Acknowledgment.—We are greatly indebted to Dr. George Van Dyke Tiers and Minnesota Mining and Manufacturing Co., St. Paul, Minn., for NMR spectra, to Dr. R. W. Kiser and Mr. Emilio Gallegos for a mass spectrum, and Dr. G. Dana Johnson for his comments.

A Study of the Thermal Cyclization of 1,7-Alkadienes and Monocyclic Dienes[1]

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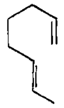
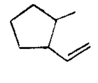
8-Methyl-1,7-nonadiene fails to cyclize at 440°, but does cyclize to an appreciable extent at 490° giving 1-methyl-2-isopropenylcyclohexane. The carbomethoxy group facilitates thermal cyclization as shown by the fact that methyl 5,9-dimethyl-2,8-decadienoate (X) cyclizes rapidly at 400°. The products are three diastereomeric methyl 8-*p*-menthene-3-acetates (XI), the major one of which is believed to be the most stable diastereomer, XII.

Monocyclic diolefins in which one double bond is contained in a six-membered ring fail to give bicyclic compounds at temperatures as high at 500°.

It was shown recently that suitably constituted 1,6-alkadienes undergo cyclization at 450° to give cyclopentane derivatives.[2] For example, 1,6-octadiene (I) gives 1-methyl-2-vinylcyclopentane (II), and 7-methyl-1,6-octadiene (III) gives 1-methyl-2-isopropenylcyclopentane (IV). Evidence has been presented which indicates that these thermal cyclizations proceed by an intramolecular mechanism.[3]


I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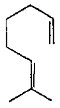
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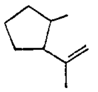
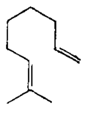
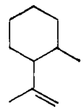

IV

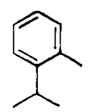
We were interested in extending this study (1) to see if cyclohexane derivatives could be obtained from 1,7-alkadienes, (2) to determine the effect of substituents other than alkyl groups, and (3) to determine if bicyclic compounds could be obtained from monocyclic dienes.

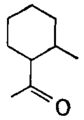
Results and Discussion

8-Methyl-1,7-nonadiene (V) was chosen for the first part of the study. No change occurred when this compound was heated at 440°, but when the temperature was increased to 490°, cyclization occurred to a significant extent. Quantitative hydrogenation indicated that the pyrolysate consisted of 25% monoolefin and 75% diolefin. The mixture was separated by chromatography over silica gel, and the diolefin was identified as unchanged starting material (V), while the monoolefin was shown to be 1-methyl-2-isopropenylcyclohexane (VI) by the following evidence.


V


VI


VII


VIII

The results of elemental analysis agreed with the formula $C_{10}H_{18}$. Strong infrared bands at 6.05 and 11.26 μ indicated a double bond of the type $R_2C{=}CH_2$.[4] *o*-Cymene (VII) was obtained when a sample of the pyrolysate was hydrogenated and then dehydrogenated over platinum-alumina. Ozonolysis gave a ketone $C_9H_{16}O$ (analyzed as the semicarbazone) which gave a positive iodoform test. Comparison of the infrared spectrum with those of authentic samples revealed that this ketone was a mixture of methyl *cis*- and methyl *trans*-2-methylcyclohexyl ketone (VIII).[5]

Methyl 5,9-dimethyl-2,8-decadienoate (X) was chosen for the study of the effect of substituents other than alkyl groups. In contrast to the behavior of V, extensive reaction occurred when X was heated at 400°, and the gas chromatography tracing of the product showed three peaks; the components are designated A, B, and C in the order of increasing retention times in the following discussion. Calculation of the approximate composition from the peak areas indicated 53% A, 29% B, and 18% C. Component C possessed a retention time identical with that of X, and was subsequently shown to be identical with it. Careful fractional

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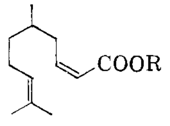
[1] Financial support by the National Science Foundation (G7379) and the Ohio University Research Fund is gratefully acknowledged.

[2] H. Pines, N. E. Hoffman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 4412 (1954); W. D. Huntsman, V. C. Solomon, and D. Eros, *ibid.*, **80**, 5455 (1958).

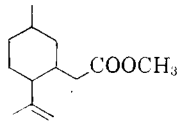
[3] W. D. Huntsman and T. H. Curry, *ibid.*, **80**, 2252 (1958).

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1958, p. 34.

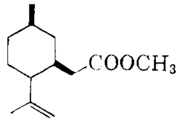
[5] It is possible that some epimerization occurred during the degradation, *e.g.*, see ref. 2. Unfortunately, a gas chromatography instrument suitable for checking the homogeneity of the cyclic olefin was not available to us at the time this work was done.



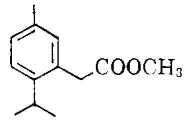
IX. R = H
X. R = CH_3



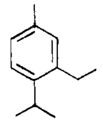
XI



XII



XIII



XIV

distillation effected the separation of these components: A, b.p. 126.5–127.5° (15 mm.); B, b.p. 132–133.5° (15 mm.); and C, b.p. 144.3–145° (15 mm.).

Results from elemental analysis and quantitative hydrogenation showed A and B to be monocyclic isomers of X, and a strong band at 11.2 μ in the spectrum of each component indicated the double bond to be present in an isopropenyl group. The product obtained by hydrogenating A gave a single peak on gas chromatography, but two peaks appeared in the tracing of the saturated product from B. A single peak appeared when B itself was subjected to gas chromatography under the usual conditions, but two incompletely resolved peaks appeared when the analysis was carried out at very low flow rates. Neither of these peaks corresponded to A.

When A was refluxed in the presence of palladium-charcoal,[6] disproportionation, rather than dehydrogenation, was the major reaction. Chromatography of the product over alumina furnished an aromatic ester shown to be methyl 3-*p*-cymeneacetate (XIII) by comparison with an authentic sample. The remainder of the product was a saturated ester; prolonged refluxing of this material with palladium-charcoal failed to effect dehydrogenation. Failure of the saturated and unsaturated esters to undergo dehydrogenation is most likely due to the fact that their boiling points are lower than the optimum temperature for dehydrogenation. It is significant that the saturated ester formed by disproportionation of A is identical with the product obtained by hydrogenation of A in the presence of platinum.

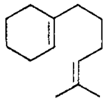
Similar results were obtained by refluxing B over palladium-charcoal; methyl 3-*p*-cymeneacetate (XIII) and saturated ester were obtained. Only one major peak appeared in the gas chromatography tracing of the saturated material, and this peak occurred at a retention time corresponding to the saturated ester obtained from isomer A. The infrared spectra of these two products corresponded closely, but all of the saturated esters encountered in this study have spectra that are very similar, rendering positive identification difficult.

The possibility remained that cyclopentane derivatives constituted part of the material which failed to dehydrogenate, and to settle this question, a more effective method of dehydrogenation was needed. Vapor phase dehydrogenation of the saturated esters over platinum-alumina proved unsatisfactory because extensive decomposition occurred. It has been shown that cyclohexane hydrocarbons are converted to aromatic hydrocarbons in high yield over platinum-alumina.[7] Consequently the saturated esters from A and B were combined and the carbomethoxy group was converted to a methyl group by the sequence: $RCH_2COOCH_3 \rightarrow RCH_2CH_2OH \rightarrow RCH_2CH_2OTs \rightarrow RCH_2CH_3$. Dehydrogenation of this product occurred rapidly over platinum-alumina at 300° furnishing 3-ethyl-*p*-cymene (XIV) in good yield. Gas chromatography showed that all but a trace of the starting material had reacted, and it may be concluded that cyclopentane derivatives were not formed in the cyclization reaction.

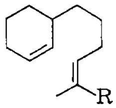
Therefore, the products of thermal cyclization of X must be stereoisomeric methyl 8-*p*-methene-3-acetates (XI). Sufficient evidence is not at hand to permit a positive configurational assignment for these isomers, but there is support for the assignment of XII to the major product A. As pointed out above, the major component of the saturated ester fraction obtained by disproportionation of the unsaturated esters over palladium charcoal was the same as the ester obtained by hydrogenating A. It is known that *cis, trans* isomerization occurs when cyclohexane derivatives are heated in the presence of dehydrogenation catalysts.[8] One would anticipate the formation of the most stable stereoisomer, *i.e.*, XII in the present case.

The mechanism of activation by the carbomethoxy group is uncertain; possibly, it may be related to the lower energy required for uncoupling the pi electrons in α,β-unsaturated carbonyl compounds than in simple alkenes. Further studies of the effect of substituents are in progress.

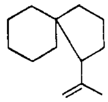
Compounds XV–XVII were chosen for the study of the thermal cyclization of monocyclic dienes.



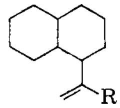
XV



XVI. R = CH_3
XVII. R = H



XVIII



XIX. R = CH_3
XX. R = H

By analogy with acyclic 1,6-alkadienes, one would expect XV to yield 1-isopropenylspiro[4.5]decane (XVIII), while XVI and XVII would be expected to give the substituted decalins XIX and XX.

1-(5-Methyl-4-hexenyl)cyclohexene (XV) failed to cyclize to a detectable extent at temperatures up to 500°. The product from a reaction carried out

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[6] M. S. Newman and H. V. Zahn, *J. Am. Chem. Soc.*, **65**, 1097 (1943).

[7] H. Pines, R. C. Olberg, and V. N. Ipatieff, *ibid.*, **70**, 533 (1948).

[8] N. D. Zelinsky and E. I. Margolis, *Ber.*, **65**, 1613 (1932).

at 450° absorbed 97% of the theoretical amount of hydrogen required for two double bonds, and 1-isopropylspiro[4.5]decane could not be detected in the saturated product by gas chromatography. Similar results were obtained at 500°, except that considerable decomposition occurred.

The 1,7-dienes, XVI and XVII, likewise failed to cyclize. The infrared spectrum of the product obtained by heating XVI at 500° showed only minor differences from that of the starting material, and gas chromatography revealed that small amounts of two compounds were present in addition to unreacted XVI. However, when this material was dehydrogenated, only 1-phenyl-5-methylhexane was formed, and it may be concluded that XIX was not among the pyrolysis products. The infrared spectrum of the pyrolysis product from XVII was identical with that of the starting diolefin.

It is likely that steric factors introduced by the ring are responsible for the failure of these monocyclic diolefins to cyclize. Models indicate that the quasi-axial hydrogens offer considerable interference in the conformations necessary for intramolecular cyclization.

Experimental[9]

8-Methyl-1,7-nonadiene (V).—4-Pentenylmagnesium bromide was prepared by the reaction of 150 g. (1 mole) of 5-bromo-1-pentene[10] with 24.3 g. (1 g.-atom) of magnesium. A solution of 92 g. (0.80 mole) of 1-chloro-3-methyl-2-butene[11] in an equal volume of ether was added dropwise, and the mixture was allowed to stand overnight. The mixture was hydrolyzed with ice–ammonium chloride, dried over calcium chloride, and the ether was stripped. Two fractions were obtained when the residue was fractionated in a 90-cm. column packed with glass helices; fraction 1, 21.8 g., b.p. 85–90° (100 mm.), $n^{25}\text{D}$ 1.4355; fraction 2, 52.5 g., b.p. 101–102° (100 mm.), $n^{25}\text{D}$ 1.4392.

Fraction 2 was shown to be the desired compound, 8-methyl-1,7-nonadiene, by the following evidence.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.95; H, 13.05. Found: C, 86.89; H, 13.05.

Infrared absorption bands appeared at 5.97, 10.08, and 10.99 μ, characteristic of a vinyl group, and at 5.97 and 12.00 μ, corresponding to a trisubstituted double bond. A 0.00899-mole sample absorbed 0.0185 mole of hydrogen (102% of the theoretical amount for two double bonds), and the infrared spectrum of the saturated product corresponded exactly to the recorded spectrum of 2-methylnonane.[12]

Fraction 1 was evidently 3,3-dimethyl-1,7-octadiene, formed by coupling of the Grignard reagent at the tertiary position of the halide. The material was refractionated in a spinning band column, b.p. 154–155°, $n^{25}\text{D}$ 1.4360. Infrared absorption bands appeared at 6.08, 10.00, and 10.98 μ ($RCH{=}CH_2$) and a doublet at 7.25 and 7.34 μ (*gem*-dimethyl group).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.95; H, 13.05. Found: C, 86.87; H, 13.25.

Methyl 5,9-Dimethyl-2,8-decadienoate (X).—Condensation of 233 g. (1.51 moles) of citronellal with 260 g. (2.50 moles) of malonic acid in the presence of 450 ml. of pyridine according to the procedure of Ruzicka and Steiger[13] gave 228 g. (77% yield) of a mixture of 5,9-dimethyl-2,8- and 5,9-dimethyl-3,8-decadienoic acids, b.p. 140–148° (2 mm.), $n^{25}\text{D}$ 1.4766–1.4780.

The mixture of isomeric acids was separated by using the partial esterification procedure described by Rydon.[14] From 225 g. of a mixture of acids, there was obtained 78.0 g. of the pure α,β-unsaturated acid (IX), b.p. 144–146° (2 mm.), $n^{25}\text{D}$ 1.4779, $\alpha^{25}\text{D}$ $-1.39°$. Gas chromatography of the ester fraction obtained in this separation showed that a substantial part of the α,β-unsaturated acid had been esterified along with the β,γ-isomer.

The α,β-unsaturated acid (IX) was converted to the methyl ester (X) by treatment with diazomethane. In a typical run, 23.0 g. (0.12 mole) of 5,9-dimethyl-2,8-decadienoic acid was dissolved in 50 ml. of anhydrous ether and the solution was cooled in an ice bath. An ethereal solution containing 0.12 mole of diazomethane[15] was added gradually with vigorous shaking. A total of 75.0 g. of the acid was esterified in this manner, and the ether solutions were combined. The ether was stripped, and distillation of the residue yielded 54.0 g. (67% yield) of methyl 5,9-dimethyl-2,8-decadienoate (X), b.p. 141.5–142° (13 mm.), $n^{25}\text{D}$ 1.4642, $\alpha^{25}\text{D}$ -0.96.

1-(5-Methyl-4-hexenyl)cyclohexene (XV).—A Grignard reagent was prepared from 60.7 g. (0.32 mole) of 1-(2-bromoethyl)cylcohexene[16] and 7.83 g. (0.32 g.-atom) of magnesium in 300 ml. of absolute ether. Unchanged magnesium was removed by filtration, and then a solution of 25.9 g. (0.25 mole) of 1-chloro-3-methyl-2-butene[11] in 100 ml. of anhydrous ether was added dropwise. The mixture was allowed to stand overnight, and was hydrolyzed with ice–ammonium chloride. The solution was dried and the ether was stripped. Distillation of the residue in a spinning band column yielded 4 g. of 1-(5-methyl-4-hexenyl)cyclohexene, b.p. 106–106.5° (4 mm.), $n^{25}\text{D}$ 1.4780. This material was shown to be homogeneous by gas chromatography, and absorbed 99% of the theoretical amount of hydrogen for two double bonds. The infrared spectrum of the saturated material was identical with that of an authentic sample of 1-cyclohexyl-5-methylhexane.

3-(5-Methyl-4-hexenyl)cyclohexene (XVI).—A Grignard reagent was prepared from 33.8 g. (0.18 mole) of 3-(2-bromoethyl)cyclohexene[17] and 4.35 g. (0.18 g.-atom) of magnesium in 175 ml. of ether. The reagent was filtered under nitrogen and a solution of 17.7 g. (0.17 mole) of 1-chloro-3-methyl-2-butene[11] in 50 ml. of ether was added dropwise. The mixture was hydrolyzed and worked up in the usual way. Fractionation in a spinning band column gave 5.0 g. of 3-(5-methyl-4-hexenyl)cyclohexene, b.p. 99° (6 mm.), $n^{25}\text{D}$ 1.4750.

Anal. Calcd. for $C_{13}H_{20}$: C, 87.56; H, 12.44. Found: C, 87.62; H, 12.40.

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[9] Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were determined on liquid films using a Perkin-Elmer Model 21 spectrophotometer. Gas chromatographic analyses were performed with a Perkin-Elmer Model 154-C Vapor Fractometer using a 4-m. column with silicone grease packing. Rotations are reported for homogeneous liquids in a 1-dm. tube at 25.0°. Unless stated otherwise, the thermal cyclization reactions were carried out by passing the material through a 2.5-cm. Pyrex tube packed with 1/8-in. Pyrex helices; packed section, 65 cm. long. The tube was heated in the thermostat previously described.[3] A slow stream (3–5 ml./min.) of prepurified nitrogen was introduced along with the compound under study.

[10] F. B. LaForge, N. Green, and W. A. Gersdoff, *J. Am. Chem. Soc.*, **70**, 3707 (1948).

[11] W. T. Jones and H. W. Chorley, *J. Chem. Soc.*, 832 (1946); A. J. Ultee, *Rec. trav. chim.*, **68**, 125 (1949).

[12] *Catalog of Infrared Spectral Data*, Serial No. 614, American Petroleum Institute Research Project **44**, Pittsburgh, Pa. (1947).

[13] L. Ruzicka and R. Steiger, *Helv. Chim. Acta*, **10**, 684 (1927).

[14] H. N. Rydon, *J. Chem. Soc.*, 1544 (1939).

[15] C. E. Redemann, F. O. Rice, P. Roberts, and H. P. Ward, *Org. Syntheses*, Coll. Vol. III, 244 (1955).

[16] L. Toldy, T. Nogradi, L. Vargha, G. Ivanovics, and I. Koczka, *Acta Chim. Acad. Sci. Hung.*, **4**, 303 (1954); *Chem. Abstr.*, **50**, 362 (1956).

[17] L. F. Fieser and co-workers, *J. Am. Chem. Soc.*, **70**, 3195 (1948).

This material absorbed 102% of the theoretical amount of hydrogen for two double bonds, and the saturated product had an infrared spectrum identical with that of an authentic sample of 1-cyclohexyl-5-methylhexane.

3-(4-Hexenyl)cyclohexene (XVII).—A Grignard reagent was prepared from 106 g. (0.562 mole) of 3-(2-bromoethyl)-cyclohexene and 13.7 g. (0.506 g.-atom) of magnesium in 450 ml. of ether. The reagent was filtered under nitrogen, cooled to −10°, and a solution of 48 g. (0.53 mole) of 1-chloro-2-butene in 100 ml. of ether was added dropwise. The mixture was allowed to stand overnight, and then was worked up in the usual way. Fractionation in a Podbielniak Mini-Cal column furnished two fractions: (1) 34 ml., b.p. 107–109° (22 mm.), $n^{25}\text{D}$ 1.4728, and (2) 15.5 ml., b.p. 123–125° (36 mm.), $n^{25}\text{D}$ 1.4740.

Fraction 2 was shown to be the desired compound, 3-(4-hexenyl)cyclohexene.

Anal. Calcd. for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.56; H, 12.45.

Infrared absorption bands occurred at 10.38 μ (*trans* RCH=CHR) and 13.93 μ (*cis* RCH=CHR). The compound absorbed 100% of the theoretical amount of hydrogen for two double bonds, and the saturated product was *n*-hexylcyclohexane.

Fraction 1 was not fully investigated, but is most likely 3-(3-methyl-4-pentenyl)cyclohexene, formed by coupling of the Grignard reagent at the secondary position of the halide. Thus, infrared absorption bands appeared at 10.05 and 11.0 μ ($RCH{=}CH_2$) and 13.90 μ (*cis* RCH=CHR).

Methyl 2-Methylcyclohexyl Ketone.—Samples of the *cis* [b.p. 67–68° (10 mm.), $n^{25}\text{D}$ 1.4538] and *trans*[b.p. 65–66° (10 mm.), $n^{25}\text{D}$ 1.4476] isomers of this ketone were prepared by the method of Turner.[18]

Methyl 3-*p*-Cymeneacetate (XIII).—Methyl 3-hydroxy-*p*-menthane-3-acetate was obtained from menthone and methyl bromoacetate by the Reformatsky reaction.[19] From 45.3 g. (0.293 mole) of *l*-menthone, 45.0 g. (0.294 mole) of methyl bromoacetate, and 19 g. (0.29 g.-atom) of zinc dust there was obtained 30.5 g. (46% yield) of the hydroxy ester, b.p. 100–112° (2 mm.), $n^{25}\text{D}$ 1.4627.

A solution of 29.3 g. (0.129 mole) of the hydroxy ester and 4.3 g. of *p*-toluenesulfonic acid monohydrate in 65 ml. of benzene was placed in a flask which was attached to a water separator. The solution was refluxed until the evolution of water was complete, and then worked up in the usual way. Distillation gave 16.8 g. of a mixture of unsaturated esters, b.p. 116–128° (10 mm), $n^{25}\text{D}$ 1.4659–1.4702.

A 7.0-g. sample of this material was mixed with 0.1 g of 20% palladium-charcoal and refluxed for 1 hr.,[6] and the mixture was centrifuged to remove the catalyst. Gas chromatography indicated the product to consist of saturated and aromatic esters. A small amount of pure methyl 3-*p*-cymeneacetate, $n^{25}\text{D}$ 1.5005, was isolated by chromatographing the mixture over alumina.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.70; H, 8.75.

3-Ethyl-*p*-cymene (XIV).—3-Ethyl-*p*-menthan-3-ol, b.p. 104–109° (15 mm.), was prepared from ethylmagnesium bromide and menthone by the procedure of Read and Watters,[20] and dehydrated by heating with iodine.[21] The mixture of double bond isomers obtained in this way had b.p. 148–152° (200 mm.), $n^{25}\text{D}$ 1.4569–1.4589. Hydrogenation of this material over platinum in acetic acid yielded a mixture of stereoisomeric 3-ethyl-*p*-menthanes, b.p. 190–196°, $n^{25}\text{D}$ 1.4510.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.37; H, 14.56.

A solution of 4.15 g. of this material in 10 ml. of benzene was passed over a platinum-alumina catalyst at 300° during a period of 35 min. Gas chromatography of the crude product showed that virtually all of the 3-ethyl-*p*-menthane had reacted, and distillation furnished 3-ethyl-*p*-cymene, b.p. 134–138° (100 mm.), $n^{25}\text{D}$ 1.5010. An analytical sample was isolated by gas chromatography.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.64; H, 11.17.

1-Cyclohexyl-5-methylhexane.—A Grignard reagent was prepared from 60.0 g. (0.274 mole) of (4-bromobutyl)cyclohexane and 6.7 g. (0.276 g.-atom) of magnesium in 300 ml. of ether. A solution of 16.5 g. (0.30 mole) of acetone in 30 ml. of ether was added, and the mixture was worked up in the usual way. Distillation gave 35 g. (65% yield) of 6-cyclohexyl-2-methyl-2-hexanol, b.p. 95–99° (2 mm.), $n^{25}\text{D}$ 1.4630.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.70; H, 13.21.

Dehydration of 22 g. of this alcohol over alumina at 350° gave 12.9 g. of an alkene mixture, b.p. 80–93° (5 mm.), $n^{25}\text{D}$ 1.4600, which, upon hydrogenation in the presence of platinum, gave 1-cyclohexyl-5-methylhexane, b.p. 95–95.5° (6 mm.), $n^{25}\text{D}$ 1.4445.

Anal. Calcd. for $C_{13}H_{26}$: C, 85.63; H, 14.37. Found: C, 85.56; H, 14.39.

1-Isopropylspiro[4.5]decane (XVIII).—Isopropyllithium was prepared from 5.6 g. (0.807 g.-atom) of lithium and 32 g. (0.408 mole) of isopropyl chloride in 850 ml. of petroleum ether (b.p. 20–40°). A solution of 18.0 g. (0.118 mole) of spiro[4.5]decan-1-one[22] in 60 ml. of petroleum ether was added dropwise, with stirring. The mixture was hydrolyzed with ice–ammonium chloride, and the organic layer was washed with sodium carbonate solution and dried over magnesium sulfate. The major component recovered by fractionation of this material was spiro[4.5]decan-1-one, 10.8 g., b.p. 64–68° (0.6 mm.); a second fraction, 3.5 g., b.p. 68–93° (0.5 mm.) consisting of 1-isopropylspiro[4.5]decan-1-ol contaminated with about 25% of the starting ketone was also obtained. No appreciable separation of the ketone and alcohol was realized by chromatography over alumina, but the ketone was removed almost completely by treatment with Girard's reagent P. 1-Isopropylspiro[4.5]decan-1-ol exhibited medium-to-strong infrared absorption bands at: 2.83, 3.42, 6.78, 6.88, 7.22, 7.32, 7.82, 8.71, 8.84, 9.76, 9.98, 10.42, 11.02, 11.31, and 11.85 μ.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.45, 79.26; H, 12.03, 12.27.

Dehydration of 1-isopropylspiro[4.5]decan-1-ol was effected by heating 1.5 ml. of the alcohol with a crystal of iodine at 160° until formation of water ceased. The organic material was washed with dilute sodium bisulfite and dried over potassium hydroxide. Distillation furnished 1 ml. of an alkene mixture, b.p. 95–105° (bath temperature) (3 mm.).

Upon hydrogenation, this material absorbed 103% of the theoretical amount of hydrogen for one double bond and gave 1-isopropylspiro[4.5]decane, $n^{25}\text{D}$ 1.4773. The amount of material was too small to permit an accurate boiling point determination; the following infrared absorption bands were observed: 3.45, 6.85, 7.22, 7.32, 7.61, 8.58, 10.94, and 11.77 μ.

Anal. Calcd. for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.73; H, 13.42.

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[18] R. B. Turner, *J. Am. Chem. Soc.*, **72**, 878 (1950).

[19] L. F. Fieser and co-workers, *ibid.*, **70**, 3206 (1948); S. Natelson and S. P. Gottfried, *ibid.*, **61**, 970 (1939).

[20] J. Read and A. J. Watters, *J. Chem. Soc.*, 2165 (1929).

[21] W. A. Mosher, *J. Am. Chem. Soc.*, **62**, 552 (1940).

[22] M. Mousseron, R. Jacquier, and H. Christol, *Compt. rend.*, **239**, 1805 (1954). Other workers[23] have experienced considerable difficulty in obtaining reasonable yields of 2-(*N*-morpholinomethyl)-cyclopentanone, the starting material for the preparation of spiro-[4.5]decan-1-one, and the same difficulty was encountered in the early stages of the present study. It was found, however, that the purity of the morpholine hydrochloride used in the condensation was critical. If the hydrochloride contained traces of free morpholine, the yield of the Mannich base was very low (0–30%). When morpholine hydrochloride which had been recrystallized from acidic ethanol was used, the Mannich base was obtained in consistently high yields (67–70%).

[23] R. K. Hill, private communication.

Pyrolysis Experiments. 8-Methyl-1,7-nonadiene.—When 27.8 g. of this diolefin was passed through the pyrolysis tube at 440° over a period of 2 hr. no change occurred. The reaction was repeated at 490°, 22 g. of diolefin being passed through the tube over a period of 1 hr. Distillation of the pyrolysate gave 19.2 g. of material, b.p. 160–166°, and the presence of a strong band at 11.26 μ in the spectrum of this material indicated that a reaction had occurred. A 0.00116-mole sample absorbed 0.00204 mole of hydrogen, corresponding to 25% monoolefin and 75% diolefin.

Careful fractionation in a spinning band column failed to effect a separation, but a reasonably good separation was achieved by chromatography over silica gel at 0°, using isopropyl alcohol as the eluent. Bands corresponding to the starting diolefin were absent from the spectrum of the best fractions obtained (n^{25}D 1.4547), and a strong, new band was present at 11.26 μ.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.95; H, 13.05. Found: C, 86.85; H, 13.17.

A solution of 5.30 g. of this material in 55 ml. of methylene chloride was ozonized, and the resulting ozonide was decomposed with 2.5 g. of zinc dust and 25 ml. of 50% acetic acid.[24] One gram of a liquid ketone was obtained, b.p. 93° (22 mm.) (bath temp.), n^{25}D 1.4518. This material gave a positive iodoform test, and its infrared spectrum corresponded to a mixture of methyl *cis*- and methyl *trans*-2-methylcyclohexyl ketone. The semicarbazone melted at 166–168°.

Anal. Calcd. for $C_{10}H_{19}N_3O$: C, 60.88; H, 9.71; N, 21.30. Found: C, 61.12; H, 9.99; N, 21.05.

A 5.5-g. sample of the original pyrolysate was hydrogenated over platinum in acetic acid, and the resulting saturated material was dehydrogenated over platinum-alumina at 300°.[7] Chromatography over silica gel served to separate the aromatic material, and, except for an extraneous band at 14.30 μ, the infrared spectrum corresponded to that reported for *o*-cymene.[25]

Methyl 5,9-Dimethyl-2,8-decadienoate.—Preliminary experiments showed that very little cyclization of this compound occurred at 350°. Pyrolysis of 52.4 g. of this material at 400° over a period of 6 hr. gave 51.1 g. of pyrolysate, n^{25}D 1.4634. The gas chromatography tracing of the pyrolysate showed three peaks, the smallest of which corresponded to the starting ester. Recycling resulted in a small additional conversion, and gas chromatography indicated the components to be present to the extent of 53%, 29%, and 18%. Fractionation of 48.9 g. of this product in a 60-cm. Podbielniak Mini-Cal column gave the following fractions: A, 24.2 ml., b.p. 126.5–127.5° (15 mm.), n^{25}D 1.4618–1.4620, α^{25}D −11.93°; B, 10.1 ml., b.p. 132.0–133.5° (15 mm.), n^{25}D 1.4653–1.4659 α^{25}D 11.88°; and C, 2.8 ml., b.p. 144.3–145° (15 mm.), n^{25}D 1.4641–1.4643. Fraction C was shown to be identical with the starting ester (X) by gas chromatography and infrared spectroscopy.

Fraction A gave a single peak on gas chromatography, exhibited strong absorption at 11.2 μ, and absorbed 103% of the amount of hydrogen required for one double bond.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.36; H, 10.46.

The saturated ester obtained by hydrogenation, n^{25}D 1.4535, α^{25}D −29.07°, gave a single peak on gas chromatography.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.77; N, 11.24.

A mixture of 3.07 g. of A and 0.2 g. of palladium-charcoal was refluxed 6 hr.; chromatography of the product over alumina gave 0.9 g. of an aromatic ester identified as methyl 3-*p*-cymeneacetate (XIII) by comparison with the synthetic material described above.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.42; H, 8.57.

The other material isolated from the chromatographic separation was a saturated ester identical with the one obtained by hydrogenation of A.

Fraction B appeared to be homogeneous upon gas chromatography under the same conditions as used for A, but when the flow rate was reduced to very low values (*e.g.*, retention time *ca.* 60 min.), two incompletely resolved peaks appeared. This material exhibited a strong infrared band at 11.2 μ and absorbed 105% of the theoretical amount of hydrogen for one double bond.

Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.55. Found: C, 74.55; H, 10.52.

The saturated ester, n^{25}D 1.4551, α^{25}D 10.83° obtained by hydrogenation exhibited two peaks on gas chromatography; both of these peaks had retention times different from the saturated ester derived from A.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.76; H, 11.30.

A 3.80-g. sample of B was refluxed 5 hr. with 0.20 g. of palladium-charcoal, and the product was chromatographed over alumina. The aromatic ester, n^{25}D 1.5013, was identified as methyl 3-*p*-cymeneacetate (XIII). The major component of the saturated ester fraction, n^{25}D 1.4531, had the same retention time as the saturated ester derived from A. The infrared spectra were also very similar.

Degradation of the Cyclic Esters.—A total of 11.9 g. of a mixture[26] of saturated and unsaturated esters was hydrogenated over platinum in acetic acid; 11.0 g. of isomeric methyl *p*-menthane-3-acetates, n^{25}D 1.4545, was obtained.

A solution of 10.9 g. of the ester mixture in 20 ml. of ether was added dropwise to a solution of 1.80 g. of lithium aluminum hydride in 50 ml. of ether, and the mixture was refluxed for 0.5 hr. The product was worked up in the usual way,[27] and distillation afforded 7.98 g. of isomeric 3-*p*-menthaneethanols, b.p. 147–148° (20 mm.), n^{25}D 1.4681.

The *p*-toluenesulfonate ester was prepared from 7.43 g. of the alcohol mixture, 15.0 g. of *p*-toluenesulfonyl chloride, and 25.0 g. of dry pyridine.[28] The crude ester, 13.2 g., n^{25}D 1.5075, was a viscous liquid, and was used without further purification. Reduction of 12.6 g. of the ester with 2.85 g. of lithium aluminum hydride in 230 ml. of tetrahydrofuran by the procedure of Mitra and Karrer[29] gave 4.66 g. of crude hydrocarbon. To remove traces of sulfur containing impurities, 4.06 g. of this material was refluxed over sodium for 2 hr. Distillation furnished 3.55 g. of 3-ethyl-*p*-menthane, b.p. 198–202°, n^{25}D 1.4485.

A solution of 3.38 g. of this material in 8 ml. of benzene was dehydrogenated over platinum-alumina at 300°; 2.62 g. of product, n^{25}D 1.5046, was obtained. The gas chromatography tracing showed only slight wiggles corresponding to the starting cycloalkanes, and the major component had a retention time identical with that of 3-ethyl-*p*-cymene. The infrared spectrum of a sample isolated by gas chromatography was identical with the spectrum of 3-ethyl-*p*-cymene.

1-(5-Methyl-4-hexenyl)cyclohexene.—Two grams of this diolefin was heated in a sealed tube at 350° for 20 min. The gas chromatography tracing of the product showed only one peak and the infrared spectrum was identical with that of the starting material.

Another sample, 17.7 g., of the diolefin[30] was pyrolyzed in the flow system at 450° over a period of 43 min. After being distilled, the pyrolysate (11 g.) absorbed 97% of the theoretical amount of hydrogen required for two double bonds. The gas chromatography tracing showed one major peak which corresponded to 1-cyclohexyl-5-methylhexane, and two minor peaks neither one of which corresponded to

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[24] A. L. Henne and P. Hill, *J. Am. Chem. Soc.*, **65**, 752 (1943).

[25] See ref. 12, Serial No. 1585.

[26] This mixture consisted of A and B, the saturated esters obtained by hydrogenation of A and B, and the saturated esters formed by disproportionation of A and B over palladium-charcoal.

[27] R. B. Moffett, *Org. Syntheses*, **33**, 82 (1953).

[28] C. S. Marvel and V. C. Sekera, *ibid.*, Coll. Vol. III, 366 (1955).

[29] A. K. Mitra and P. Karrer, *Helv. Chim. Acta*, **38**, 1 (1955).

1-isopropylspiro[4.5]decane. Similar results were obtained when the reaction was repeated at 500°.

3-(5-Methyl-4-hexenyl)cyclohexene.—The pyrolysis of 17.5 g. of this diolefin[30] in the flow system at 500° over a period of 35 min. gave 13.0 g. of product whose infrared spectrum was the same as that of the starting material, except for minor differences in band intensities. A 4.5-g. sample was hydrogenated and the saturated product was dehydrogenated over platinum-alumina at 300°. The gas chromatography tracing showed only one peak, and the material was identified as 1-phenyl-5-methylhexane. 1-Isopropylnaphthalene could not be detected in the product.

3-(4-Hexenyl)cyclohexene.—Over a period of 45 min., 10 g. of this diolefin was passed through the flow system at 500°. The infrared spectrum of the product was practically identical with that of the starting diolefin, and this material was not studied further.

(30) The diolefin used in this experiment was synthesized by a *route different from the one described above, and contained a small* amount (10–15%) of double bond isomers.

The Thermal Cyclization of 6-Octen-1-yne[1]

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6-Octen-1-yne cyclizes rapidly at 400° giving 1-methylene-2-vinylcyclopentane. The structure of this product was established by infrared spectroscopy, degradation, and hydrogenation.

It was shown in earlier studies that 1,6-alkadienes undergo thermal cyclization at 450–500° to give cyclopentane derivatives.[2,3] The results of a kinetics study indicate that this reaction proceeds by an intramolecular mechanism.[4]

It was of interest to determine if this reaction could be extended to compounds possessing a carbon-carbon triple bond in place of one of the olefinic linkages. 6-Octen-1-yne (I) was chosen for this study because it has the necessary structural features, and an inspection of molecular models reveals that the molecule can assume the proper conformation for intramolecular cyclization.[4]

Results and Discussion

6-Octen-1-yne was obtained in 65% yield by the alkylation of sodium acetylide with 6-bromo-2-hexene in liquid ammonia solution

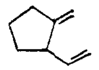
$$\mathrm{CH_3CH{=}CHCH_2CH_2CH_2Br + HC{\equiv}CNa \longrightarrow \underset{\textstyle I}{CH_3CH{=}CH(CH_2)_3C{\equiv}CH}}$$

This material gave a single peak on gas chromatography and exhibited infrared absorption at 2.99 (acetylenic C—H); 4.70 (RC≡CH); 5.97 and 10.34 μ (*trans* RCH=CHR).[5]

Extensive change occurred when this material was heated at 400° as evidenced by a drastic reduction in intensity of the infrared bands corresponding to acetylenic, methyl, and *trans* olefinic groups and the appearance of several new, intense bands. Unchanged 6-octen-1-yne was removed from the pyrolysate by precipitation as the silver salt, and the new hydrocarbon which remained was shown to be homogeneous by gas chromatography.

The results of elemental analysis agreed with the formula C_8H_{12}. A sample absorbed 2.0 moles of hydrogen per mole of hydrocarbon, thus demonstrating it to be a cyclic isomer of the starting alkenyne. Strong infrared absorption bands at 10.06 and 10.99 μ indicated the presence of a vinyl group, $RCH{=}CH_2$, while a strong band at 11.37 μ pointed to the presence of an alkene of the type $R_2C{=}CH_2$.[5] These assignments were substantiated by the detection of formaldehyde upon ozonolysis. It is also significant that the characteristic absorption band (7.25–7.30 μ) for methyl groups was absent from the spectrum.

These results are in agreement with II, the structure anticipated for the product on the basis of the behavior of 1,6-alkadienes. Confirmation of this assignment was obtained by hydrogenating a sample of the pyrolysate; the saturated product was shown to consist of 62% *cis*- and 38%-*trans*-1-ethyl-2-methylcyclopentane by comparison with authentic samples.



II

The crude pyrolysate contained approximately 65% II as determined by quantitative hydrogenation and infrared spectroscopy. This is considerably greater than the extent of cyclization previously observed for 1,6-alkadienes, even at higher temperatures. For example, 1-methyl-2-vinylcyclopentane was formed in 35% yield from 1,6-

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(1) Financial support by the National Science Foundation (G-7379) and the Ohio University Research Fund is gratefully acknowledged.

(2) H. Pines, N. E. Hoffman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **76**, 4412 (1954).

(3) W. D. Huntsman, V. C. Solomon, and D. Eros, *ibid.*, **80**, 5455 (1958).

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

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1958, pp. 34, 58.