was separated from the supernatant liquid after some time and dissolved in dilute hydrochloric acid. The acid solution, after being shaken with benzene and filtered through a wet filter paper, was made alkaline cautiously with caustic soda solution with cooling and stirring. The benzene layer was washed and dried and the solvent was removed in vacuo in a hydrogen atmosphere. The reddish residue thus obtained was dissolved in methanol (50 ml.) and reduced over Raney nickel (1.5 g.), *ca.* 2 molar equivalents of hydrogen being absorbed. The catalyst and the solvent were removed and the residue was dissolved in benzene and purified through an alumina column. After evaporation of the solvent there remained a yellow oily base, which was again dissolved in methanol, neutralized with hydrobromic acid and evaporated. The residue solidified on scratching and was purified from a minimum amount of hot water (charcoal) to give the hydrobromide salt of 1-*p*-methoxybenzyl-1,2,3,4,5,6,7,8-octahydroisoquinoline as colorless prisms, m.p. 197–198°, undepressed when admixed with an authentic specimen, yield 1.55 g. or 41.3%. Both specimens also gave the identical IR spectra.

Anal. Calcd. for $C_{17}H_{23}ON\cdot HBr$: C, 60.4; H, 7.1; N, 4.1. Found: C, 60.0; H, 6.7; N, 4.1.

Catalytic reduction of the 2-methyl quaternary salt of the tetrahydro base did not give a satisfactory result. Methylation was accomplished by catalytic reduction in the presence of formaldehyde and the 1-*p*-methoxybenzyl-2-methyl-1,2,3,4,5,6,7,8-octahydroisoquinoline was converted to 3-hydroxy-*N*-methylmorphinan, m.p. 250–252°, by the procedure of Schnider and Hellerbach.[3] Its identity was confirmed by mixed melting point with an authentic sample.

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Pyrolysis of 1,1-Dichloro-2-vinylcyclopropane. Synthesis of 2-Chlorocyclopentadiene

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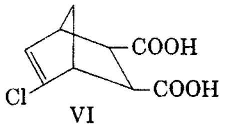
The reaction of chloroform with butadiene in the presence of potassium *t*-butoxide gives 1,1-dichloro-2-vinylcyclopropane (I).[1] This material is remarkably stable, being resistant to the action of bases, to zinc and magnesium in refluxing ethanol or tetrahydrofuran and is not attacked by molecular oxygen.[2] However, on vacuum pyrolysis at about 500° (5 mm. nitrogen atmosphere), the compound was converted essentially completely to a mixture of new chloroolefins. Low temperature vacuum distillation of the mixture permitted isolation in about 90% purity of a monochlorocyclopentadiene (II) which on the basis of its Diels-Alder reactions was concluded to have the chlorine atom in the 2- position.

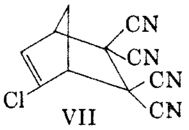
Vapor phase chromatography of the reaction product on a silicone column resulted in separation into four major peaks and several additional minor ones. While the structures of these materials have not been conclusively demonstrated, evidence was obtained for the existence of 4,4-dichlorocyclopentene (III), 1,1-dichloropenta-1,4-diene (IV), and 1,1-dichloropenta-1,3-diene (V) in the pyrolysis mixture.

Evidence for the interesting chlorocyclopentadiene structure consisted of hydrogenation with palladium on charcoal in alcoholic potassium hydroxide to cyclopentane; a mass spectrum indicating a molecular weight of 100 and the presence of one chlorine atom (from the size of the isotopic 102 peak); the infrared spectrum showing a strong band at 6.3μ attributable to a conjugated diene structure; the nuclear magnetic resonance spectrum which showed the presence of two types of hydrogens in the ratio of 3 to 2 with resonance at +9.0 and +42.5 parts per ten million from benzene, respectively; the ultraviolet spectrum with maxima at 254 (ϵ 3200) and 250 (ϵ 3200) with a shoulder at 238 (ϵ 2500) mμ; the exothermic reactions with maleic anhydride and tetracyanoethylene; and the spontaneous dimerization of the material on standing.

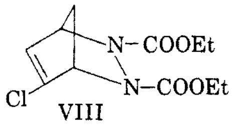
The conclusion that the molecule reacted as if the chlorine atom were in the 2- rather than the 1-position on the cyclopentadiene ring was made on the basis of the absence of the 14.2μ *cis*-hydrogen band in the infrared spectra of all the Diels-Alder derivatives which were prepared. This band was present in all authentic bicyclo(2,2,1)hept-5-ene derivatives unsubstituted in the 5- and 6-positions which were examined.



VI



VII



VIII

In addition, the nuclear magnetic resonance (NMR) spectrum of VI showed the presence of four kinds of hydrogens in the approximate ratios of 4:2:2:1. The lone hydrogen atom had its resonance peak at the position of resonance of the olefinic hydrogens in bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid. The existence of a dynamic equilibrium between 1- and 2-chlorocyclopentadiene with more rapid reaction of the 2- isomer cannot be ruled out, however, though an attempt to find even a small amount of an isomeric adduct in the maleic anhydride reaction was unsuccessful.

The evidence for the 4,4-dichlorocyclopentene (III) consisted of the infrared, NMR, and mass spectrum of a fraction which had been collected by vapor phase chromatography. Also in a series of

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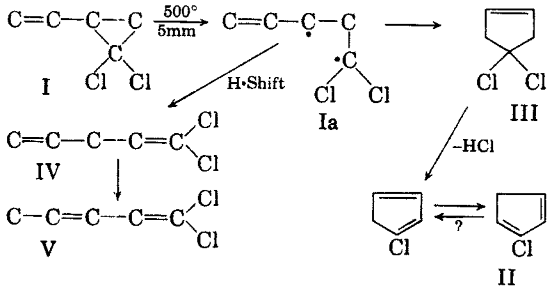
[1] R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, 79, 2542 (1957).

[2] All of these observations are in sharp contrast to the behavior of 1,1-dibromo-2-vinylcyclopropane, N. P. Neureiter, unpublished results; see also W. E. Doering and P. M. LaFlamme, *Tetrahedron*, 2, 75 (1958).

pyrolyses the yield of III decreased in direct proportion to an increase in II with an increase in the pyrolysis temperature. This suggested that at the higher temperatures III was dehydrochlorinating to give II. Such a precursor to the cyclopentadiene structure would mean that initially 1-chlorocyclopentadiene was formed, followed either by immediate rearrangement to the 2- isomer or the existence of the two compounds in dynamic equilibrium.

The most plausible course for the transformation would involve initial rupture of the cyclopropane ring to form the resonance stabilized diradical Ia which then has a number of alternate paths by which it can subsequently react.



One path of reaction of Ia leading to the linear structures IV and V is indicated. A small amount of isopentane which was obtained on hydrogenation of the reaction mixture can be explained through formation of a different initial diradical.

It has recently been concluded that carbenes add to double bonds by a three-center transition state.[3] Perhaps as a result of such a mechanism no 1,4-additions of carbenes to conjugated double bond systems have been observed.[4] It seems reasonable to interpret the present work as further evidence for the reaction of carbene species in the singlet state. If a carbene were a true diradical one might fairly expect some conjugate addition. It appears that when the diradical intermediate Ia does exist, conjugate addition can be observed. Of course, in the present work, the three-membered ring is unstable with regard to the diradical Ia at the high temperatures of the reaction. This, then, is one way of forcing the 1,4- addition of a carbene to a conjugated system.

EXPERIMENTAL[5]

Chlorocyclopentadiene. The 1,1-dichloro-2-vinylcyclopropane was obtained by the method of Woodworth and Skell.[1] In a typical pyrolysis run 16.8 g. (0.123 mol.) of this product was introduced during 1 hr. to an empty 28 × 300 mm. (heated length) Vycor tube inclined at a 40° angle through a furnace heated to 475–500°. A slow stream of nitrogen (100 ml./min.) was passed through the tube, while a vacuum pump was regulated to hold the total pressure at about 5 mm. The sample was charged in two different ways. A small three-neck flask equipped with dropping funnel, nitrogen inlet, and heating mantle was attached *via* a short, bent exit tube to the pyrolysis tube. The material could be added through the dropping funnel at any desired rate and immediately vaporized. Later the dropping funnel was eliminated by placing the full charge in the precooled flask and slowly warming to vaporize the material into the nitrogen stream. The exit gases from the pyrolysis tube were passed directly into a Dry Ice trap, then to a liquid nitrogen trap which was attached to the vacuum pump. The liquid product remained in the Dry Ice trap while the hydrogen chloride collected in the liquid nitrogen trap. At the end of the reaction the product in the Dry Ice trap (13.7 g., brown liquid) was dried over a little calcium chloride to remove some cloudiness and distilled immediately under nitrogen through an 8 × 200 mm. Vigreux column. The distillate was collected in a Dry Ice trap at 33 mm. pressure until the vapor temperature reached 39° (b.p. of starting material). The distillate (6.3 g.) was immediately redistilled (after removing a little cloudiness with calcium chloride) under nitrogen through a 14-cm. Vigreux column. The fractions were collected at 0°. After a small forerun, a fraction (1.92 g.) was collected, b.p. 30.7–35.5° (60 mm.) (flat at 33°), n_D^{27} 1.4822. From mass spectral data the material was estimated to be about 90% pure monochlorocyclopentadiene, though in the low voltage mass spectrum there were small peaks at mass 136, 104, and 88. The NMR spectrum at 60 megacycles on the neat liquid showed two kinds of hydrogen (peaks at +9.0 and +42.5 parts per ten million from benzene) in the ratio of 3 to 2. There were some smaller impurity bands —in part ascribable to the presence of some of the dimer. The infrared spectrum showed bands at 3.23 (mw), 3.47 (mw), 6.17 (vw), 6.32 (s), 6.69 (s), 7.30 (s), 7.42 (s), 7.89 (s), 8.02 (ms), 8.19 (m), 8.90 (s), 9.00 (m), 9.29 (ms), 9.34 (ms), 10.21 (ms), 10.60 (ms), 10.90 (ms), 11.23 (s), 11.62 (s), 11.76 (s), 12.48 (m), 13.40 (s), 14.60 (ms), 14.95 (s) μ. The ultraviolet spectrum in isooctane showed λ_{max} 254 mμ (ϵ 3200), 250 mμ (ϵ 3200), and 238 mμ (ϵ 2500).

For rapid, rough analyses of the product mixture vapor phase chromatography on an 8 ft. silicone grease on firebrick column operated at 80° with 22 lb. of helium pressure was used. There were only four significant peaks with at least five minor ones (all less than 5%). The first peak corresponded to chlorocyclopentadiene.

The second large peak (whose relative percentage was strongly dependent on the temperature of the pyrolysis) had a mass of 136 and contained two chlorine atoms. In the mass spectrometer from the size of the 100 and 101 peaks it was clear that the material had a structure which readily lost hydrogen chloride. The infrared spectrum had a C—H stretching pattern in the 3–4μ range similar to cyclopentene. Also, the shape of the C=C band at 6.18μ and the broad band at 14.35μ were similar to cyclopentene. The NMR spectrum in carbon disulfide at a frequency of 30 megacycles showed two kinds of hydrogens in the ratio of about 2 to 1 with bands centered at +38.0 and +13.0 parts per ten million from benzene. On the basis of these data this material has been assigned the structure 4,4-dichlorocyclopentene.

The third and fourth large peaks overlapped slightly. A mixture of the two was hydrogenated with palladium (10%) on charcoal in ethanol containing potassium hydroxide to give *n*-pentane. Both compounds had mass 136 and contained two chlorine atoms. The materials did not readily lose hydrogen chloride in the mass spectrometer. The third compound appeared to have a vinyl group and no methyl group from the infrared. No evidence was obtained for the

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(3) W. von E. Doering and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **80**, 5274 (1958). P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(4) The evidence for the small amount of 1,4- addition of :CCl_2 to isoprene reported by M. Orchin and E. C. Herrick, *J. Org. Chem.*, **24**, 139 (1959), hardly seems sufficient to warrant the conclusion.

(5) All boiling points and melting points are uncorrected. Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

location of the chlorine atoms. It was felt that the material was a linear, nonconjugated, dichloropentadiene. The fourth compound was thought to be the conjugated isomer of the third, but no conclusive information was obtained.

In a series of pyrolyses using only 1 or 2 ml. samples the effect of temperature on the pyrolysis was examined. Under the conditions described above, varying only the temperature produced a change in the composition of the product. Below 300° there was no conversion, at 325° it was only 0.5%. At 375° with 12% conversion there was 5% of peak 1, 5% of peak 2 and 2% of peak 3. Peak 4 appeared (2%) at 425° (∼50% conversion). In the 400–450° range, the relative amounts of 1 and 2 were essentially the same; however, above 500° as the temperature was raised to 570° the percentage of 2 dropped sharply as 1 increased. The percentage and number of small by-product peaks increased at these high temperatures. In the normal pyrolysis range (475–525°) a typical product (by relative peak areas in the vapor phase chromatograms) showed 25–30% peak 1, 15–20% peak 2, 30–35% peak 3, 10% peak 4, and 10–20% others.

Hydrogenation of reaction mixture. A sample of the pyrolysis product (0.8971 g.) was dissolved in 30 ml. of ethanol containing 1.3 g. of potassium hydroxide pellets and 80 mg. of 10% palladium on charcoal catalyst. The mixture was stirred in a hydrogen atmosphere at room temperature for 20 hr. Hydrogen absorption was very rapid at the beginning —but in the last 12 hr. only 10 ml. was absorbed. The mixture was filtered and distilled through a short Vigreux column until the vapor temperature reached 78°. The distillate was transferred to a narrow tube and water added. The supernatant layer (0.1–0.2 ml.) was analyzed by vapor phase chromatography. It was about 30% cyclopentane, 70% *n*-pentane. In a larger run 2.039 g. of pyrolysis mixture gave 0.35 ml. of hydrocarbon. This was analyzed as 61% *n*-pentane, 2% isopentane, 37% cyclopentane. From treatment of the residue with nitric acid and silver nitrate 2.47 g. of silver chloride was recovered corresponding to 0.61 g. of chloride ion having been eliminated from the original material. This suggests that hydrogenolysis under the reaction conditions was not complete.

From a fractional distillation of the pyrolysis product mixture the first fraction was hydrogenated as described above. The recovered hydrocarbon was 73% cyclopentane, 15% *n*-pentane and 12% a combination of several smaller peaks (C_1's to C_4's).

Isolation of dimer. The pyrolysis mixture from 20 g. of 1,1-dichloro-2-vinylcyclopropane was distilled giving 5.0 g., b.p. up to 30° (28 mm.). This was added to 15 ml. of ethyl ether containing a pinch of hydroquinone and let stand at room temperature for 5 days. The ether was removed under a column and the brown residue distilled giving 3.1 g. of colorless liquid, b.p. 85–93° (3 mm.). This was redistilled giving 2.4 g., b.p. 78–84° (2.2 mm.), n_D^{20} 1.5388.

Anal. Calcd. for $C_{10}H_{10}Cl_2$: C, 59.7; H, 5.0; Cl, 35.3. Found: C, 59.6; H, 4.9; Cl, 29.0, 29.2.

Hydrogenation of dimer. A sample of this dimer (0.9586 g., 4.77 mmol.) was dissolved in 30 ml. of ethanol with 2.5 g. of potassium hydroxide and 130 mg. of 10% palladium on charcoal. The mixture was stirred at room temperature for several hours in 1 atmosphere of hydrogen—uptake being very rapid. After about 200 ml. had been absorbed, continued hydrogen absorption became very slow even though the temperature was raised to 60°. At the end of 4 days 351 ml. (15.65 mmol.) of hydrogen had been absorbed. Most of the ethanol was removed under a small column at slightly reduced pressure. The residue was added to 4 vol. of water and extracted with petroleum ether. Washing the extracts with water, drying with calcium chloride and distilling gave 0.46 g. of material distilling to 120° (20–30 mm.). About $^2/_3$ of this material solidified on standing. The mass spectrum showed it to be a mixture of masses 136 and 170. The 170 material still contained one chlorine atom as evidenced by the 172 isotope peak, while the 136 peak was apparently due to the saturated hydrocarbon. This shows that the hydrogenolysis was not complete. The odor of the product was similar to that of tetrahydrodicyclopentadiene.

Reaction with maleic anhydride. From the initial distillation of the pyrolysis mixture 2.4 g. of the first cut was added to 2.6 g. of maleic anhydride in 12 ml. of benzene. Within 1 min. there was a considerable development of heat. The solution was left standing overnight and concentrated *in vacuo.* The highly viscous residue was boiled with 20 ml. of water for 1 hr. The clear solution was concentrated *in vacuo* until crystals formed (1.0 g.). The slightly moist material was recrystallized from an ether–petroleum ether mixture giving 0.35 g. of white crystals of *5-chlorobicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid* (VI), m.p. 140.1–141.3°. It was interesting that the material was insoluble in ether when dry, but readily dissolved on the addition of a drop of water. The only other product present from subsequent crops seemed to be maleic acid.

Anal. Calcd. for $C_9H_9ClO_4$: C, 49.9; H, 4.2; Cl, 16.4. Found: C, 49.8; H. 4.5; Cl, 16.2.

The NMR spectrum of the compound was recorded in 1,4-dioxane and deuterated acetone. There were four kinds of hydrogens present with resonance at −6(COOH), +12(=CH), +40 and +43(α and β to COOH), and +59 (bridge) parts per ten million from benzene. The relative ratios were 2.3:0.9:3.9:1.9 (theor. 2:1:4:2), respectively. The spectrum of bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid (in 1,4-dioxane) showed essentially the same peaks but in the order of 2.3:1.7:4.3:1.7 (theor. 2:2:4:2). In the monochloro compound there was one less olefinic hydrogen.[6] Though no conclusive information was obtained concerning the *endo* or *exo* configuration of the adduct, the apparent absence of splitting of the bridge hydrogens in the NMR spectrum suggests the *endo* form.

Reaction with tetracyanoethylene. Immediately upon mixing tetracyanoethylene (1.3 g.) with the crude chlorocyclopentadiene (1.3 g.) in tetrahydrofuran (12 ml.), there was sudden development of heat. After standing overnight the mixture was concentrated *in vacuo* leaving 2.0 g. of dark solid. A portion of the material was decolorized with norite and recrystallized from ethyl acetate–petroleum ether. On standing in the refrigerator, a very small quantity of white crystals of *5-chloro-2,2,3,3-tetracyanobicyclo(2,2,1)hept-5-ene* (VII) was obtained, m.p. 202–204° (dec.), darkening at 183°.

Anal. Calcd. for $C_{11}H_5ClN_4$: C, 57.8; H, 2.2; N, 24.5. Found: C, 57.8; H, 2.4; N, 24.6.

Reaction with diethyl azodicarboxylate. When the crude chlorocyclopentadiene (1.3 g.) was mixed with the azodicarboxylic ester (1.7 g.) in 15 ml. of ether, there was no development of heat whatsoever. After 4 days at room temperature the solvent was removed *in vacuo* leaving a viscous orange residue. After standing for 3 weeks at −10° the material crystallized (1.7 g. of yellow-white solid). The crystals were washed with ether which removed the color (excess azodicarboxylic ester). The residue (0.13 g.) after two recrystallizations from ethyl acetate–petroleum ether gave white crystals of *5-chloro-2,3-dicarbethoxy-2,3-diazabicyclo(2,2,1)hept-5-ene* (VIII), m.p. 81–83°.

Anal. Calcd. for $C_{11}H_{15}ClN_2O_4$: C, 48.1; H, 5.5; N, 10.2. Found: C, 47.9; H, 5.4; N, 10.1.

The infrared spectra of all three adducts were recorded. None had the band near 14.2μ which is present in norbornylene and in bicyclo(2,2,1)hept-5-ene-2,3-dicarboxylic acid and which is characteristic of the two *cis*-hydrogen atoms in the bridged six-membered ring.

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(6) The author is indebted to N. F. Chamberlain and associates for the NMR spectrum and its interpretation.