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.

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[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

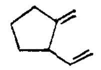
$$CH_3CH{=}CHCH_2CH_2CH_2Br + HC{\equiv}CNa \longrightarrow \underset{\textstyle \text{I}}{CH_3CH{=}CH(CH_2)_3C{\equiv}CH}$$

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.

octadiene at 460°. If, as seems likely, the same mechanism operates for the cyclization of both compounds, then the greater rate of reaction of the alkenyne may be a result of the smaller amount of energy required for the rupture of one bond of an acetylenic linkage than that required for the rupture of one bond in an ethylenic linkage.

Experimental[6]

4-Hexen-1-ol was obtained in 90% yield by the reaction of sodium with 1-methyl-2-bromo-tetrahydropyran according to the procedure of Brandon, Derfer, and Boord[7]; b.p. 155–159°, $n^{25}\text{D}$ 1.4411.

6-Bromo-2-hexene was prepared in 54% yield from 4-hexen-1-ol and phosphorus tribromide[8]; b.p. 54.3-56.0° (20 mm.), $n^{21}\text{D}$ 1.4681.

6-Octen-1-yne.—The procedure for preparing this compound was modeled after the one described for 1-octyne.[9] From 84.9 g. (0.52 mole) of 6-bromo-2-hexene and sodium acetylide, prepared by dissolving 15.0 g. (0.65 g.-atom) of sodium in a saturated solution of acetylene in liquid ammonia, there was obtained 36.3 g. (64% yield) of 6-octen-1-yne, b.p. 79–80° (150 mm.), $n^{25}\text{D}$ 1.4344. This material gave a single peak upon gas chromatography, and a sample absorbed 3.02 moles of hydrogen per mole of hydrocarbon upon quantitative hydrogenation.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.96; H. 11.21.

trans-**1-Methyl-2-ethylcyclopentane**, $n^{25}\text{D}$ 1.4194, was obtained by hydrogenating a sample of *trans*-1-methyl-2-vinylcyclopentane[3] over platinum.

cis-**1-Methyl-2-ethylcyclopentane**, $n^{25}\text{D}$ 1.4269, was obtained by hydrogenating a sample of *cis*-1-methyl-2-vinylcyclopentane[3] over platinum.

Pyrolysis of 6-Octen-1-yne.—The pyrolysis of 6-octen-1-yne was carried out at 400° in a Pyrex tube, 1.5 cm. × 64 cm., packed with glass helices. A slow stream of nitrogen, 3 ml. per minute, was passed through the tube during the pyrolysis. A total of 18.9 g. of 6-octen-1-yne was added over a period of 2 hr.; the crude product recovered amounted to 18.1 g. Two incompletely resolved peaks, the smaller of which corresponded to 6-octen-1-yne, appeared in the gas chromatography tracing.

The crude product was distilled through a short Vigreux column, and the material boiling below 122° was collected (16 g.). Upon quantitative hydrogenation, a sample of the distillate absorbed 2.26 moles of hydrogen per mole of hydrocarbon; this corresponds to 74% cyclic diene and 26% alkenyne. The unchanged 6-octen-1-yne was removed by adding ethanolic silver nitrate until precipitation of the silver salt was complete. The mixture was filtered, and the filtrate was diluted with water and extracted with petroleum ether (20–40°). 1-Methylene-2-vinylcyclopentane, b.p. 118°, $n^{27}\text{D}$ 1.4557, was obtained by fractionation of the extract.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.02; H, 11.22.

A sample of this hydrocarbon absorbed 2.0 moles of hydrogen per mole of hydrocarbon upon quantitative hydrogenation. Two peaks with retention times corresponding to *cis*- and *trans*-1-methyl-2-ethylcyclopentane appeared in the gas chromatography tracing of the saturated product. On the basis of the areas under the peaks, the composition was estimated to be 66% *cis* and 34% *trans* isomer. The infrared spectrum of the mixture was compared with that of a synthetic mixture containing 62% of the *cis* and 38% of the *trans* isomer. All of the bands in the spectra coincided, except for minor differences in intensities amounting to 1–2% transmission in a 0.1-mm. cell.

A solution of the cyclic diene in pentane was ozonized, and the formaldehyde formed was trapped by passing the exit gas through water. The formaldehyde-methone derivative was prepared in the usual way, and after recrystallization melted at 188°. Admixture with an authentic sample of formaldehyde-methone did not depress the melting point.

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(6) Analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were determined on liquid films using a Perkin-Elmer Model 21 spectrophotometer, and gas chromatographic analyses were performed with a Perkin-Elmer 154 C Vapor Fractometer.

(7) R. C. Brandon, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **72**, 2120 (1950).

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(9) K. N. Campbell and B. K. Campbell, *Org. Syntheses*, **30**, 15 (1950).

The Production of 4-*cis* Isomers in the Irradiation of 3-Methyl-5-aryl-2,4-pentadienoic Acids

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Ultraviolet irradiation of the 2-*cis*-4-*trans* or 2-*trans*-4-*trans* isomers of 3-methyl-5-phenyl- or 5-*p*-chlorophenyl-2,4-pentadienoic acids gives mixtures of all four geometric isomers with up to 37% of the 4-*cis*-structure as determined by n.m.r.

The observation[1] that the n.m.r. absorption maxima for the methyl protons in the four geometrical isomers of 3-methyl-5-phenyl-2,4-pentadienoic acid occur at four characteristic positions has made possible a study of the iodine-catalyzed, ultraviolet irradiation-induced isomerizations in this series. The rather remarkable result of this study has been the observation that under these conditions equilibrating mixtures of all four of the isomers are obtained in which 22–37% of the mixture is of the 4-*cis* configuration.

The n.m.r. absorption maxima for the methyl protons in 3-methyl-5-phenyl-2,4-pentadienoic acid occur at 7.42 τ for the *trans-trans;* 7.61 τ for the 2-*trans*-4-*cis;* 7.95 τ for the 2-*cis*-4-*trans;* and 8.18 τ for the *cis-cis* isomers. These values are for the acids in pyridine; the esters in carbon tetrachloride give values of 7.67; 7.88; 8.00; and 8.27, respectively,

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(1) R. H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, **27**, 1535 (1962).