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}_{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}_{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}_{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}_{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}_{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}_{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).

[8] M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1788 (1957).

[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).

and the acids in carbon tetrachloride give values equivalent to those observed for the esters in carbon tetrachloride. The presence of these four characteristic sets of methyl proton absorptions provides an analytical method for establishing both the purity of a given sample and the composition of mixtures thought to contain mixtures of isomers. The presence of 2–3% of one constituent in an isomeric mixture is readily apparent in the spectrum.

The irradiation of the *trans-trans* isomer of 3-methyl-5-phenyl-2,4-pentadienoic acid in benzene with iodine for six hours produces a mixture of 38% *trans-trans;* 2% *trans-cis;* 48% *cis-trans;* and 12% *cis-cis* isomers. After twelve hours the relative amounts[2] are 34; 6; 42; and 18%. In benzene–ethanol solution with iodine and benzophenone, the relative amounts after twelve hours irradiation were 30; 15; 30; and 25%. The 2-*cis*-4-*trans* isomer irradiated 12 hours in benzene with iodine gave a mixture of 25; 4; 38; and 33% of the four isomers. Irradiation of 2-*cis*-4-*trans* 3-methyl-5-(*p*-chlorophenyl)-2,4-pentadienoic acid in benzene–ethanol with iodine gave after three hours: 36; –; 64; and –%; after eight hours: 41; 3; 42; and 15%; and after fifty-two hours: 37; 6; 41; and 16% of the isomers. The τ values for the 3-methyl protons in the *p*-chlorophenyl acids (acid in pyridine) are: 7.47; 7.69; 7.98; and 8.24 for the respective isomers. The relative percentages were determined by measurement of peak heights and widths and are capable of more precise measurements with a recording integrator. These experiments are in progress.

The iodine-catalyzed, ultraviolet-induced isomerization of 3-methyl-5-aryl-2,4-pentadienoic acids has been used previously[3,4] for the isomerization of 2-*cis*-4-*trans* isomers to the *trans-trans* isomers. It is not always successful, however, probably because it is difficult to follow empirically the course of the isomerization and of the fractional crystallization. The n.m.r. data, indicating the presence of all four isomers, confirm the probability of encountering difficulties in such empirical studies, but they also provide techniques which should be of assistance in isolation of such isomers.

Isolation of the previously unknown *trans-trans* isomer of 3-methyl-5-(*p*-chlorophenyl)-2,4-pentadienoic acid, m.p. 195°, from irradiation experiments provides an interesting example. It is now apparent that this *trans-trans* isomer in this series is, in fact, less soluble than the 2-*cis*-4-*trans* isomer, m.p. 215°, and hence can be obtained by recrystallization techniques only from solutions from which the less soluble 2-*cis* isomer has been removed by precipitation. N.m.r. characterization of the course of the irradiation experiment determines the optimum time for production of maximal amounts of the *trans-trans* isomer. N.m.r. characterization of the fractions separated during fractional recrystallization locates the isomer of interest. The 4-*cis* isomers can presumably be isolated by similar techniques.

Experimental

The n.m.r. measurements were made with a Varian high resolution (Model HR-4302) spectrometer with 60 Mc. oscillator with superstabilizer and field homogeneity control. The calibrations were made by the side band technique at several frequencies. Tetramethylsilane was used as an internal reference standard. Values are given in τ units.[5] The areas under the peak were estimated from measurements of peak height and width at half maximum intensity.

The 2-*trans*-*4*-*trans*- (m.p. 160°) and 2-*cis*-4-*trans*- (m.p. 158°) 3-methyl-5-phenyl-2,4-pentadienoic acid[1,4] and 2-*cis*-4-*trans*- (m.p. 215°) 3-methyl-5-(*p*-chlorophenyl)-2,4-pentadienoic acid[3] were prepared as previously described. The *trans-trans* isomer of the last is new.

The following example is typical of the procedures used in the irradiation experiments. A solution of 7.65 g. of 2-*cis*-4-*trans*-3-methyl-5-(*p*-chlorophenyl)-2,4-pentadienoic acid m.p. 214–215°, and 40 mg. of iodine in 75 ml. of benzene was irradiated in a quartz flask supported over a Hanovia mercury vapor lamp so as to maintain the solution at gentle reflux. At stated time intervals samples were withdrawn and evaporated in vacuum at room temperature. The residue was taken up in pyridine and examined in the n.m.r. spectrometer.

After 3.5 hr. irradiation, evaporation of the total sample left a residue which was recrystallized from acetone–cyclohexane. The first crop was mostly 2-*cis*-4-*trans* isomer (by n.m.r.); the second mostly *trans-trans.* Repeated recrystallization of the second crop gave 0.74 g. (9%) of the pure (by n.m.r.) *trans-trans* isomer, m.p. 195–196°.

Anal.[6] Calcd. for $C_{12}H_{11}ClO_2$: C, 64.72; H, 4.98. Found: C, 64.43; H, 4.83.

The methyl ester was obtained by reaction with diazomethane, m.p. 99.5–100.5° from methanol–water.

Anal.[6] Calcd. for $C_{13}H_{13}ClO_2$: C, 65.91; H, 5.54. Found: C, 65.91; H, 5.71.

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[2] In each case the percentages are listed in order for the *trans-trans;* 2-*trans*-4-*cis;* 2-*cis*-4-*trans;* and *cis-cis* isomers.

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[5] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[6] Analyses by Micro Tech Laboratories.