *ibid.*, [5] **18**, 106 (1951); **19**, 467 (1952); **20**, 634 (1953).

[13] A. Guillemonat, *Ann. chim. (Paris)*, [11] **11**, 170 (1939).

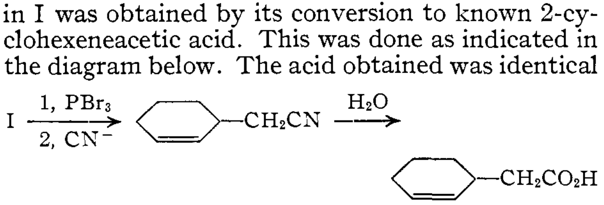
[14] M. Mousseron, R. Jacquier, A. Fontaine and R. Zagdoun, *Bull. soc. chim. France*, [5] **21**, 1246 (1954).

[15] H. Pommereau, *Compt. rend.*, **174**, 685 (1922).

[16] "Catalogue of Selected Infrared Absorption Spectrograms," American Petroleum Institute Research, Project 44, National Bureau of Standards, Washington, D. C.

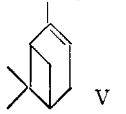
double bond. Reduction of I gave known cyclohexanemethanol, identical in all respects with an authentic sample.

Confirmation of the position of the double bond in I was obtained by its conversion to known 2-cyclohexeneacetic acid. This was done as indicated in the diagram below. The acid obtained was identical

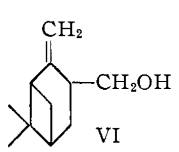


in all respects with an authentic sample prepared from 3-bromocyclohexene and diethyl malonate.

Although β-pinene reacts readily with formaldehyde to give nopol (V) in high yield, Bain reports that α-pinene[4] is relatively unreactive toward formaldehyde. We have found that *pure* α-pinene reacts with paraformaldehyde at 180° in the absence of solvent to afford 2-methylene-6,6-dimethylbicyclo[3.1.1.]heptane-3-methanol (VI) in 12% yield. Commercial samples of α-pinene give only



V

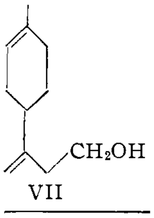


VI

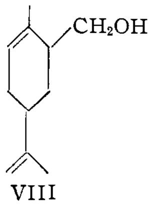
nopol (V), undoubtedly due to contaminating β-pinene in the starting material. This probably accounts also for the products reported by earlier workers.[17,18]

Elementary analysis of VI and its hydrogen phthalate were in accord with the postulated structure. The infrared spectrum of VI showed strong absorption at 11.40 μ, characteristic of an exocyclic double bond, and reductive ozonolysis of VI gave formaldehyde, isolated as its dimedone derivative in 45% yield. Finally, the alcohol VI absorbed 95% of the theoretical amount of hydrogen required for one double bond when reduced in ethanol using Adams catalyst. One attempt to dehydrate VI to a diene by the method used to prepare the isomeric nopadiene[19] gave only a polymer.

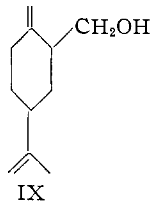
The thermal condensation of *d*-limonene and paraformaldehyde[20] gave in 28–35% yield an inseparable mixture of unsaturated alcohols to which we have assigned the name "homolimonenol." Although rigorous proof is lacking, preliminary evidence points to VII as the major constituent of *homolimonenol* while VIII and IX are probably present to a much smaller extent.



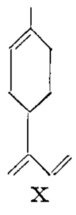
VII



VIII



IX

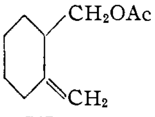


X

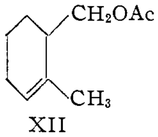
This result is to be expected in view of the enhanced reactivity of an acyclic double bond in this reaction.

Hydrogenation data indicated that at least 90% of the mixture from *d*-limonene and formaldehyde contained a ring double bond, thus limiting the amount of IX to <10%. Oxidation of the dihydro derivatives produced at least two aldehydes, one of which was of the α,β-unsaturated type. Pyrolysis of *homolimonenol acetate* at 500–510° resulted in the formation of a triene whose infrared absorption spectrum (λ_{max} 6.08, 6.25, 10.05, 10.80 and 11.25 μ) was in accord with structure X but the material polymerized on attempted characterization.

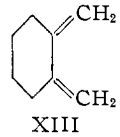
The condensation of 1-methylcyclohexene at 165° in solvent acetic acid–acetic anhydride gave, in 45% yield, an approximately equal and inseparable mixture of 2-acetoxymethyl-1-methylenecyclohexane (XI) and 3-acetoxymethyl-2-methylcyclohexene (XII). Although the physical constants for this product were very similar to those recorded for pure XI,[21] the presence of another isomer was indicated by the infrared spectrum (λ_{max} *6.03*, 6.10, 11.26 and *12.54* μ) and by the experiments described below.



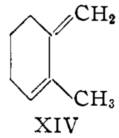
XI



XII



XIII



XIV

Hydrogenation of the mixture of acetates afforded a single compound which was identical with an authentic sample of 2-acetoxymethyl-1-methylcyclohexane. Upon pyrolysis, a mixture of 1,2-dimethylenecyclohexane (XIII) and 3-methylene-2-methylcyclohexene (XIV) was formed. This composition was indicated by the isolation of glutaric and adipic acid from oxidative ozonolysis of the pyrolyzate. By selective reaction of XIII in the pyrolysis mixture with maleic anhydride[22] and by titration of the diene mixture with perbenzoic acid,[23] it was estimated that the composition was approximately 50–55% XIII and 45–50% XIV. Concomitant experiments conclusively demonstrated that XI did not isomerize to XII during the conditions of the formaldehyde condensation. For this reason it was possible to use the established composition of the diene mixture (XIII and XIV) to represent the composition of the original mixture of acetates produced in the thermal condensation of formaldehyde with 1-methylcyclohexene.

Mechanism.—The results of these thermal condensations of formaldehyde with cyclic olefins may be rationalized by a mechanism involving a planar six-membered ring as the transition state, as proposed earlier.[2,24] Because of its symmetry, cyclohexene can form only one transition state in noncatalyzed condensation with formaldehyde (XV,

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(17) O. Kriewitz, *Ber.*, **32**, 57 (1899).

(18) H. J. Prins, *Chem. Weekblad*, **16**, 1510 (1919).

(19) L. J. Kitchen, This Journal, **73**, 2368 (1951).

(20) While this work was in progress, G. Ohloff [*Arch. Pharm.*, **287**, 258 (1954)] reported the condensation of *d*-limonene and formaldehyde in refluxing acetic acid. The products to be described agree well in physical properties with those obtained by Ohloff.

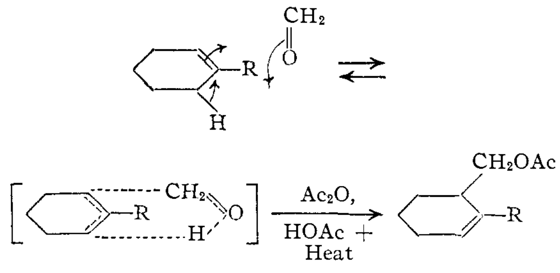
(21) W. J. Bailey and H. R. Golden, This Journal, **75**, 4780 (1953).

(22) Such a Diels–Alder reaction is known to proceed essentially quantitatively for 1,2-conjugated exocyclic dienes; *cf.* A. T. Blomquist, *et al.*, *ibid.*, **78**, 6057 (1956). This treatment, incidentally, permitted us to isolate pure XIV, *i.e.*, uncontaminated with XIII.

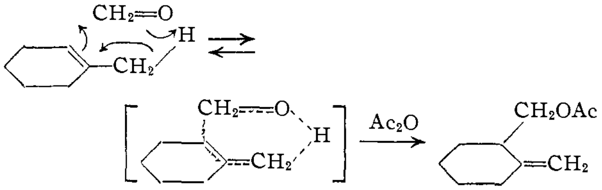
(23) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 220 (1947).

(24) R. T. Arnold and J. F. Dowdall, This Journal, **70**, 2590 (1948).

R = H) but 1-methylcyclohexene can form two transition states, one of which is analogous to that from cyclohexene and leads to XVI (R = CH_3) while the other (XVII) involves a methyl hydrogen and hence gives rise to XI. As mentioned earlier in the Discussion, *both* compounds (XI and XII) are formed in this reaction, a fact that lends support to the proposed mechanism. For obvious steric reasons, α-pinene is restricted to a transition state similar to XVII and as a consequence, only that product with an exocyclic double bond is realized.



XV XVI



XVII XI

It should be stressed that although transition state XV involves the formation of an incipient double bond at a bridgehead carbon atom, the same situation undoubtedly obtains in the *para*-Claisen rearrangement,[25] so that this postulate is not without analogy.

Experimental Part[26]

Materials.—Eastman Kodak Co. α-pinene gave only nopol (V) when condensed with formaldehyde but a pure grade that contained no β-pinene was obtained from Techniservice, Inc.[27] 1-Methylcyclohexene, b.p. 110° (atm.), $n^{20}D$ 1.4503, was prepared in 79% yield by Vogel's method.[28]

Condensation of Cyclohexene with Formaldehyde.—A mixture of 1000 g. (12.2 moles) of cyclohexene, 300 g. (10 moles) of paraformaldehyde, 360 g. (6 moles) of glacial acetic acid and 300 g. (3.3 moles) of acetic anhydride was heated with shaking in a stainless steel bomb at 175–180° for 86 hours. Unreacted cyclohexene (703 g.) was stripped from the reaction mixture by distillation and the residue was taken up in ether, washed well with sodium carbonate solution and water and the dried ethereal solution was then evaporated. Fractional distillation of the residual oil gave 143.8 g. (9%) of crude Ia, b.p. 108–122° (38–45 mm.), $n^{25}D$ 1.4555–1.4598, and 28 g. of a high-boiling product, b.p. 120–130° (1–10 mm.).

The crude acetate Ia was transesterified by heating under reflux in methanol containing dibutyltin oxide. Distillation of the reaction mixture afforded 96.3 g. of the corresponding alcohol I, b.p. 85–90° (10–25 mm.), $n^{25}D$ 1.4782–1.4840. A portion of this alcohol was distilled through a Podbielniak column and there was obtained, after a small forerun, pure I, b.p. 184–187° (atm.), $n^{25}D$ 1.4825, d^{25}_4 0.9697.

Anal. Calcd. for $C_7H_{12}O$: C, 74.95; H, 10.79; *MR*D, 33.41. Found: C, 74.76; H, 10.78; *MR*D, 33.01.

Crystallized from ethanol, the **p-nitrobenzoate** derivative had m.p. 49–50°.

Anal. Calcd. for $C_{14}H_{15}O_4N$: C, 64.35; H, 5.79. Found: C, 63.98; H, 5.93.

The phenylurethan derivative had m.p. 61–63° after crystallization from hexane.

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.70; H, 7.41. Found: C, 72.69; H, 7.43.

After three crystallizations from hexane, the **α-naphthylurethan** derivative had m.p. 87–88°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 76.66; H, 6.82.

A pure sample of the **acetate** derivative was prepared by the acetic anhydride–pyridine method and was purified by distillation through a Podbielniak column, b.p. 104–107° (35 mm.), $n^{25}D$ 1.4564, d^{25}_4 0.9870.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15; *MR*D 42.74. Found: C, 70.17; H, 9.56; *MR*D 42.54.

Hydrogenation of I.—A solution of 10.0 g. (0.09 mole) of I in ethyl acetate was hydrogenated at 50 lb. pressure in a Parr apparatus. The usual workup gave 8.6 g. (86%) of **cyclohexanemethanol**, b.p. 176–178° (atm.), $n^{25}D$ 1.4618. The literature values[29] for this compound are b.p. 183° (760 mm.), $n^{25}D$ 1.4638.

The hydrogen phthalate derivative had m.p. 115–116° when crystallized from benzene–hexane; lit.[29] m.p. 109° and 119–120°.

2-Cyclohexeneacetic Acid. A. From Diethyl Malonate.—To a solution of diethyl sodiomalonate (from 3.75 g. of sodium and 26 g. (0.16 mole) of diethyl malonate) was added 26 g. (0.16 mole) of 3-bromocyclohexene. The mixture was allowed to stir at room temperature for two hours and, after standing overnight, it was subjected to the usual workup. Distillation afforded 33.3 g. (86%) of diethyl 2-cyclohexenylmalonate, b.p. 108–112° (0.8 mm.), $n^{25}D$ 1.4598. This was hydrolyzed in the usual fashion with methanolic potassium hydroxide and the corresponding malonic acid, m.p. 165–166°, was obtained in 90% yield.

Distillation of 20 g. of this dibasic acid gave 13.4 g. (89%) of 2-cyclohexeneacetic acid, b.p. 150–152° (24 mm.), $n^{25}D$ 1.4787; lit.[30] b.p. 76° (0.01 mm.), 135–136° (15 mm.), $n^{25}D$ 1.4783, $n^{16}D$ 1.4798.

The p-bromophenacyl ester derivative had m.p. 88–89° after crystallization from ethanol.

Anal. Calcd. for $C_{16}H_{17}O_3Br$: C, 56.98; H, 5.08. Found: C, 57.56; H, 5.23.

B. From 2-Cyclohexenemethanol (I).—To 18.2 g. (0.067 mole) of phosphorus tribromide at 0° was added with stirring 15 g. (0.137 mole) of 2-cyclohexenemethanol. The reaction mixture was allowed to warm to room temperature and then was heated at 60–80° overnight. After the addition of water the product was extracted with methylene chloride which was in turn washed with carbonate, dried and distilled, to give 3.9 g. of monobromide, b.p. 73–78° (20–25 mm.), $n^{25}D$ 1.5182–1.5250. There was also obtained 9.1 g. of unidentified material, b.p. 110–122° (10 mm.), $n^{25}D$ 1.5420, which was probably a dibromide.

The monobromide (2.2 g.) was heated under reflux overnight with 3.1 g. of potassium cyanide in 25 ml. of ethanol. The crude nitrile was extracted from the diluted reaction mixture with ether and hydrolyzed by heating for two days in methanolic sodium hydroxide solution followed by two more days of heating in aqueous methanol. The acid was then extracted from the acidified solution and distilled to give 0.8 g. of 2-cyclohexeneacetic acid, b.p. *ca.* 134° (12 mm.), $n^{25}D$ 1.4807. The infrared absorption spectrum of this acid was identical with that of the authentic material described above and on admixture of the corresponding *p*-bromophenacyl esters, there was no depression in melting point.

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(25) H. J. Conroy and R. A. Firestone, This Journal, **78**, 2290 (1956), and earlier references contained therein.

(26) All melting points and boiling points are uncorrected. Infrared absorption spectra were determined using a Perkin–Elmer double beam infrared spectrophotometer, model 21. Ultraviolet absorption spectra were measured on a Beckman model DK automatic recording spectrophotometer. Rotations were obtained by use of a Rudolph high precision polarimeter.

(27) This α-pinene showed no infrared absorption at 11.40 μ characteristic of β-pinene. It had αD +19.45° (neat) and b.p. 152–155°.

(28) A. I. Vogel, *J. Chem. Soc.*, 1323 (1938).

(29) W. Huckel and V. Wenge, *Z. physik. Chem.*, **193**, 146 (1944).

(30) M. Mousseron and F. Winternitz, *Bull. soc. chim.*, **13**, 604 (1946); R. B. Moffett, C. A. Hart and W. M. Hoehn, This Journal, **69**, 1854 (1947).

Examination of the High-boiling Fraction from Cyclohexene and Formaldehyde.—The crude acetate described above, b.p. 120–130° (1–10 mm.), was transesterified by heating in methanol containing dibutyltin oxide. Distillation afforded 9.4 g. of a viscous oil, b.p. *ca.* 134° (2–8 mm.), n^{25}D 1.4960.

This alcohol was unsaturated and absorbed 75% of the theoretical amount of hydrogen for one double bond. The saturated material had b.p. 110.5–117° (0.85 mm.) and n^{25}D 1.4850. A small amount of the phenylurethan of this alcohol, m.p. 156–158.5°, could be obtained but the major portion of the derivative was a non-crystallizable oil. The properties of this phenylurethan were similar to those reported for 2-hydroxymethyl-1-cyclohexanol.[31]

Condensation of α-Pinene with Formaldehyde.—A mixture of 580 g. (4.26 moles) of pure α-pinene and 100 g. (3.33 moles) of paraformaldehyde was heated with shaking for 9 hours at 175–180°. The reaction mixture was washed with water and distilled to give 520 g. of unreacted α-pinene, 66.8 g. (12%) of crude VI, b.p. 115–126° (7–15 mm.), n^{25}D 1.4893, and 37.5 g. of a viscous oil, b.p. *ca.* 130° (1–5 mm.).

The crude alcohol (which contained some formate ester) was added to 25 g. from another run and the combined mixture was transesterified as described above. Distillation afforded 78.3 g. of the alcohol VI, b.p. 90–92° (0.75 mm.), n^{25}D 1.4930–1.4982. The analytical sample showed b.p. 62–62.8° (0.1 mm.), n^{20}D 1.4958, d^{25}_4 0.9755, $[\alpha]$D −16° (*c* 4.4, ethanol), λ_{max} 6.12 and 11.40 μ.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.53; H, 10.85.

The hydrogen phthalate of VI had m.p. 144–144.5° when crystallized from hexane, $[\alpha]$D −22.4° (*c* 1.2, ethanol).

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.50; H, 6.99.

Ozonolysis of VI.—A stream of ozonized oxygen was passed through a solution of 0.34 g. (2 mmoles) of the alcohol VI in 15 ml. of methylene chloride at −70°. The resultant solution of ozonide was added with stirring to a slurry of 2 g. of zinc dust in 10 ml. of acetic acid and the mixture was allowed to stand for one hour. The zinc was removed by filtration and the solution was brought to 50 ml. by the addition of alcohol. To an aliquot (37 ml.) of this solution was added excess dimedone in alcohol containing several drops of piperidine. The methylene chloride was removed by distillation and the cooled residue deposited 0.19 g. of adduct, m.p. 187–190°, undepressed on admixture with an authentic sample of the formaldehyde–dimedone derivative.

Attempts to characterize the larger fragment by forming a 2,4-dinitrophenylhydrazone derivative failed.

Hydrogenation of VI.—An alcoholic solution containing 10 g. of the alcohol VI and 0.5 g. of Adams catalyst was hydrogenated at 3 atm. pressure in a Parr apparatus. The reaction stopped after the uptake of 95% of the theoretical amount of hydrogen required for one double bond and the saturated alcohol resulting was isolated by distillation. In this way there was obtained 7.3 g. (72%) of 2,6,6-trimethylbicyclo[3.1.1]heptane-2-methanol, b.p. 76–78° (0.2 mm.), n^{25}D 1.4847, d^{25}_4 0.9659, $[\alpha]$D −15.7° (*c* 8.7 ethanol).

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.09; H, 11.95.

After several crystallizations from hexane the **hydrogen phthalate** derivative melted at 139.5–141°, $[\alpha]$D −11.9° (*c* 3.9, ethanol).

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.13; H, 7.64. Found: C, 71.91; H, 7.80.

Condensation of *d*-Limonene with Formaldehyde.—A mixture of 1000 g. (7.58 moles) of *d*-limonene and 200 g. (6.66 moles) of paraformaldehyde was shaken in a stainless steel bomb for 10 hours at 180°. The crude reaction mixture was distilled to give 569 g. of unreacted *d*-limonene, 317.3 g. (31%) of a crude unsaturated alcohol, b.p. 108–115° (3–7 mm.), and 166 g. of a high-boiling residue.

The crude alcohol (953 g.) from three experiments was transesterified in the usual fashion to give 761 g. of **homolimonenol**, b.p. 95–98° (2.2 mm.), n^{25}D 1.4978–14990. A center cut was retained for analysis; b.p. 97° (2.2 mm.), n^{25}D 1.4988, d^{25}_4 0.9517, $[\alpha]$D 65.50° (neat); reported values[20] are b.p. 125–126° (9 mm.), n^{20}D 1.5014, d^{20}_4 0.9541, $[\alpha]$D 67.5°.

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.03; H, 10.85.

The acetate derivative, b.p. 95–100° (1.4 mm.), n^{25}D 1.4775, d^{25}_4 0.9691, $[\alpha]$D 53.4° (neat) was prepared in the usual fashion using acetic anhydride and pyridine.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.77; H, 9.64.

The 3,5-dinitrobenzoate derivative crystallized from ethanol as colorless crystals, m.p. 78–79° (Ohloff[20] reported m.p. 79.5–80.5°), $[\alpha]$D 48.1° (*c* 1.1, chloroform). The formation of at least two derivatives was observed in this reaction but only one could be obtained in a pure condition.

Anal. Calcd. for $C_{18}H_{20}O_6N_2$: C, 59.99; H, 5.59. Found: C, 60.01; H, 5.65.

The hydrogen phthalate derivative, $[\alpha]$D 45.5° (*c* 1.5, ethanol), melted at 60.6–61.6° after four recrystallizations from hexane.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.58; H, 7.06. Found: C, 72.64; H, 7.19.

When crystallized from benzene, the **3-nitrophthalate** derivative formed colorless crystals, m.p. 134.5–135.5°, $[\alpha]$D 38.9° (*c* 0.64, ethanol).

Anal. Calcd. for $C_{18}H_{21}O_6N$: C, 63.50; H, 5.89. Found: C, 63.09; H, 5.85.

The phenylurethan derivative crystallized from hexane as a colorless solid, m.p. 55.5–57°, $[\alpha]$D 59.5° (*c* 1.66, hexane).

Anal. Calcd. for $C_{18}H_{23}O_2N$: C, 75.76; H, 8.12. Found: C, 75.72; H, 8.03.

Hydrogenation of Homolimonenol.—A solution of 0.296 g. (1.5 mmoles) of homolimonenol in ethyl acetate containing Adams catalyst absorbed 90.9 ml. of hydrogen (100.6% required for two double bonds). The first equivalent was absorbed in 40 minutes whereas the second required 20 hours. When a plot of hydrogen absorbed *vs.* time was made and the level portion of the curve was extrapolated to zero time the intercept with the hydrogen ordinate occurred at 49 ml. It could thus be estimated that at least 90% of homolimonenol contained an endocyclic double bond.

When prepared on a larger scale and purified by distillation, **dihydrolimonenol**, b.p. 99–103° (1.5 mm.), n^{25}D 1.4838, d^{25}_4 0.9310, $[\alpha]$D 47.5° (neat) and **tetrahydrolimonenol**, b.p. 104–107° (4.1 mm.), n^{25}D 1.4680, d^{25}_4 0.9110, $[\alpha]$D 2.24° (*c* 41, ethanol) were obtained readily. The properties cited above are in good agreement with those obtained by Ohloff.[20] Several attempts to prepare solid derivatives of dihydro and tetrahydrolimonenol failed.

Oxidation of Dihydrolimonenol.—The chromic acid oxidation of dihydrolimonenol produced a complex mixture from which it was possible to isolate a red 2,4-dinitrophenylhydrazone derivative, m.p. 187–188°, λ_{max} 377–383 mμ, ϵ 32,600, and an orange 2,4-dinitrophenylhydrazone derivative, m.p. 90–95°, λ_{max} 365–370 mμ, ϵ 18,000. The orange derivative was analyzed.

Anal. Calcd. for $C_{17}H_{22}O_4N_4$: C, 58.94; H, 6.40. Found: C, 59.27; H, 6.37.

These properties of the hydrazone derivatives are characteristic of an α,β-unsaturated aldehyde and an unconjugated aldehyde, respectively, but it was not possible in this experiment to determine the relative proportion of each in the mixture.

Pyrolysis of Homolimonenonyl Acetate.—The acetate (123 g., 0.6 mole) was dropped slowly (*ca.* 20 drops per minute) through a Pyrex tube, packed with glass helices, in which the temperature was maintained at 500–510° by an electrically heated furnace. The pyrolysate was washed free of acetic acid and distilled to give 4.4 g. of forerun; b.p. 28–76° (25 mm.), n^{25}D 1.4838–1.4881; 43 g. of crude triene, b.p. 77–94° (20 mm.), n^{25}D 1.4960–1.5020, and 45 g. of unreacted acetate.

A second distillation of the triene afforded a purer product; b.p. 70–73° (10 mm.), n^{25}D 1.5017. There was a broad plateau in the ultraviolet absorption spectrum of this material between 210 and 230 mμ, ϵ 8,700. The infrared absorption spectrum showed strong absorption at 6.08, 6.25, 10.05, 10.80 and 11.25 μ. The 10.05 and 10.80 μ bands

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(31) J. Wolinsky, unpublished results.

are especially important because these are characteristic[32] of the vinyl group which would indicate that VII is the main constituent in homolimonenol.

All attempts to prepare a maleic anhydride adduct produced polymeric material.

Condensation of 1-Methylcyclohexene with Formaldehyde.—A mixture of 240.5 g. (2.5 moles) of 1-methylcyclohexene, 39.6 g. (1.25 moles) of paraformaldehyde, 75.5 g. (1.25 moles) of acetic acid and 45.2 g. (0.42 mole) of acetic anhydride was heated to 165° for 12 hours. After the acetic anhydride and acetic acid had been washed from the reaction mixture, unreacted 1-methylcyclohexene (121 g.) was distilled and the residue was acetylated completely by heating with excess acetic anhydride and pyridine. The acetates were then subjected to a fractional distillation through a 30-cm. Vigreux column and after a small forerun there was obtained 113.7 g. (54%) of a mixture of XI and XII, b.p. 95–106° (20 mm.), $n^{20}\text{D}$ 1.4660–1.4682.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.98; H, 9.62.

Most of the material had b.p. 105–106° (20 mm.) and $n^{20}\text{D}$ 1.4660, properties that are very reminiscent of those reported[21] for pure 2-acetoxymethylmethylenecyclohexane (XI). The infrared absorption spectrum ($\lambda_{\max}$ *6.03*, 6.10, 11.26 and *12.54* μ) strongly suggested the presence of another olefin, however, the italicized maxima being characteristic of an endocyclic double bond.[32] Following the procedure of Kolthoff,[23] the mixture of acetates was titrated with perbenzoic acid and from the curve obtained in a plot of percentage double bonds reacted *vs.* time it was estimated that the mixture of acetates comprised *ca.* 64% XII and 36% XI.

The acetates, mixed XI and XII, were subjected to the transesterification conditions described above to give the corresponding alcohols which also formed a constant-boiling mixture; b.p. 113–114° (28 mm.), $n^{20}\text{D}$ 1.4882.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.82; H, 11.21.

Hydrogenation of Mixed XI and XII.—A solution of 6.1 g. (0.036 mole) of the mixture XI and XII in 25 ml. of ethyl acetate was hydrogenated at 50 p.s.i. in the presence of 0.3 g. of Adams catalyst. The usual workup gave 5.5 g. of 2-methylacetoxymethylcyclohexane; b.p. 113–114° (24 mm.), $n^{20}\text{D}$ 1.4498, identical in all respects with an authentic sample prepared by the hydrogenation of pure XI.[21]

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.74; H, 10.63.

Pyrolysis of the Mixed Acetates XI and XII.—The acetates (67.2 g., 0.39 mole) were pyrolyzed at 525° as described above for homolimonenonyl acetate. The pyrolysate (65 g.) was washed free of acetic acid and distilled to give 16.3 g. of diene mixture (XIII and XIV), b.p. 80–82° (110 mm.), $n^{20}\text{D}$ 1.4765–1.4850, $\lambda_{\max}^{\text{isooctane}}$ 235 mμ, log ϵ 3.74; and 29.2 g. of unreacted acetate. Infrared examination of the unpyrolyzed material indicated that it was essentially pure starting material. A center cut of the diene mixture was retained for analysis; b.p. 74–75° (90 mm.).

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.84; H, 11.26.

The infrared absorption spectrum of the dienes XIII and XIV ($\lambda_{\max}$ 6.15, 6.25, 11.25, 12.54 μ) clearly showed that two constituents were present, one containing an exocyclic and the other an endocyclic double bond.

Reaction of the Mixture of Dienes XIII and XIV with Maleic Anhydride.—To a solution of 2.3 g. (0.023 mole) of maleic anhydride and 0.1 g. of hydroquinone in benzene was added at 0° 4.26 g. (0.035 mole) of the diene mixture. The reaction mixture was kept at 0° for one hour and was then allowed to stand at room temperature for two days. The adduct was precipitated by the addition of pentane and after crystallization from hexane showed m.p. 142–143°. It was identical in all respects with an authentic specimen of the adduct prepared from pure 1,2-dimethylenecyclohexane.[21]

The mother liquor from the above filtration was concentrated *in vacuo* to a small volume and the resultant yellow mobile oil was taken up in pentane and washed well with dilute potassium hydroxide solution. Evaporation of the solvent and distillation of the residue gave 1.5 g. of diene XIV, b.p. 129–130°, $n^{20}\text{D}$ 1.4925, $\lambda_{\max}^{\text{isooctane}}$ 235 mμ, log ϵ 4.16; lit.[33] b.p. 135.5° (760 mm.), $n^{20}\text{D}$ 1.4925. Although no spectral data are available for this compound, a similarly constituted diene, 7-methylenecholesterol, has $\lambda_{\max}$ 236 mμ, log ϵ 4.3.[34]

The selective reaction of the diene XIII with maleic anhydride indicated that the diene mixture was about 50% XIII and 50% XIV. The original mixture of acetates (XI and XII) probably had the same approximate 50–50 composition.

Ozonolysis of the Mixture of Dienes XIII and XIV.—A solution of 1.0 g. of diene mixture in 25 ml. of methylene chloride was ozonized in the usual fashion at −70°. The solvent was removed *in vacuo* and 3 ml. of 30% hydrogen peroxide in 20 ml. of acetic acid was added. The resultant solution was heated on a steam-bath for four hours and evaporated to dryness *in vacuo*. The residue was taken up in ether and the slow addition of hexane caused the precipitation of a solid which, when crystallized from water, had m.p. 150–151°. Comparisons of this acid as well as its *p*-bromophenacyl ester (m.p. 153–154°) with adipic acid showed the two to be identical.

The filtrate was evaporated to an oil which was then chromatographed on a small column of silicic acid. The crystalline material eluted with ether had m.p. 98–100° after one crystallization from benzene. The usual comparisons with authentic glutaric acid and its *p*-bromophenacyl ester established their identity.

Attempted Isomerization of XI to XII.—In a 30-ml. Pyrex bomb was placed 10.0 g. (0.06 mole) of pure XI,[21] 3.5 g. (0.06 mole) of acetic acid and 2.1 g. (0.06 mole) of acetic anhydride. The contents were heated with shaking for 12 hours at 160°. The product was isolated as described above for the various thermal condensations and distilled to give 9.5 g. of unreacted XI, b.p. 95–96° (17 mm.), $n^{20}\text{D}$ 1.4646. This experiment conclusively demonstrated that XII is not an artifact arising from XI and hence must result *via* a different reaction path.

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[32] N. Sheppard and D. M. Simpson, *Quart. Rev.* (*Chem. Soc.*), **6**, 1 (1952).

[33] J. E. Faraday, "Encyclopedia of Hydrocarbon Compounds," Chemical Publishing Co., Inc., Brooklyn, N. Y., p. F. 221.

[34] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 186.