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Thermal Rearrangement of 5-Methylenebicyclo[2.2.1]hept-2-ene[1]

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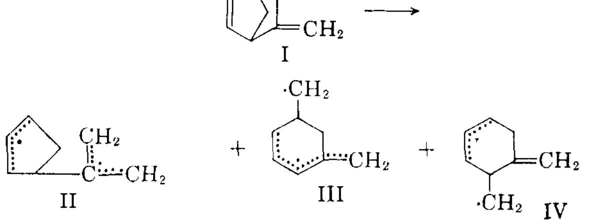
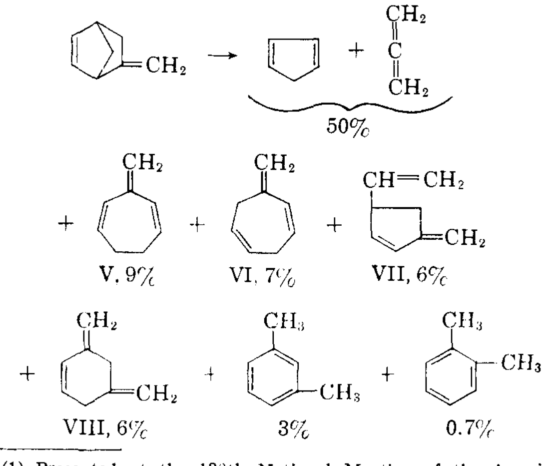
3-Methylene-1,4-cycloheptadiene and 3-methylene-1,5-cycloheptadiene are obtained when 5-methylenebicyclo[2.2.1]-hept-2-ene is pyrolyzed at 660–690° and low pressures. Two other C_8H_{10} isomers, 3-methylene-5-vinylcyclopentene and 3,5-dimethylenecyclohexene, are also obtained. About half of the starting hydrocarbon is converted to cyclopentadiene and allene. In addition, numerous minor products are formed, among which *m*-xylene, *o*-xylene, benzene and methylenecycloheptatriene have been identified spectroscopically.

The development of an easy synthesis of 5-methylenebicyclo[2.2.1]hept-2-ene[3] (I) led us to an examination of the chemistry of this compound. We were particularly interested in high-temperature reactions because the bicyclic system would be expected to cleave to give the allyl diradicals II, III and IV, and it has been shown[4,5] that allylic radicals often undergo unusual transformations.



When 5-methylenebicyclo[2.2.1]hept-2-ene is pyrolyzed in a tube that is heated to 660–690° and evacuated to a pressure of approximately 1–5 mm., about half of the material is cleaved to cyclopentadiene and allene, about 40% is converted to a mixture of C_8H_{10} hydrocarbons, and 10% is transformed to higher-boiling products. Gas chromatography of the C_8H_{10} fraction revealed the presence of 19 components, but 85–90% were accounted for in the four largest fractions. The major components of these four fractions have been identified as 3-methylene-1,4-cycloheptadiene (V), 3-methylene-1,5-cycloheptadiene (VI), 3-methylene-5-vinylcyclopentene (VII) and 3,5-dimethylenecyclohexene (VIII). Xylenes were also present and, because of coincidence of retention times, *m*-xylene appeared in the same fraction with V, and *o*-xylene appeared with VI.

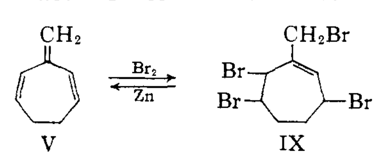


Partial separation of the C_8H_{10} isomers was achieved by distillation through a three-foot packed column under reduced pressure. The most volatile major component was 3-methylene-5-vinylcyclopentene (VII) which amounted to 60–65% of a fraction boiling at 10–17° (12 mm.). This compound was isolated by preparative scale gas chromatography. Its structure is supported by ultraviolet and infrared spectra. The carbon skeleton and the presence of three double bonds were confirmed by quantitative hydrogenation to a mixture of *cis*- and *trans*-1-methyl-3-ethylcyclopentane.

The next most volatile major component was 3,5-dimethylenecyclohexene (VIII), which distilled in a fraction boiling at 17–28° (12 mm.). This compound was isolated by gas chromatography of the unfractionated mixture of C_8H_{10} isomers and found to have the same infrared spectrum as that of an authentic sample.[6]

The seven-membered ring compounds V and VI were separated from a fraction boiling at 28–32° (12 mm.). Very slow redistillation gave a lower-boiling fraction enriched in 3-methylene-1,5-cycloheptadiene (VI) and a higher-boiling fraction enriched in 3-methylene-1,4-cycloheptadiene (V). However, the boiling points of these compounds are too close for complete separation by distillation. Separation was readily accomplished by gas chromatography. However, under the conditions employed, *m*-xylene was inseparable from V and *o*-xylene was inseparable from VI. Accordingly, special methods were developed to obtain pure samples of V and VI.

Preparation of pure 3-methylene-1,4-cycloheptadiene (V) was facilitated by the discovery that distilled fractions rich in V react with excess



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[1] Presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[2] To whom inquiries regarding this paper should be addressed.

[3] 5-Methylenebicyclo[2.2.1]hept-2-ene has been reported by P. von R. Schleyer and R. E. O'Connor, Abstracts of Papers, 134th Meeting of the American Chemical Society, Chicago, Ill., 1958, p. 39P. It is easily synthesized from allene and cyclopentadiene, and detailed description of this preparation will be published by Dr. H. N. Cripps.

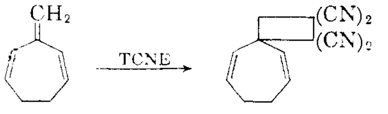
[4] J. J. Drysdale, H. B. Stevenson and W. H. Sharkey, THIS JOURNAL, **81**, 4908 (1959).

[5] W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

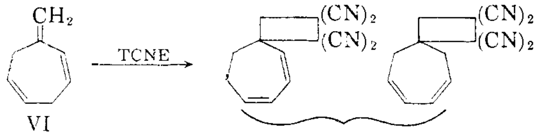
[6] R. E. Benson and R. V. Lindsey, THIS JOURNAL, **81**, 4250 (1959).

bromine to yield a crystalline tetrabromide, from which pure V can be recovered by debromination with zinc. The infrared spectrum of the tetrabromide is consistent with the postulated structure, 1-bromomethyl-3,6,7-tribromocycloheptene (IX).

The presence of three double bonds in V was established by quantitative hydrogenation. The product formed by hydrogenation was methylcycloheptane. In addition to these facts, the infrared and ultraviolet spectra of V agree with those reported for 3-methylene-1,4-cycloheptadiene by Doering and Wiley[7] if a small number of bands in the infrared spectrum of the latter sample that are not in the spectrum of V are attributed to an impurity. Further evidence for structure V is its reaction with tetracyanoethylene (TCNE) to give a 1:1 adduct not having conjugated double bonds. This adduct is believed to be the spiro compound X.[8]



V X



VI XI

Purification of 3-methylene-1,5-cycloheptadiene (VI) by gas chromatography was complicated by the presence of *o*-xylene, which had the same retention time as VI on the column used. However, VI forms a water-soluble complex with silver nitrate and *o*-xylene does not. Accordingly, a fraction of C_8H_{10} hydrocarbons containing VI was dissolved in aqueous silver nitrate and washed with pentane to remove *o*-xylene. The xylene-free hydrocarbons were regenerated from their silver nitrate complexes and subjected to gas chromatography to separate pure VI. As a check on the homogeneity of the material, VI was also purified by fractional crystallization of its silver nitrate complex, followed by regeneration and distillation.

The structure of 3-methylene-1,5-cycloheptadiene (VI) was assigned on the basis of the following evidence. As with V, catalytic quantitative hydrogenation showed the presence of three double bonds and yielded methylcycloheptane. Infrared and ultraviolet spectra indicate that the exomethylene group is conjugated with a double bond in the ring. Ultraviolet absorption, which was observed at 235 mμ, is too low for a conjugated triene, unless for steric reasons the plane of one double bond is approximately perpendicular to the plane of the other two. The nuclear magnetic resonance spectrum is also consistent with a planar triene structure. It is possible the linear triene, which would be 5-methylene-1,3-cycloheptadiene, could have a non-planar configuration. However, a compound that should be sterically analogous to it, 2,4-cycloheptadienone,[9] has an ultraviolet spectrum indicating all the double bonds are planar.

Unexpectedly, the tetracyanoethylene adduct of VI was shown by its ultraviolet spectrum to have a conjugated pair of double bonds. However, the infrared spectrum indicated that the expected loss of the exocyclic bond had occurred. In view of the above, it appears that rearrangement occurred during reaction with tetracyanoethylene, possibly to give one of the isomers depicted by XI.

An interesting minor product from the pyrolysis of 5-methylenebicyclo[2.2.1]hept-2-ene (I) is methylenecycloheptatriene[7] (XII). Since this red hydrocarbon polymerizes spontaneously on standing, even in dilute solutions, it was not isolated but was identified by its characteristic visible spectrum. The amount present was estimated to be 0.1% of the C_8H_{10} fraction, with which it codistilled on rapid, simple distillation at room temperature. Since the methylenecycloheptatriene was probably formed by dehydrogenation of the methylenecycloheptadienes, its synthesis by catalytic vapor-phase dehydrogenation of a mixture of V and VI was examined. Passage of the mixture over base-treated chromia–alumina at 490° and 1 mm. and thence into a trap cooled to $-75°$ yielded up to 18% of what appeared to be polymer of methylenecycloheptatriene.[7] However, the largest amount of monomer observed was less than 1% and then only in the presence of pyridine as a stabilizer. Without pyridine, the initial red color of the dehydrogenation products in the $-75°$ trap faded very rapidly. A platinum-on-charcoal catalyst gave lower yields of methylenecycloheptatriene (0.1%), but the product was stable enough for spectroscopic examination without any basic stabilizer. Reaction of XII prepared in this manner with methyl acetylenedicarboxylate yielded 1,2-dicarbomethoxyazulene, as reported by Doering and Wiley.[7]

Experimental[10]

Pyrolysis of 5-Methylenebicyclo[2.2.1]hept-2-ene (I).[11]—The pyrolysis tube consisted of a 75-cm. length of 25-mm. diameter Vycor tubing mounted vertically with an 8-mm. Vycor tube, open only to the outside, running up the center for a thermocouple well. The pyrolysis tube was packed with chips of 6-mm. Vycor tubing for a length of 50 cm., the bottom 30 cm. of which was heated with an electric furnace. An addition funnel was connected to the top and a suitable receiver to the bottom with ground joints. The receiver was cooled in liquid nitrogen and the system evacuated to below 2 mm. on the pump side of the receiver. The pyrolysis tube was heated to 660–690° at the hottest point, and 5-methylenebicyclo[2.2.1]hept-2-ene (I), b.p. 55–57° (100 mm.), $n^{25.5}{}_D$ 1.4830, was admitted to the top of the pyrolysis tube at the rate of about 100 g./hour. Faster addition did not allow all the liquid to vaporize before entering the hot zone and appeared to increase formation of high-boiling by-products. It was also found important to use acid-free glassware. A pyrolysis tube that had previously been used with fluorocarbons gave products that decomposed on at-

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[7] William von E. Doering and D. W. Wiley, Abstracts of Papers, 126th Meeting of the American Chemical Society, September, 1954, p. 10-O; D. W. Wiley, Ph.D. Thesis, Yale University, 1954.

[8] For reports on the formation of four-membered rings by reaction of tetracyanoethylene with conjugated olefins incapable of reacting in the normal manner see: J. K. Williams, THIS JOURNAL, **81**, 4013 (1959); A. T. Blomquist and Y. C. Meinwald, *ibid.*, **79**, 5316 (1957); **81**, 667 (1959); and Abstracts of Papers, 133rd Meeting of the American Chemical Society, San Francisco, Calif., 1958, p. 77-N.

[9] E. E. van Tamelen and G. T. Hildahl, THIS JOURNAL, **78**, 4405 (1956).

[10] All melting and boiling points are uncorrected.

[11] J. J. Drysdale, U. S. Patent 2,886,608, May 12, 1959.

tempted distillation. Material in the trap, which amounted to 495 g. when 500 g. of I was pyrolyzed, was subjected to simple distillation to yield 236 g. of cyclopentadiene plus allene, b.p. −26° (atm.) to −35° (10 mm.); 208 g. of C_8H_{10} isomers, b.p. up to 10° (0.5 mm.); and 51 g. of residue.

Gas Chromatographic Analysis of Pyrolysis Products.—The C_8H_{10} fraction was gas chromatographed at 90–100° on a 2-meter column of 25% 1,1-bis-(2-cyanoethyl)-nitroethane on 30–60 mesh Fisher Columpak with helium as the carrier gas. Nineteen peaks were observed, but 85% of the material was accounted for in four peaks. With a 2-meter column made from $^1/_4$-in. o.d. copper tubing, a helium flow rate of 24 ml./min. and a column temperature of 91°, the retention times of the four major components and their percentages in the mixture were found to be 24.1 min., 16%; 58.7 min., 16%; 69.0 min., 32%; 89.3 min., 21%. A peak at 7.3 min., presumably cyclopentadiene, accounted for 5% of the mixture, and all other products were present in lesser amounts. After initial examination of the pyrolysis mixture, higher helium flow rates were used for rapid routine analyses. At a flow rate of about 40 ml./min. at 100°, 3-methylene-1,4-cycloheptadiene (V) had a retention time of 17.9 minutes and *m*-xylene 17.0 minutes, too close to permit separation. Under similar conditions, the retention time of *o*-xylene was 23.7 minutes and that of 3-methylene-1,5-cycloheptadiene (VI) was 24.1 minutes. Since *o*- and *m*-xylene are present in the pyrolysis products, gas chromatographic analytical results for methylenecycloheptadienes in the present work include the indistinguishable xylenes in the values reported.

Preparative Scale Gas Chromatography of Pyrolysis Products.—The C_8H_{10} fraction described in the preceding paragraph was gas chromatographed on a column similar to the analytical column but of wider bore for 0.1–0.5-g. scale separations. The first major peak ($n^{25.5}\mathrm{D}$ 1.4892) represented 3-methylene-5-vinylcyclopentene (VII). The second major peak ($n^{25.5}\mathrm{D}$ 1.5119) represented largely 3,5-dimethylenecyclohexene[6] (VIII), identified by its known infrared spectrum, with a small amount of an unknown contaminant. The third major peak ($n^{25.5}\mathrm{D}$ 1.5325) represented a mixture of 75% 3-methylene-1,4-cycloheptadiene (V) and 25% *m*-xylene (percentages calculated from the refractive indices of the pure materials). That the dependence of refractive index on concentration is nearly linear was verified by making up a mixture of 29% (by weight) *m*-xylene and 71% purified V (see below), which gave $n^{25.0}\mathrm{D}$ 1.5315 as compared to a calculated value of 1.5299. The infrared spectrum of the mixture was similar to that of the crude gas chromatographed sample. The fourth major peak ($n^{25.5}\mathrm{D}$ 1.5183) represented a mixture of 89% 3-methylene-1,5-cycloheptadiene (VI) and 11% *o*-xylene (percentages calculated from the refractive indices of the pure materials). The presence of *o*-xylene in the mixture was indicated by a strong infrared band at 744 cm.$^{-1}$, absent in the spectrum of purified VI. From the results described above, the calculated composition of a typical C_8H_{10} fraction of pyrolysis products was 25% 3-methylene-1,4-cycloheptadiene (V), 20% 3-methylene-1,5-cycloheptadiene (VI), 17%, 3-methylene-5-vinylcyclopentene (VII), 17% 3,5-dimethylenecyclohexene (VIII), 8% *m*-xylene, 2% *o*-xylene and remainder unknown products, the most prevalent of which was present to the extent of 3%.

Separation of C_8H_{10} Isomers.—The C_8H_{10} fraction was distilled at reduced pressure through a 3-ft. vacuum-jacketed column, 1 cm. in diameter, packed with Podbielniak stainless steel helices and having the condenser cooled to −75°. The reflux ratio was kept above 50:1 during most of the distillation, which required 100 hours of continuous operation. The following fractions were obtained: 17 g. of forerun that was mostly cyclopentadiene with 1–2 g. of benzene, which solidified in the condenser and was identified by infrared; 26.3 g. of 60–65% (by gas chromatography) 3-methylene-5-vinylcyclopentene (VII), b.p. 10–17° (12 mm.); 43 g. of intermediate fractions that were complex mixtures containing largely 3,5-dimethylenecyclohexene (VIII) and, slightly higher boiling, *m*-xylene, b.p. 17–28° (12 mm.); 82.6 g. containing methylenecycloheptadienes (V and VI), b.p. 28–32° (12 mm.); and 32 g. of residue. Unlike the earlier fractions, the methylenecycloheptadienes were distilled very rapidly, and the material held up on the column was removed at 1-mm. pressure. The methylenecycloheptadienes were then redistilled at a reflux ratio of 40–50:1, which required 55 hours. The fractions obtained, analyzed by gas chromatography, fell in the following categories: 7.9 g., b.p. 22–26.5° (11 mm.), 50–55% 3-methylene-1,5-cyclo-heptadiene (VI), 10% 3,5-dimethylenecyclohexene (VIII), 10% unknown, and the rest *m*-xylene and 3-methylene-1,4-cycloheptadiene (V); 22.6 g., b.p. 26.5–27° (11 mm.), 49–54% VI, 23–34% V, 12% unknown and <4% VIII; 9.6 g., b.p. 27° (11 mm.), 41% V and 48% VI; 22.1 g., distilled at 4:1 reflux ratio, b.p. 27.7–28.2° (11 mm.), 71% V, 25% VI, 3% unknown and 1% VIII. An additional 11.8 g. of a complex mixture containing a considerable amount of V was stripped out of the column at 1 mm., and 6.2 g. of residue remained.

Partitioning V and VI between Pentane and Aqueous Silver Nitrate.—A distilled 5-g. sample containing the isomers V, VI, VIII, and small amounts of xylenes was equilibrated at 0° between 50 ml. of commercial pentane and a solution of 25 g. of silver nitrate in 50 ml. of water. Recovery of the olefins from each phase followed by gas chromatographic analysis indicated the following ratios of material in the pentane phase to material in the aqueous phase: VI, 0.27; VIII, 1.1; V, 2.2; unknown, 8.4. Thus, it was possible to separate V and VI by an appropriate sequence of equilibrations, but VIII contaminated both products unless excessive effort was expended. The distribution coefficients measured for V and VI are only approximate, inasmuch as the xylenes in the mixture, which are insoluble in aqueous silver nitrate, are not separated from V and VI by gas chromatography.

Purification of 3-Methylene-1,5-cycloheptadiene (VI).—A 29.3-g. sample of distilled pyrolysis products containing approximately 55% VI was stirred with 30 ml. of pentane and a solution of 100 g. of silver nitrate in 200 ml. of water at 0°. The pentane phase was washed with a small second portion of aqueous silver nitrate and the combined aqueous solutions were washed with 20 ml. of pentane. The olefins were liberated from the silver nitrate by addition of 250 ml. of 7 *M* ammonium hydroxide at 0° and extracted with pentane. Distillation in a spinning band column yielded 15.1 g. of products, b.p. 52° (24 mm.). The VI in the mixture was separated by gas chromatography and distilled, b.p. 51° (25 mm.), $n^{25.5}\mathrm{D}$ 1.5205; infrared spectrum (cm.$^{-1}$), significant bands[12]: 884(s), 1770(m), (C=CH_2); 1600(s), (conjugated C=C); 1640(ms), (C=C); 653(s), 692(s), 781(s), 852(s), (unassigned).

Anal. Calcd. for C_8H_{10}: C, 90.51; H, 9.49; quant. hydrogenation, 0.0570 g. H_2/g. sample. Found: C, 90.64; H, 9.77; quant. hydrogenation, 0.0553, 0.0559.

As a check on its homogeneity, VI was also isolated by fractional crystallization of its silver nitrate complex. A 41-g. sample of distilled pyrolysis product, containing approximately 35% VI, 55% V and 5% VIII, and 30.8 g. of silver nitrate were dissolved in 200 ml. of methanol and 200 ml. of 2-propanol, decolorized with charcoal, and cooled. The solution was seeded with crystals of the silver nitrate complex obtained from VI that had been purified by gas chromatography and was allowed to crystallize at −15° for 10 days. The crude complex, approximately 25 g., was recrystallized from methanol and 2-propanol to yield 13.9 g. of complex, which was recrystallized from methanol to yield 10.0 g. The olefin was liberated from the complex with aqueous ammonium hydroxide, extracted with methylene chloride and distilled, b.p. 24–25° (9 mm.), yield 1.7 g., $n^{25.2}\mathrm{D}$ 1.5199. The infrared spectrum was identical with that of the analytical sample of VI described above. The ultraviolet spectrum (in ethanol) showed $\lambda_{\max}$ 235 mμ, $\epsilon_{\max}$ 13,900.

1-Bromomethyl-3,6,7-tribromocycloheptene (IX).—An 18.2-g. sample of distilled pyrolysis products containing 11.3 g. of 3-methylene-1,4-cycloheptadiene (V) (by gas chromatographic analysis) was dissolved in 72 ml. of methylene chloride. The solution was stirred at −75° and 54.5 g. of bromine in 55 ml. of methylene chloride was added over a period of 40 minutes. Crystallization of the tetrabromide was completed by adding 100 ml. of toluene and allowing the mixture to stand for 1 hour at −78°. The yield of tetrabromide of V, m.p. 114–116°, was 22.1 g. (49%). Recrystallization from 80 ml. of toluene yielded 16.1 g., m.p. 125–128° (35%). Addition of a small amount of calcium carbonate before heating the tetrabromide in toluene prevented darkening of the solution. An analytical sample was obtained

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[12] Infrared interpretations are based on L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

by recrystallization from methylcyclohexane. The infrared spectrum (potassium bromide pellet) contained no band near 890 cm.$^{-1}$ (exo-methylene) and only weak absorption near 1670 cm.$^{-1}$ (C=C must have nearly symmetrical *trans* substitution). The compound reacted slowly with potassium permanganate in acetone.

Anal. Calcd. for $C_8H_{10}Br_4$: C, 22.57; H, 2.37; Br, 75.07. Found: C, 22.65; H, 2.57; Br, 75.35; 75.24.

When samples containing lower proportions of V were brominated, yields of tetrabromide were lower. Thus, bromination of the entire C_8H_{10} fraction from pyrolysis of 500 g. of I yielded only 10 g. of V tetrabromide. Rapid fractionation (3-ft. packed column, 5:1 reflux ratio) of the C_8H_{10} products before bromination greatly improved the yield. For example, a solution of 170.9 g. of fractionated pyrolysis products containing 84.7 g. of V (by gas chromatography) in 350 ml. of methylene chloride was added to 515 g. of bromine in 800 ml. of methylene chloride at −75° to yield 100 g. (29%) of IX. If the calculated amount of V includes 25% *m*-xylene, the yield of tetrabromide is 39%. Considerable amounts of HBr were evolved from reaction of the bromine with lower-boiling components, *e.g.*, VIII, in the mixture. In spite of the lower yields of tetrabromide, use of rapidly fractionated V was preferred because of the time saved.

Debromination of 1-Bromomethyl-3,6,7-tribromocycloheptane.—A mixture of 40 g. of zinc dust, 5 g. of calcium carbonate and 150 ml. of *t*-butyl alcohol was stirred vigorously and heated under reflux during the addition of 42.6 g. of 1-bromomethyl-3,6,7-tribromocycloheptane in small portions over a period of 20 minutes. The mixture was stirred and heated under reflux 0.5 hour longer and then filtered with gentle suction. The zinc residue was washed with 100 ml. of hot *t*-butyl alcohol and the combined filtrates were poured into 1 l. of water acidified with 5 ml. of acetic acid. The product was extracted with three 100-ml. portions of pentane, washed with dilute sodium bicarbonate (50 ml.) and water (two 50-ml. portions), and dried over magnesium sulfate and potassium carbonate. Distillation through a spinning band column yielded 7.77 g. (73%) of 3-methylene-1,4-cycloheptadiene (V), b.p. 54–57° (30.5 mm.), $n^{25.0}\mathrm{D}$ 1.5418–1.5442. An analytical sample was prepared from a center cut of the above material by vacuum distillation from anhydrous calcium sulfate; $n^{25.0}\mathrm{D}$ 1.5443; infrared spectrum (cm.$^{-1}$), significant bands:[12] 890(s), 1780 (m), ($C{=}CH_2$); 1575(s), 1610(ms), 1640(w), (conjugated C=C); 1430(s), 1450(m), 1415(m), ($-CH_2-$); 665(s), 730(s), (unassigned). The 788 cm.$^{-1}$ strong band observed by Doering and Wiley[7] was evidently due to an impurity, as the present sample shows an absorption minimum at that point; ultraviolet spectrum (in isoöctane): λ_{max} 284 mμ, ϵ_{max} 11,800, shape of curve the same as that described by Doering and Wiley.[7]

Anal. Calcd. for C_8H_{10}: C, 90.51; H, 9.49; quant. hydrogenation, 0.057 g. H_2/g. sample. Found: C, 90.87, 90,63; H, 9.74, 9.56; quant. hydrogenation, 0.0573, 0.0577.

Gas chromatography indicated the presence of 2% of an impurity, presumably an isomer, having a retention time of 12.5 minutes when the main peak was at 17.9 minutes. The largest other impurity was 0.1%. It is believed that these impurities were derived from impurities in the tetrabromide. Use of ethanol instead of *t*-butyl alcohol as the solvent for the debromination of a different batch of tetrabromide led to formation of a small amount of higher-boiling material, b.p. 74° (24 mm.), as well as a 59% yield of V, b.p. 78° (81 mm.), $n^{24.5}\mathrm{D}$ 1.5453–1.5462, a center cut of which yielded slightly low carbon and hydrogen analyses. The largest impurity detected by gas chromatography was 0.2% and the infrared spectrum was identical with that of the analytical sample.

Addition of Tetracyanoethylene (TCNE) to 3-Methylene-1,4-cycloheptadiene (V).—To a solution of 0.53 g. of V in 10 ml. of toluene at room temperature was added 0.64 g. of TCNE. After 5 days, the solution was filtered to remove an amorphous solid (0.13 g.). The filtrate was concentrated and the product was precipitated by addition of ether. The yield of TCNE adduct X, m.p. 140–143°, was 0.30 g. (25%). Sublimation at 80–100° (0.1 mm.) yielded 0.18 g., m.p. 150–154°. A sample prepared in the same way and having an identical infrared spectrum, but melting at 165–170°, was submitted for analysis. The reason for the large variation in the melting point is not known. The infrared spectrum showed double bond absorption at 1640 cm.$^{-1}$ and no exomethylene band near 890 cm.$^{-1}$. The ultraviolet spectrum (in acetonitrile) showed only end absorption below 225 mμ, indicating that the double bonds were not conjugated.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.80; H, 4.30; N, 23.90. Found: C, 71.40; H, 4.44; N, 24.16.

Addition of Tetracyanoethylene (TCNE) to 3-Methylene-1,5-cycloheptadiene (VI).—A mixture of 0.53 g. of IX and 0.64 g. of TCNE in 10 ml. of toluene was allowed to stand 5 days at room temperature. The solution was concentrated and the products were precipitated with ether and pentane. The yield of TCNE adducts of IV, m.p. 118–124°, was 0.97 g. (83%). Sublimation at 100° (0.1 mm.) of 0.71 g. yielded 0.14 g. of sublimed material and 0.45 g. of residue. The sublimed material was recrystallized from ether–pentane, then methylcyclohexane, then resublimed to yield 0.08 g., m.p. 115–116°. The infrared spectrum showed double-bond absorption at 1625 cm.$^{-1}$ and no exomethylene band near 890 cm.$^{-1}$. The ultraviolet spectrum (in acetonitrile) showed λ_{max} at 265 mμ, ϵ_{max} 4450, consistent with a conjugated diene in a ring.

Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.80; H, 4.30; N, 23.90. Found: C, 71.62; H, 4.19; N, 24.24.

Hydrogenation of the Methylenecycloheptadienes V and VI.—Dilute solutions of 1-g. analytical samples of the methylene-cycloheptadienes (V and VI) in ethanol were hydrogenated over a platinum catalyst. Reaction mixtures were poured into water, extracted with pentane, and the pentane extracts were distilled. From VI there was obtained a 40% yield of methylcycloheptane, b.p. 133–135°, $n^{25.8}\mathrm{D}$ 1.4390 (reported[13] b.p. 135–136°, $n^{25}\mathrm{D}$ 1.4388), and V gave a 35% yield, b.p. 134–136°, $n^{25}\mathrm{D}$ 1.4385. The infrared spectrum of each sample was identical with that of methylcyclo-heptane prepared by Doering and Wiley.[7]

Isolation of 3-Methylene-5-vinylcyclopentene (VII).—The largest component (60–65%) of the distillation cut of b.p. 10–17° (12 mm.) was separated by preparative scale gas chromatography. The analytical sample was distilled rapidly in a spinning band column, b.p. 51° (65 mm.), $n^{25}\mathrm{D}$ 1.4887. Gas chromatography indicated 96% of the material to be under one peak; infrared spectrum (cm.$^{-1}$), significant bands: 913(s), 993(s), 1840(w), 1970(w) ($-CH{=}CH_2$); 860(s), 1745(m) ($C{=}CH_2$ conjugated with a cyclopentane; for comparison, the $C = CH_2$ bands in 1-methyl-3-methylenecyclobutene[14] occur at 851 and 1700 cm.$^{-1}$); 1645(s), (C=C) 799(s), 677(s) (unassigned); ultraviolet spectrum: in ethanol, λ_{max} 237 mμ, ϵ_{max} 16,500; in isoöctane, λ_{max} 237 mμ, ϵ_{max} 19,800. (Since 1-methyl-3-methylenecylobutene[14] has λ_{max} 224, ϵ_{max} 14,000, this small ring structure is excluded.) The nuclear magnetic resonance spectrum was complex and was not interpreted in detail, but showed an approximate ratio of aliphatic to olefinic hydrogen of 3:7.

Anal. Calcd. for C_8H_{10}: C, 90.51; H, 9.49; quant. hydrogenation, 0.0570 g. H_2/g. sample. Found: C, 90.81; H, 9.76; quant. hydrogenation, 0.0579.

Hydrogenation of 3-Methylene-5-vinylcyclopentene (VII).—A 10.27-g. sample obtained by gas chromatography and containing 90–95% VII was hydrogenated in 100 ml. ethanol over 0.2 g. of platinum. The hydrogenation was complete in 15 minutes, but shaking with the catalyst was continued for 20 hours. Isolation of the product was accomplished by pouring the solution into water, extracting with pentane, and distilling the pentane extract in a spinning band column. The yield of 1-methyl-3-ethylcyclopentanes, b.p. 120.5–121°, $n^{25}\mathrm{D}$ 1.4177–1.4186, was 7.58 g. (64%); reported:[15] *cis*-1-methyl-3-ethylcyclopentane, b.p. 121.4°, $n^{25}\mathrm{D}$ 1.4179, d^{25} 0.768; *trans*-1-methyl-3-ethylcyclopentane, b.p. 120.8°, $n^{25}\mathrm{D}$ 1.4162, d^{25} 0.758; *trans*-1-methyl-2-ethylcyclopentane, b.p. 121.2°, $n^{25}\mathrm{D}$ 1.4195, $d^{25}{}_4$ 0.765. Comparison of the infrared spectrum with an American Petroleum Institute reference curve (serial number 534) for *cis*-1-methyl-2-ethylcyclopentane (b.p.[15] 128.05°, $n^{25}\mathrm{D}$ 1.42695) indicated that this isomer was not present. The Raman spectrum

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[13] G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1940, Vol. II, p. 178.

[14] J. K. Williams and W. H. Sharkey, THIS JOURNAL, **81**, 4269 (1959).

[15] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Washington, D. C., 1953, p. 112.

(only the stronger bands were observed) was inconsistent with the presence of either *cis*- or *trans*-1-methyl-2-ethylcyclopentane,[16] but was consistent with that of a mixture containing 50% or more *trans*-1-methyl-3-ethylcyclopentane[17] together with an unknown component, presumably the *cis* isomer. Gas chromatography on a column of 10% squalane on Columpak showed 92% of the sample under one peak, with all of the contaminants higher-boiling materials except for 0.1%. Most hydrocarbons boiling higher than the 1-methyl-3-ethylcyclopentanes have higher refractive indices, so the value found for the present material may be considered a probable upper limit. In addition, the infrared spectrum showed changes only in weak bands in going from the lowest-boiling to highest-boiling distillation fractions, indicating that the bulk of the material had a uniform boiling point and that substances changing the refractive index from one cut to the next were impurities, not major constituents. The sample described above was redistilled in a spinning band column at a reflux ratio of 40:1 and a center cut taken, b.p. (± 0.5°) 121.2°, $n^{25}{}_{D}$ 1.4170, $d^{25}{}_{4}$ 0.7614. Gas chromatography on a column of 25% cyanoethyl glyceryl ether on Columpak, indicated that 94% of the material was under one peak, three higher-boiling major impurities (2%, 3% and 1%) were present, and lower-boiling impurities amounted to 0.1%. Thus, the observed physical constants exclude *trans*-1-methyl-2-ethylcyclopentane, but are consistent with those of a mixture containing largely *trans*- probably mixed with some *cis*-1-methyl-3-ethylcyclopentane.

7-Methylene-1,3,5-cycloheptatriene (XII).—A distilled mixture of pyrolysis products containing approximately 71% V and 25% VI, was passed over approximately 20 ml. of heated catalyst at reduced pressure and trapped at −75°. Dehydrogenation of this crude mixture of methylenecycloheptadienes at 530° (2 mm.) over 1% platinum-on-granular charcoal catalyst that had been treated with alkaline hydrogen peroxide yielded a bright red solution having absorption maxima at 600, 550 and 500 mμ. Comparison with the extinction coefficients determined by Doering and Wiley[7] indicated that the concentration of methylenecycloheptatriene was 0.03%. In another experiment, 1. g. of crude mixture of methylenecycloheptadienes was dehydrogenated at 610° (1 mm.) and collected in a solution of 1 ml. of dimethylacetylene-dicarboxylate in 10 ml. of tetrahydrofuran. Then the methylene-cycloheptatriene was converted to 1,2-bis-(methoxycarbonyl)-azulene by the method of Doering and Wiley.[7] The azulene was partially purified by chromatography, and the yield was estimated to be 0.1% on the basis of the ultraviolet spectrum. Dehydrogenation of the crude mixture of methylenecycloheptadienes at 490° (1 mm.) over chromia–alumina catalyst that had been treated with methanolic potassium hydroxide yielded red solutions which faded very rapidly. Addition of pentane to the product precipitated a white polymer, presumably poly-(methylenecyclo-heptatriene), in 18% yield. An attempt to get a carbon and hydrogen analysis failed because the polymer exploded in the combustion tube, probably because of formation of peroxides. When a solution of 0.5 g. of the crude mixture of methylene-cycloheptadienes in 2 ml. of pyridine was passed over the alkali-treated chromia–alumina catalyst at 490° (1 mm.), the methylene-cycloheptatriene formed was stabilized somewhat. In this case, the yield of monomer, as determined spectroscopically, was 0.9%, and the yield of polymeric product was about the same as in the absence of pyridine. Pyrolysis of 5-methylenebicyclo-[2.2.1]-hept-2-ene (I) over the 1% platinum-on-charcoal catalyst at 650–675° (2 mm.) yielded a 0.1% solution of methylenecycloheptatriene. The yield of methylenecycloheptatriene from the usual pyrolysis of the hydrocarbon I over a Vycor or carbon surface appeared to be about 0.05%.

Acknowledgment.—We wish to thank Dr. D. W. Wiley of this Laboratory for many helpful discussions on the chemistry of methylenecycloheptatriene and methylenecycloheptadienes.

WILMINGTON, DEL.

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[16] G. Chiurdoglu and A. Guillemonat, *Bull. soc. chim. France*, [5] **5**, 1328 (1938).

[17] P. A. Bazhulin, A. V. Koperina, A. L. Liberman, V. A. Ovodova and B. A. Kazanskii, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. S.S.R.*, 607 (1954) (Engl. translation).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Highly Strained Bicyclic Systems. I. The Synthesis of Some Bicyclo[2,1,1]hexanes of Known Stereochemistry[1]

BY JERROLD MEINWALD[2] AND PAUL G. GASSMAN[3]

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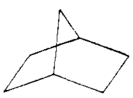
The stereospecific synthesis of a series of 2-substituted bicyclo[2,1,1]hexanes, starting from (±)-α-pinene, is described.

Introduction.—Chemical investigations of the bicyclo[2,2,1]heptanes (I) have led to some of the most interesting discoveries in the classical area of natural products as well as in the field of physical organic chemistry.[4] All of the possible types of monosubstituted derivatives of I are known; each has some unique, characteristic behavior. In addition, olefinic and aromatic variants of I have been the subject of much recent attention.[4]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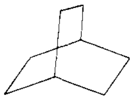
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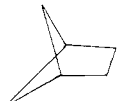
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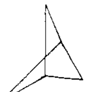
IV

A good deal of the unusual chemistry associated with the bicyclo[2,2,1]heptyl system may be attributed ultimately to the strain incorporated in the rigid, bridged carbon skeleton; the analogously constituted but less strained bicyclo[2,2,2]-octanes (II) show much more classical behavior. In this context, a study of the synthesis, properties and reactions of the bicyclo[2,1,1]hexanes (III) and bicyclo[1,1,1]pentanes (IV) should be of special significance, since these molecules must be considerably more strained than I itself. It is remarkable that no systematic effort to study the chemistry of these systems seems to have been made, although compounds with carbon skeleton III have been prepared in a few instances. With

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[1] A portion of this work was presented at the Boston Meeting of the American Chemical Society, April 5–10, 1959; Abstracts of Papers Presented, p. 14-O.

[2] Fellow of the Alfred P. Sloan Foundation.

[3] National Science Foundation Coöperative Fellow, 1959–1960.

[4] For an interesting historical survey of this field see L. Ruzicka in A. Todd's "Perspectives in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 265–314. See also S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957); J. Meinwald, H. Nozaki and G. A. Wiley, *ibid.*, **79**, 5597 (1957); J. Meinwald and G. A. Wiley, *ibid.*, **80**, 3667 (1958).