Anal. Calcd. for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.72; H, 5.78.

Oxidation of 2,3-Diphenylindone with 9-Hydroperoxy-9-benzylfluorene.—A solution of the hydroperoxide (0.80 g., (0.0028 mole) in pyridine (5 ml.) was added to an ice-cooled solution of the indone (0.70 g., 0.0025 mole) and Triton B (0.1 ml.) in the same solvent (5 ml.), and the mixture was left at room temperature for 2 hours, acidified with acetic acid and poured into water. The precipitated product was filtered, dried, washed with cold alcohol (10 ml.) and recrystallized from the same solvent to afford 0.56 g. (yield 67%) of 2,3-diphenylindone epoxide, m.p. and mixed m.p.[15] 144.5–155.5°. Evaporation of the alcoholic solutions and recrystallization of the residue from benzene–heptane, 1:3, gave 0.60 g. (yield 88%) of 9-benzylfluorenol, m.p. 141–144°.

Acknowledgment.—The author is indebted to Mr. Abraham Deshe for his capable assistance in carrying out the oxidation experiments.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

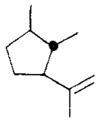
Reactions of Diolefins at High Temperatures. II. The Cyclization of 1,6-Octadiene and 7-Methyl-1,6-octadiene[1]

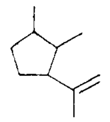
BY WILLIAM D. HUNTSMAN, VICTOR C. SOLOMON AND DONALD EROS

RECEIVED APRIL 18, 1958

1,6-Octadiene undergoes cyclization at 457° to give 1-methyl-*cis*-2-vinylcyclopentane, and under the same conditions 7-methyl-1,6-octadiene furnishes 1-methyl-*cis*-2-isopropenylcyclopentane. 1,6-Heptadiene fails to cyclize even at 500°. These results lend support to the intramolecular mechanism previously proposed for the thermal cyclization of 1,6-diolefins.

At elevated temperatures, properly substituted 1,6-diolefins undergo cyclization to give substituted cyclopentanes. For example, 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane (I) and 1-*cis*-2-dimethyl-*cis*-3-isopropenylcyclopentane (II) are formed from 3,7-dimethyl-1,6-octadiene (III) at 400-500°.[2] Evidence was presented recently which indicates that the cyclization of III proceeds by an intramolecular mechanism involving hydrogen transfer from position 8 to position 1 simultaneously with bond formation between positions 2 and 6.[3] According to this scheme a hydrogen-bearing group at position 8 is a requisite for thermal cyclization; consequently it was anticipated that 1,6-octadiene (IV) would cyclize, but 1,6-heptadiene (V) would not.


I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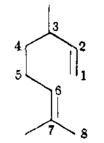
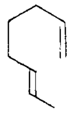
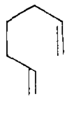


III


IV


V

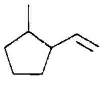
Results

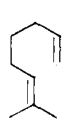
1,6-Heptadiene failed to cyclize at 450 or 500°. The infrared spectra of the pyrolysis products were identical with the spectrum of V and, upon quantitative hydrogenation, the hydrogen consumption corresponded to two double bonds per molecule.

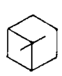
A cyclic olefin (A) was formed in approximately 35% yield when IV was pyrolyzed at 457° with a contact time of 56 seconds. The separation of A from unreacted IV was accomplished by chromatography over silica gel at 0°. Strong absorption bands at 10.00 and 10.99 μ in the infrared spectrum of A indicated the presence of a monosubstituted double bond,[4] RCH=CH$_2$, and the spectrum of the product obtained by hydrogenation of A was identical with the recorded spectrum of 1-methyl-*cis*-2-ethylcyclopentane.[5] These results provide strong evidence that A is 1-methyl-*cis*-2-vinylcyclopentane (VI); this was confirmed by comparison with a sample of VI obtained by an independent synthesis. Analysis of the pyrolysate by careful fractional distillation and vapor–liquid partition chromatography showed that 1-methyl-*trans*-2-vinylcyclopentane (VII) was absent.

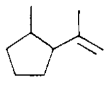
The 1,6-octadiene used in this study was apparently a mixture of the *cis* and *trans* isomers as evidenced by infrared absorption bands at 14.38 and 10.35 μ.[4] Evidently both isomers underwent cyclization since the ratio of the intensities of these bands was essentially the same for the pyrolysate as for the starting diolefin. Models reveal that both isomers should be able to assume the proper conformation for cyclization with nearly equal facility.

A cyclic olefin (B), b.p. 147.5-148.5°, n^{25}_D 1.4480, was obtained by the pyrolysis of 7-methyl-1,6-octadiene (VIII) at 457°. These properties, as well as the infrared spectrum, are in agreement with those reported (b.p. 149-150°, n^{20}_D 1.4496) for a cyclic olefin (C) obtained by the pyrolysis of 6,6-


VI *cis*
VII *trans*


VIII


IX


X *cis*
XI *trans*

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(1) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)546.

(2) H. Pines, N. E. Hoffman and V. N. Ipatieff, THIS JOURNAL, **76**, 4412 (1954).

(3) W. D. Huntsman and T. H. Curry, *ibid.*, **80**, 2252 (1958).

(4) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

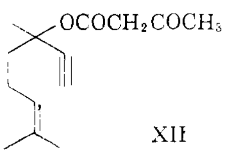
(5) Catalog of Infrared Spectral Data, Serial No. 534, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1946.

dimethylnorpinane (IX), to which the structure 1-methyl-*trans*-2-isopropenylcyclopentane (XI) was assigned.[6] The properties of B, however, differed markedly from those of a sample of XI obtained by an independent synthesis (b.p. 141.1-141.8°, $n^{25}D$ 1.4430).[7] Furthermore, hydrogenation of B gave a hydrocarbon which was identical with an authentic sample of 1-methyl-*cis*-2-isopropylcyclopentane and it may be concluded that B and C are 1-methyl-*cis*-2-isopropenylcyclopentane (X).

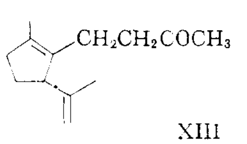
The assignment of the *trans* configuration to C by Pines and Hoffman was based on the formation of methyl *trans*-2-methylcyclopentyl ketone (XIV) upon ozonolysis. The identity of XIV was established by comparison with an authentic sample, and appears to be beyond question. Consequently epimerization must have occurred during the degradation, possibly during the decomposition of the ozonide with zinc and acetic acid.[8]

Models of IV and VIII can be arranged in the conformations required for the formation of either the *cis* (VI, X) or the *trans* (VII, XI) cyclic products. The exclusive formation of VI and X, however, indicates the former to be favored. Evidently the factors responsible for the fact that *cis*-1,2-dialkylcyclopentanes are less stable than the corresponding *trans* isomers[9] have not developed sufficiently in the transition state to govern the course of cyclization of these diolefins. In contrast to the behavior of IV and VIII, the major product of the cyclization of III is the *trans* isomer I.[2] Models of III reveal that this may be due to a greater amount of steric interference by the C_3-methyl group when the conformation corresponds to that leading to II.

It was shown recently that XIII is one of the products formed by heating dehydrolinalyl acetoacetate (XII).[10] The similarity between this ring closure and that observed for 1,6-diolefins makes the hypothesis that both occur by the same mechanism attractive. Models of alk-6-ene-1-ynes such as XII possess geometries even more favorable than 1,6-diolefins for intramolecular cyclization. Experiments designed to test this hypothesis are in progress. It should be pointed out that the temperature required for the formation of XIII from XII (150-200°) is much lower than that required for the cyclization of 1,6-diolefins (380°). This may possibly be due to a more suitable geometry in the acetylenic analog, or to the electron-withdrawing acetoacetoxy group at position 3 in XII.



XII



XIII

It is interesting to consider the possibility of closing larger rings by the thermal isomerization of higher diolefins. Models show favorable geometries for the cyclization of 1,7- and 1,8-diolefins. This possibility will be investigated in the near future.

Synthesis of Diolefins.—The synthesis of 1,6-heptadiene was accomplished by coupling allyl bromide with 3-butenylmagnesium bromide. The properties of the diolefin

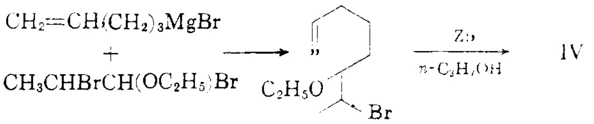
$$CH_2{=}CHCH_2Br + CH_2{=}CHCH_2CH_2MgBr \longrightarrow V$$

prepared in this way agreed with previously reported values. An analogous coupling reaction involving the same Grignard reagent and isoprene hydrochloride furnished 7-methyl-1,6-octadiene. Considerable difficulty was encountered in re-

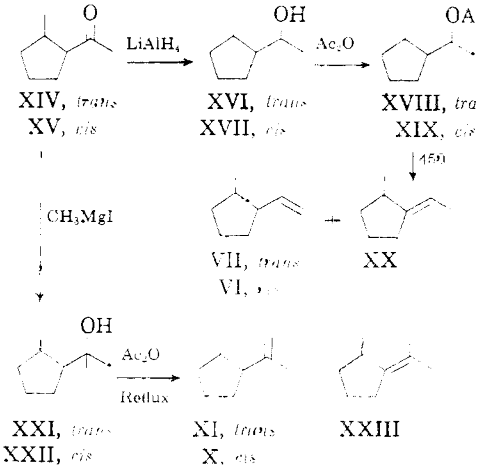
$$(CH_3)_2C{=}CHCH_2Cl + CH_2{=}CHCH_2CH_2MgBr \longrightarrow VIII$$

moving halogen-containing impurities from this hydrocarbon.

The classical Boord olefin synthesis[11] proved to be the most satisfactory of several schemes investigated for the synthesis of 1,6-octadiene. The reaction of 4-pentenylmagnesium bromide with ethyl 1,2-dibromopropyl ether gave 6-ethoxy-7-bromo-1-octene which, upon treatment with zinc dust in refluxing *n*-propyl alcohol, furnished 1,6-octadiene.



Synthesis of 1-Methyl-2-alkenylcyclopentanes.—The methods used for the synthesis of the various cyclopentane derivatives for comparison with the cyclization products are outlined



Methyl *trans*-2-methylcyclopentyl ketone (XIV), obtained by the reaction of acetyl chloride with cyclohexane in the presence of aluminum chloride,[6,12] was reduced by lithium aluminum hydride to the corresponding alcohol XVI. Pyrolysis of the acetate ester XVIII gave the desired olefin VII accompanied by a small amount of an isomeric olefin, assumed to be 1-methyl-2-ethylidenecyclo-

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(6) H. Pines and N. E. Hoffman, This Journal, **76**, 4417 (1954).

(7) B. Shive, J. Horeczy, G. Wash and H. L. Lochte, *ibid.*, **64**, 385 (1942), report b.p. 140°, $n^{22}D$ 1.4452 for XI.

(8) D. H. R. Barton, P. de Mayo and M. Shafiq, *J. Chem. Soc.*, 929 (1957), have noted epimerization during the cleavage of the ozonide of isophotosantonic lactone.

(9) M. S. Newman, editor, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 36.

(10) W. Kimel, J. D. Surmatis, J. Weber, G. O. Chase, N. W. Sax and A. Ofner, *J. Org. Chem.*, **22**, 1611 (1957); G. Saucy, L. H. Chopard-dit-Jean, W. Guex, G. Ryser and O. Isler, *Helv. Chim. Acta*, **41**, 160 (1958).

(11) B. H. Shoemaker and C. E. Boord, This Journal, **53**, 1505 (1931).

(12) C. D. Nenitzescu and I. P. Cantuniari, *Ann.*, **510**, 269 (1934).

pentane (XX) on the basis of a strong infrared absorption band at 12.30 μ.[4] There is evidence that unlike the behavior of simple alkyl acetates,[13] elimination during the pyrolysis of 1-cyclopentylalkyl acetates does not proceed exclusively toward the least substituted position. For example, both vinylcyclopentane and ethylidenecyclopentane are produced by the pyrolysis of 1-cyclopentylethyl acetate.[14]

A similar synthesis, starting with the *cis*-ketone-XV, was used for VI. In this case, however, the olefinic product from the acetate pyrolysis contained a large amount of the *trans* isomer VII in addition to the expected olefins VI and XX. The origin of VII is uncertain; conceivably the starting ketone might have contained some of the *trans* isomer, but this is believed unlikely. The ketone was obtained by hydrogenating methyl 2-methylcyclopentenyl ketone in the presence of palladium black and was purified by recrystallizing the semicarbazone to constant melting point.[15] The physical constants agreed with those reported by Turner for the *cis*-ketone and the infrared spectrum, although quite similar in gross features to that of the *trans* isomer, indicated that the latter was no more than a minor component. The lithium aluminum hydride used for the reduction of XV contained a large amount of ether-insoluble material which may have caused epimerization. Unfortunately, sufficient ketone was not available to repeat the reduction with a pure sample of lithium aluminum hydride.

The dimethyl-2-methylcyclopentylcarbinols (XXI) and (XXII), upon dehydration by refluxing with acetic anhydride, furnished the corresponding isopropenyl derivatives XI and X, respectively, along with small amounts of 1-methyl-2-isopropylidenecyclopentane XXIII. It was possible to separate the *trans* isomer (XI) from XXIII by fractional distillation, but the boiling point of the *cis* isomer (X) was too close to that of XXIII to permit its separation. In this case, the mixture of X and XXIII was hydrogenated in the presence of platinum oxide to give 1-methyl-*cis*-2-isopropylcyclopentane.

Experimental[16]

Methyl *trans*-2-Methylcyclopentyl Ketone (XIV).[6,12]—The reaction of 1600 ml. of cyclohexane, 375 g. of acetyl chloride and 750 g. of aluminum chloride gave 209 g. of crude XIV, b.p. 94–97° (72 mm.), $n^{25}\mathrm{D}$ 1.4395. The pure ketone, obtained by fractionation through column B, b.p. 90° (70 mm.), $n^{25}\mathrm{D}$ 1.4385, was unchanged by treatment with sodium ethoxide in ethanol.[15]

Methyl *cis*-2-methylcyclopentyl ketone (XV) was prepared and purified by the procedure of Turner.[15] The semicarbazone had m.p. 165–166° (uncor.). The ketone obtained by hydrolysis of the semicarbazone in the presence of phthalic anhydride was fractionated through column C, b.p. 64–65° (18 mm.), $n^{25}\mathrm{D}$ 1.4428.

1-(*trans*-2-Methylcyclopentyl)-ethanol (XVI).—A solution of 25.7 g. (0.20 mole) of XIV in an equal volume of dry ether was added dropwise to a stirred solution of 2.28 g. (0.060 mole) of lithium aluminum hydride in 100 ml. of dry ether. After hydrolyzing with 10% sulfuric acid and drying over potassium carbonate, there was obtained 22.4 g. of XVI, b.p. 74–75° (13 mm.), $n^{25}\mathrm{D}$ 1.4530.

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.78; H, 12.37.

1-(*trans*-2-Methylcyclopentyl)-ethyl Acetate (XVIII).—A mixture of 22 g. (0.172 mole) of XVI, 20 g. (0.196 mole) of acetic anhydride and 0.7 ml. of anhydrous pyridine was refluxed for 3 hr. Water (2 ml.) was added to hydrolyze the excess acetic anhydride and refluxing was continued for 15 minutes. The cold reaction mixture was washed with water, 5% sodium carbonate and again with water. After drying over sodium sulfate, there was obtained 24.8 g. of 1-(*trans*-2-methylcyclopentyl)-ethyl acetate, b.p. 79–80° (13 mm.), $n^{25}\mathrm{D}$ 1.4340.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.52; H, 10.55.

1-(*cis*-2-Methylcyclopentyl)-ethyl Acetate (XIX).—Acetylation of 9.0 g. (0.070 mole) of XVII by the same procedure as for the *trans*-alcohol gave 10.2 g. of 1-(*cis*-2-methylcyclopentyl)-ethyl acetate, b.p. 80–81° (13 mm.), $n^{25}\mathrm{D}$ 1.4358.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.14; H, 10.01.

1-Methyl-*trans*-2-vinylcyclopentane (VII).—Pyrolysis of 18.5 g. of XVIII at 440° in a Pyrex tube packed with glass helices according to the procedure of Bailey and King[13] gave 8.20 g. of olefin, b.p. 112–125°, $n^{25}\mathrm{D}$ 1.4331. Fractional distillation (column C) gave 5.7 ml. of 1-methyl-*trans*-2-vinylcyclopentane, b.p. 114.5–115.2°, $n^{25}\mathrm{D}$ 1.4300.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.28; H, 12.74.

A small amount (1.0 ml.) of a higher boiling olefin, b.p. 127.2–128.0°, $n^{25}\mathrm{D}$ 1.4450, also was obtained. A strong infrared absorption band at 12.30 μ indicated this fraction to be 1-methyl-2-ethylidenecyclopentane (XX), but weak bands at 10.05 and 10.98 μ indicated the presence of a small amount of VII.

1-Methyl-*cis*-2-vinylcyclopentane (VI).—Pyrolysis of 9.8 g. of XIX by the same procedure as for the *trans*-ester gave 4.0 g. of olefin, b.p. 118–122°, $n^{25}\mathrm{D}$ 1.4373. The following fractions were obtained by fractionation through column C: cut 1, 1.3 ml., b.p. 114.2–115.5°, $n^{25}\mathrm{D}$ 1.4300; cut 2, 1.2 ml., b.p. 115.5–120°, $n^{25}\mathrm{D}$ 1.4340; cut 3, 0.5 ml., b.p. 120–122.7°, $n^{25}\mathrm{D}$ 1.4375; cut 4, 0.6 ml., b.p. 122.7–127.5°, $n^{25}\mathrm{D}$ 1.4420; and cut 5, 1.1 ml., b.p. 127.5–128°, $n^{25}\mathrm{D}$ 1.4450. These fractions were examined by vapor-liquid partition chromatography and infrared spectroscopy. Cut 1 was identified as 1-methyl-*trans*-2-vinylcyclopentane (VII) and cut 5 as 1-methyl-2-ethylidenecyclopentane (XX). Cut 3 consisted of 1-methyl-*cis*-2-vinylcyclopentane (VI), 85%, the remainder being the *trans* isomer VII.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.82; H, 12.97.

2-(*trans*-2-Methylcyclopentyl)-2-propanol (XXI).—A solution of 37.8 g. (0.3 mole) of methyl *trans*-2-methylcyclopentyl ketone in an equal volume of dry ether was added dropwise to a stirred solution of methylmagnesium bromide prepared from 7.3 g. (0.3 gram atom) of magnesium. The mixture was hydrolyzed with ammonium chloride and ice, and the ether layer was washed with water, 10% sodium carbonate, and again with water. After drying over potassium carbonate there was obtained 36.9 g. of XXI, b.p. 68–69° (9 mm.), $n^{25}\mathrm{D}$ 1.4542.

Anal. Calcd. for $C_9H_{18}O$: C, 76.01; H, 12.76. Found: C, 75.55; H, 12.18.

2-(*cis*-2-Methylcyclopentyl)-2-propanol (XXII).—From 25.2 g. (0.20 mole) of methyl *cis*-2-methylcyclopentyl ketone and methylmagnesium iodide prepared from 4.86 g. (0.20 gram-atom) of magnesium, there was obtained 23.6 g. of XXII, b.p. 76–77° (14 mm.) (column C), $n^{25}\mathrm{D}$ 1.4590.

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[13] W. J. Bailey and C. King, THIS JOURNAL, **77**, 75 (1955).

[14] J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952); K. W. Greenlee and V. G. Wiley, Abstracts of Papers presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, 1955, page 10-N.

[15] R. B. Turner, THIS JOURNAL, **72**, 878 (1950).

[16] These various columns were used for fractional distillations: column A, 50 cm., packed with 1/8 in. glass helices; column B, 90 cm., packed with 1/8 in. glass helices; column C, spinning band column H. S. Martin Co., Evanston, Ill. A Fisher–Gulf partitioner equipped with a 20-ft. column packed with C-22 firebrick impregnated with tricresyl phosphate was used for the vapor–liquid partition analyses. Microanalyses were performed by the Clark Microanalytical Laboratory, Urbana, Ill., and by the Galbraith Laboratories, Knoxville, Tenn. The authors acknowledge with gratitude the financial aid provided by the National Science Foundation for the purchase of the Perkin–Elmer model 21 infrared spectrophotometer used in this study (NSF G3912).

Anal. Calcd. for $C_9H_{18}O$: C, 76.01; H, 12.76. Found: C, 75.44; H, 12.28.

1-Methyl-*trans*-2-isopropenylcyclopentane (XI).—A solution of 35.6 g. (0.250 mole) of XXI, 28.0 g. (0.274 mole) of acetic anhydride and 1 ml. of pyridine was refluxed for 5 hr. After working up in the usual manner, there was obtained 15.4 g. of crude olefin, b.p. 142–144°, $n^{25}D$ 1.4443, and 17.6 g. of a mixture of unreacted alcohol and its acetate ester, b.p. 83–87° (13 mm.), $n^{25}D$ 1.4420. Pure 1-methyl-*trans*-2-isopropenylcyclopentane, b.p. 141.1–141.8°, $n^{25}D$ 1.4430, was isolated by fractionation of the crude olefin in column C.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.33; H, 12.60.

A small amount (0.7 ml.) of an isomeric olefin, b.p. 147.8–150.4°, $n^{25}D$ 1.4532, which was apparently 1-methyl-2-isopropylidenecyclopentane (XXIII) also was obtained. Kishner reports b.p. 149–151°, n_D 1.4518 for XXIII.[17]

1-Methyl-*cis*-2-isopropylcyclopentane.—Dehydration of 11.4 g. of XXII by the same procedure as for the *trans* isomer gave 7.0 g. of olefin, b.p. 147–150°, $n^{25}D$ 1.4480–1.4510. This material was mixed with acetic acid (7 ml.) and hydrogenated at 3 atm. pressure in the presence of platinum oxide. After working up in the usual way, fractionation in column C gave pure 1-methyl-*cis*-2-isopropylcyclopentane, b.p. 147.5–148.5°, $n^{25}D$ 1.4312.

Anal. Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.68; H, 14.39.

1,6-Heptadiene (V).—A solution of 217 g. (1.79 moles) of allyl bromide in an equal volume of anhydrous ether was added dropwise to a stirred solution of 3-butenylmagnesium bromide prepared from 242 g. (1.79 moles) of 4-bromo-1-butene[18] and 43.5 g. (1.79 gram-atoms) of magnesium. The mixture was allowed to stand overnight and then hydrolyzed with ice and ammonium chloride. The ether layer was washed with water, 10% sodium carbonate, again with water, and dried over calcium chloride. Distillation furnished 124 g. of crude 1,6-heptadiene, b.p. 83–90°. The pure diolefin, b.p. 88.5–89°, $n^{25}D$ 1.4118, was obtained by fractionating the crude product through column A; literature[19] b.p. 90.0°, $n^{20}D$ 1.4142.

1,6-Octadiene (IV).—A solution of 221 g. (0.9 mole) of ethyl 1,2-dibromopropyl ether[11] in an equal volume of anhydrous ether was added dropwise to a stirred, cooled solution of a Grignard reagent prepared from 152 g. (1.02 moles) of 5-bromo-1-pentene[20] and 24.0 g. (0.99 gram-atom) of magnesium. The mixture was stirred for 4 hr., allowed to stand overnight, and then poured over crushed ice. The ether layer was washed three times with water, dried over calcium chloride and the ether removed. After adding 10 g. of potassium hydroxide, distillation of the residue under reduced pressure gave 140 g. of crude 6-ethoxy-7-bromo-1-octene, b.p. 90–100° (9 mm.).

The crude bromo ether was dissolved in 250 ml. of *n*-propyl alcohol and placed in a one-liter, three-necked flask equipped with a mercury-sealed Hershberg stirrer and a 30-cm. Widmer column with distillate-takeoff head. Zinc dust (150 g.) was added, stirring was started, and the mixture was heated to reflux. The vapor temperature dropped rapidly from 97 to 83° (azeotrope of *n*-propyl alcohol and 1,6-octadiene) and distillate was withdrawn slowly so that the vapor temperature did not rise above 85°. At the end of the reaction (14 hr.) the last traces of olefin were removed by withdrawing distillate until the vapor temperature reached 97°. The distillate was poured into water, and the organic layer that separated was washed with several small portions of water. After drying over calcium chloride, there was obtained 40 g. of 1,6-octadiene, b.p. 121.5–122°, $n^{25}D$ 1.4255.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.43; H, 12.72.

7-Methyl-1,6-octadiene (VIII).—A solution of 142 g. (1.36 moles) of isoprene hydrochloride[21] in an equal volume of anhydrous ether was added dropwise to a Grignard reagent prepared from 184 g. (1.36 moles) of 4-bromo-1-butene[18] and 33 g. (1.36 gram-atoms) of magnesium. The mixture was stirred for 2 hr., allowed to stand overnight, and hydrolyzed with ammonium chloride–ice. After washing and drying, there was obtained 89.5 g. of crude 7-methyl-1,6-octadiene, b.p. 130–144°, $n^{25}D$ 1.4361. A solution of this material and 5 g. of lithium aluminum hydride in 200 ml. of tetrahydrofuran was refluxed for 8 hr. in order to remove the halogen-containing impurities.[22] After working up in the usual way, fractionation in column B gave 7-methyl-1,6-octadiene, b.p. 143–144°, $n^{25}D$ 1.4345; literature[6] b.p. 143.5–144.0°, $n^{20}D$ 1.4369. The infrared spectrum agreed with that reported by Pines and Hoffman.[6]

Pyrolysis of 1,6-Heptadiene.—Twenty-three grams of 1,6-heptadiene was added dropwise over a period of 2.5 hours to a Pyrex tube (1.8 cm. × 75 cm.) packed with copper pellets[6] and thermostated at 450°. Distillation of the pyrolysate gave 19 g. of material, b.p. 87–90°, $n^{25}D$ 1.4122. The infrared spectrum of this material was identical with that of 1,6-heptadiene. Upon hydrogenation of a sample in the presence of platinum oxide, the hydrogen consumption amounted to 102% of that calculated for two double bonds per molecule. Similar results were obtained when the pyrolysis was carried out at 495°.

Pyrolysis of 1,6-Octadiene.—The apparatus was the one previously described.[3] Nitrogen (32.5 ml./min.) was passed through the reactor during the addition of 27.0 g. of 1,6-octadiene over a period of 140 min. The reactor temperature was 457°. Distillation of the pyrolysate (24 g.) gave 19 g. of material, b.p. 119.5–121.5°, $n^{25}D$ 1.4340. Chromatography over silica gel at 0° furnished 5.7 g. of a cyclic olefin, b.p. 121–122°, $n^{25}D$ 1.4400.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.29; H, 12.73.

Vapor-liquid partition chromatography and infrared spectroscopy showed this material to be identical with the major component of the "synthetic" 1-methyl-*cis*-2-vinylcyclopentane (Cut 3). Minor bands in the spectrum of the latter which were due to the presence of the *trans* isomer were absent from the spectrum of the olefin obtained by pyrolysis.

A 0.185-g. sample absorbed 3.17 × 10^{-3} mole of hydrogen (95% of the theoretical amount for 1 double bond) in the presence of platinum oxide, and the spectrum of the saturated product was identical with that of 1-methyl-*cis*-2-ethylcyclopentane.[5]

The remainder of the material from the chromatographic separation consisted of IV (60%) and VI (40%).

Pyrolysis of 7-Methyl-1,6-octadiene.—The pyrolysis of 20.9 g. of this diolefin at 457° with a contact time of 56 seconds gave 19.2 g. of product, $n^{25}D$ 1.4463. Fractionation through column C furnished 12.8 g. of material, b.p. 141–148.5°, $n^{25}D$ 1.4432–1.4480. A cyclic olefin, b.p. 147.5–148.5°, $n^{25}D$ 1.4480, was isolated by chromatography over silica gel at 0°.

A 0.394-g. sample of this substance absorbed 3.13 × 10^{-3} mole of hydrogen (98.5% of the theoretical amount for 1 double bond) upon hydrogenation in the presence of platinum oxide, and the infrared spectrum of the saturated product ($n^{25}D$ 1.4300) was identical with that of the synthetic 1-methyl-*cis*-2-isopropylcyclopentane.

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