mixture cooled, poured into excess dilute hydrochloric acid and filtered, gave 580 mg. (45%) of N-phenyl-1,2-naphthalimide (XIII). The analytical sample, m.p. 163–163.5°, was crystallized from 1:5 benzene–ethanol.

Anal. Calcd. for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 79.21; H, 4.22; N, 5.24.

N-Phenyl-2,3-naphthalimide (XIV).—A mixture of 1.0 g. (2.81 m*M*) of *cis*-1,2-diiodobenzocyclobutene and 1.5 g. of N-phenylmaleimide was melted and heated at 190° (bath temperature). After an induction period of 2–3 min. (gradual formation of iodine), the reaction became vigorous and gave off a stream of violet vapor. The residue was cooled and dissolved in 600 ml. of benzene. The benzene solution was washed with excess aqueous sodium thiosulfate solution, dried, reduced to 75 ml. on the steam-bath, and cooled to give 0.125 g. of the fully aromatic adduct, N-phenyl-2,3-naphthalimide (XIV), m.p. 278–285°. Two subsequent crops, obtained by boiling off benzene and adding Skellysolve F, raised the yield to a total of 0.269 g. (35%). The melting point was not depressed by an authentic sample of XIV,[10] and the infrared spectra of the two samples were identical.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE HOOKER CHEMICAL CORPORATION RESEARCH LABORATORIES]

A Study of the Diels–Alder Addition Products of Hexachlorocyclopentadiene with: 1,4-Dichlorobutene-2, 3,4-Dichlorobutene-1 and 1,4-Dichlorobutyne-2

BY PAUL E. HOCH[1] AND JOHN M. CLEGG

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The Diels–Alder addition of *cis*- and *trans*-1,4-dichlorobutene-2, 3,4-dichlorobutene-1 and 1,4-dichlorobutyne-2 to hexachlorocyclopentadiene have been studied. *cis*-1,4-Dichlorobutene-2, 3,4-dichlorobutene-1 and 1,4-dichlorobutyne-2 undergo the normal addition and yield the expected products. *trans*-1,4-Dichlorobutene-2 does not add but apparently undergoes rearrangement predominantly to 3,4-dichlorobutene-1 which isomer then undergoes normal addition. Alcoholic base treatment of the *cis*-1,4-dichlorobutene-2 adduct yields the exocyclic diene. Structure proof data for the diene are presented. Chemical reactions and polymerization data for the diene are discussed. Alcoholic base treatment of the 3,4-dichlorobutene-1 adduct is believed to yield the acetylenic compound. Structural proof data are presented.

Introduction

The activity of hexachlorocyclopentadiene as a diene in the Diels–Alder reaction with many dienophiles is well established. Two review articles on the chemistry of hexachlorocyclopentadiene have appeared recently.[2,3]

A study of the Diels–Alder addition of hexachlorocyclopentadiene and various chlorolefins was made by McBee[4] and Fields.[5] This work is concerned with chlorolefins in which the chlorine was attached to one of the double bonded carbons. Allyl chloride and propargyl bromide have been successully added to hexachlorocyclopentadiene.[5,6] The adduct of 1,4-dichlorobutene-2 has been reported in a German patent.[7]

The present investigation deals with the Diels–Alder adduct of 1,4-dichlorobutene-2, 3,4-dichlorobutene-1 and 1,4-dichlorobutyne-2 with hexachlorocyclopentadiene. With the exception of the 1,4-dichlorobutene-2 adduct, the other adducts have not been reported.

Discussion

In the early phase of the work, a mixture of *cis*- and *trans*-1,4-dichlorobutene-2 was allowed to react with hexachlorocyclopentadiene. A solid product (I, m.p. 101–102°) and a liquid product (II, b.p. 140–144° (0.1 mm.)) were obtained. Both of these products had the composition expected for the adduct. It was also demonstrated that the adduct of 3,4-dichlorobutene-1 and hexachlorocyclopentadiene was identical to the liquid product II.

Treatment of compound I with hot ethanolic potassium hydroxide yielded a product which differed from that obtained from compound II when treated with the same reagent. Both products contained the same percentage chlorine. In each case two equivalents of hydrogen chloride were removed. Compound I yielded a crystalline solid (m.p. 85–86°, III) of strong camphor-like odor and compound II yielded a viscous oil (b.p. 103–106° (1.5 mm.)).

In view of the fact that 3,4-dichlorobutene-1 condensed with hexachlorocyclopentadiene to form II it was logical to assume that under the conditions of the experiment *trans*-1,4-dichlorobutene-2 resists a Diels-Alder addition as such and rearranges to the isomeric 3,4-dichlorobutene-1 which undergoes addition. To prove that this was the case, an alternate synthesis of II was carried out. The monoadduct[6] of butadiene and hexachlorocyclopentadiene was chlorinated actinically to yield an oil identical with II. These transformations are outlined in Fig. 1.

It was reasonable to assume that the product IV obtained from II by treatment with alcoholic base was the acetylenic compound. The infrared spectrum indicates an absorption at 3.1 μ for an acetylenic hydrogen. The compound absorbs two moles of hydrogen rapidly to form an oil (IV, b.p. 129–130° (5 mm.)) which was identical in infrared spectrum with the product obtained from the Diels–Alder adduct of butene-1 and hexachlorocyclopentadiene (see Experimental) namely 1,4,5,6,7,7-hexachloro-2-ethylbicyclo[2.2.1]heptene-5.

1,4-Dichlorobutyne-2 adds to hexachlorocyclopentadiene to form the expected adduct VII. 1,4,5,6,7,7-hexachloro-2,3-bis-(chloromethyl)-bicyclo[2.2.1]heptadiene-2,5. The allylic chlorines in this compound react with sodium acetate and acetic acid to form the diacetate VIII (m.p. 54–55°).

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[1] To whom all correspondence on the paper be forwarded.

[2] C. W. Roberts. *Chemistry & Industry*, 110 (1958).

[3] H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

[4] E. T. McBee, H. Rakoff and R. K. Meyers, THIS JOURNAL, **77**, 4427 (1955).

[5] E. Fields, *ibid.*, **76**, 2709 (1954).

[6] S. H. Herzfeld, R. E. Lidov and H. Bluestone, U. S. Patent 2,606,910 (August 12, 1952).

[7] German Patent 1,002,341 (February 14, 1957).

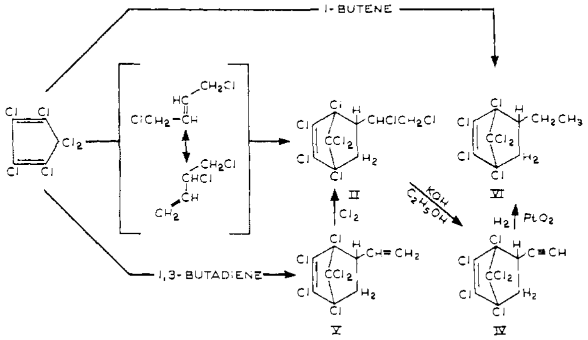


Fig. 1.

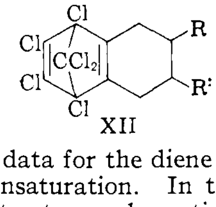
The diacetate VIII hydrolyses readily to the diol IX (m.p. 155–156°) by refluxing it with methanolic hydrochloric acid.

The diacetate VIII above has also been prepared by the Diels–Alder reaction of 1,4-diacetoxybutyne-2 with hexachlorocyclopentadiene. The melting points of the diacetate VIII and the diol IX agreed with those reported.[2] The infrared spectra of the diacetate VIII prepared by the two different synthetic routes outlined are identical.

The compound III obtained from I by dehydrohalogenation is undoubtedly the expected exocyclic diene as will be demonstrated below. It does, however, exhibit unexpected chemical properties.

The diene III adds two moles of hydrogen using Adams catalyst with low hydrogen pressure to yield a solid (XI, m.p. 86–87°). An attempt was made to prove this structure by adding a mixture of *cis*- and *trans*-butene-2 to hexachlorocyclopentadiene. Two solid products were obtained from this reaction; one, m.p. 238–242°, was identified as the bis-adduct of butadiene and hexachlorocyclopentadiene (see Experimental). The butenes must have been contaminated with small amounts of butadiene. The other product (m.p. 200–202°, XIa), gives the proper chlorine analysis for the butene adduct, but the physical and spectral properties are different from the reduced diene XI.[8]

The diene III resisted epoxidation with peracetic acid in acetic acid. No Diels–Alder adducts have been isolated. Dieneophiles that have been tried include maleic anhydride, *p*-benzoquinone, bicycloheptadiene, cyclopentadiene and tetracyanoethylene. The attempted reactions yielded polymer, or starting materials in spite of inhibitors. These observations are in marked contrast to the observed case that exocyclic dienes undergo the Diels–Alder reaction in the literature.[9,10] The resistance of this diene III to enter into a Diels–Alder reaction may be attributed to excessive steric strain in the expected product or resistance to normal alignment of the reactants for a Diels–Alder reaction. Chlorinated tricyclic structures that would result as in XII below appear to be unknown. It is improbable that the exocyclic double bond system in the diene could be twisted out of plane because of the inherent rigidity of the bicyclic ring system.



XII

The spectral data for the diene III does support a conjugated unsaturation. In the infrared spectrum, medium to strong absorption is indicated at 10.96 μ, weak absorption at 5.44, 3.22 and 3.52 μ indicating unsaturated vinyl hydrogen. A strong absorption occurs at 6.26 μ which is characteristic of the double bond in the bicyclic ring, with two very weak bonds at 6.15 and 6.37 μ, which may be due to conjugated unsaturation.

The ultraviolet spectrum for III showed the following: maxima occurred at 222 mμ, log $\epsilon_{\max}$ 4.23 with shoulders at 236 mμ, log $\epsilon_{\max}$ 4.082, and 245 mμ, log $\epsilon_{\max}$ 3.802. This spectrum is difficult to interpret in view of the fact that the double bond in the bicyclic ring also shows absorption in this region of the spectrum.[11] For example, octachlorocyclopentene shows absorption between approximately 270 and 220 mμ with a maximum at 224 mμ, log $\epsilon_{\max}$ 4.0 and 1,2,3,4,5,6,7,7-octachlorobicyclo-[2.2.1]hept-2-ene absorbs from 260 to below 212 mμ with a shoulder at approximately 235 mμ, log $\epsilon_{\max}$ 3.5. Previous workers[12] have reported absorption spectra for the exocyclic dienes with maxima ranging from 220 to 248 mμ.

Several attempts were made to prepare the diene III from VII by a 1,4-elimination with iodide ion and with zinc metal. No diene was isolated; only polymer resulted in every case. The polymer was identical in its infrared spectra with that obtained from the diene.

The diene III polymerizes very readily above its melting point. The presence of a peroxide catalyst greatly accelerates the polymerization and cure. Suspension polymers have also been prepared using a polyvinyl alcohol suspending agent. Emulsion polymerization of the pure monomer proved impractical. The polymer dropped out of the emulsion minutes after starting the polymerization. The castings obtained by bulk polymerization were clear, pale yellow, high softening (> 180°) materials. The castings and the beads obtained from the suspension polymerization were not completely solvent soluble, indicating considerable 1,2-polymerization with subsequent crosslinking. The polymers did not exhibit any degree of crystallinity as observed by Bailey[13] for 1,2-dimethylenecyclohexane polymers.

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(8) The infrared spectra for the compounds XI and XIa are similar. each possessing absorption at 6.24 μ characteristic of the double bond in the chlorobicycloheptenes. No attempt was made to prove the structures but it would appear reasonable to assume that these are *exo, endo* isomers.

(9) For example, 2,3-dimethylenebicyclo[2.2.1]heptane readily undergoes a Diels–Alder addition with maleic anhydride at 0° (W. J. Bailey and W. B. Lawson, THIS JOURNAL, **77**, 1606 (1955)); 1,2-dimethylenecyclopentane adds benzoquinone in refluxing benzene (W. J. Bailey and W. R. Sorenson, *ibid.*, **76**, 5421 (1954)); 1,2-dimethylenecyclohexane undergoes Diels–Alder addition spontaneously with diethyl acetylenedicarboxylate (W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953)).

(10) A. T. Blomquist and co-workers have added 1,2-dimethylenecyclobutane to maleic anhydride (*ibid.*, **77**, 1806 (1955)).

(11) J. D. Idol, C. W. Roberts and E. T. McBee, *J. Org. Chem.*, **20**, 1743 (1955).

(12) For example, 1,2-dimethylenecyclohexane has an ϵ_{max} at 220 mμ (W. J. Bailey, *et al.*, THIS JOURNAL, **75**, 4780 (1953)) and 2,3-dimethylenebicyclo[2.2.1]heptane possesses an ϵ_{max} at 248 mμ (*ibid.*, **77**, 1606 (1955)).

(13) W. J. Bailey, *et al.*, *ibid.*, **76**, 5418 (1954).

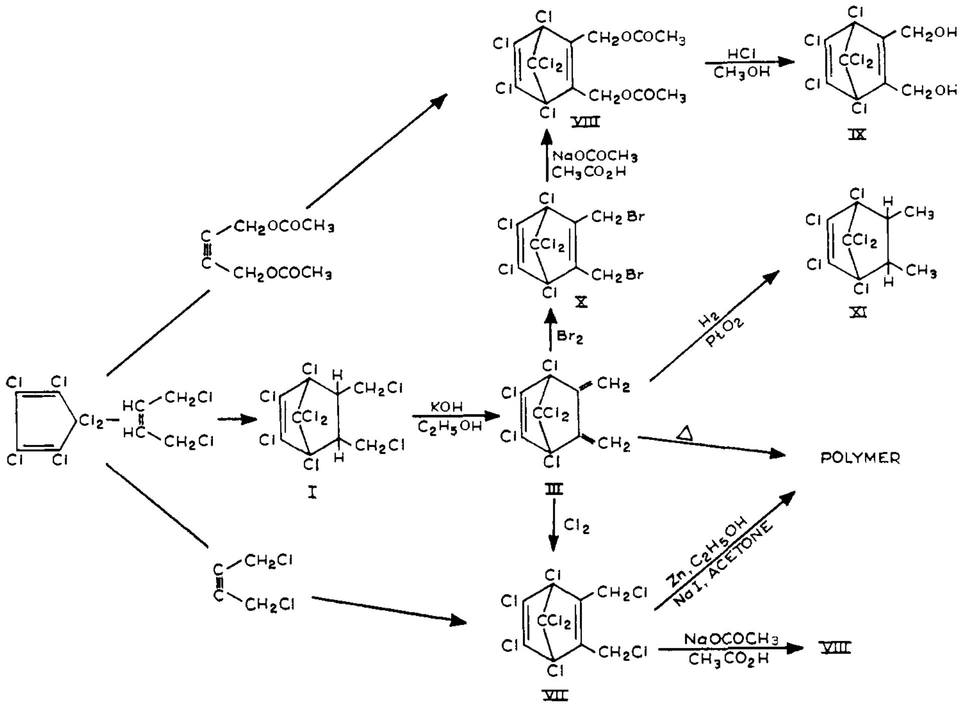

Fig. 2.

Experimental[14]

Preparation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(chloromethyl)-bicyclo[2.2.1]heptene-5 (VII).[15]—A solution of 553 g. (4.4 moles) of butene dichloride[16] (1.7% 3,4-dichlorobutene-1, 88% *cis* 1,4-dichlorobutene-2 and 6.8% *trans* 1,4-dichlorobutene-2 plus unknown impurities) and 1208 g. (4.47 moles) of hexachlorocyclopentadiene were stirred and brought to reflux. After approximately 11 hr. the pot temperature had risen to 165°. The reaction was continued for a total of 24–25 hr. at which time there was very little reflux and the pot temperature was 179°. The dark brown reaction mixture was distilled through a modified Claisen head under reduced pressure. A forerun of butene chlorides was collected weighing 100 g. (b.p. 45–75° (10 m.)). After removal of a hexachlorocyclopentadiene fraction (172 g., b.p. 85–97° (3.5 mm.)), the main fraction distilled (b.p. 150–167° (3 mm.)). The crude product, weighing 1409 g., consisted of solid and liquid products. It was treated with refluxing ethanol containing a small amount of methylene chloride to effect complete solution. After recrystallization and decolorization the product isolated weighed approximately 1000 g., m.p. 100–101°. The combined filtrates upon evaporation gave 200 g. of oil from which more solid crystallized on standing. The infrared spectrum of the oil was identical with that of the product obtained from the 3,4-dichlorobutene-1 adduct.

Anal. Calcd for $C_9H_6Cl_8$ (solid): Cl, 71.35. Found: Cl, 71.6.

The forerun of butene chlorides in the distillation above was submitted to a vapor phase chromatographic analysis. It analyzed approximately as follows: 41% *cis*, 41.5% *trans*-1,4-dichlorobutene-2 and 7.8% 3,4-dichlorobutene-1. This indicates a considerable amount of rearrangement during the reaction.

Preparation of 1,4,5,6,7,7-Hexachloro-2-(1,2-dichloroethyl)-bicyclo[2.2.1]heptene-5 (II).—A flask was charged with 125 g. (1.0 mole) of 3,4-dichlorobutene-1, 273 g. (1.0 mole) of hexachlorocyclopentadiene and 200 g. of *o*-dichlorobenzene. The solution was heated with stirring to the reflux point (161°) for 12 hr. The reaction mixture was distilled under diminished pressure through a 6″ Vigreux column. After removal of solvent and a forerun of butene chloride and hexachlorocyclopentadiene, the main fraction was collected, b.p. 140–144° (0.1 mm.), 233 g. (58.5%), n^{25}_D 1.5770, d^{25}_4 1.680.

Anal. Calcd. for $C_9H_6Cl_8$: Cl, 71.4. Found: Cl, 71.2.

Preparation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(methylene)-bicyclo[2.2.1]heptene-5 (III).—A solution of alcoholic potassium hydroxide was prepared from 370 g. (5.6 moles) of potassium hydroxide (85%) and 2.5 l. of ethanol (anhydrous). Picric acid (3 g.) was added as a free radical inhibitor, and the solution was stirred and heated to 45–50°. Into this solution was added portionwise 1005 g. (2.52 moles) of compound II during 35 min. The reaction was exothermic, and the temperature was permitted to rise to 75–82° during the addition. After addition was complete, the suspension was stirred for 2.5 hr. at 65–72, cooled and filtered. The filtrate was submitted to a vacuum stripping to remove two-thirds of the alcohol. A crystalline tan solid was collected weighing 813 g. The air-dried crude solid was recrystallized with decolorization from ethanol to give 460 g. (56%) of product, m.p. 85–86° (with polymerization).

Anal. Calcd. for $C_9H_4Cl_6$: Cl, 65.4. Found: Cl, 65.3.

Hydrogenation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(methylene)-bicyclo[2.2.1]heptene-5.—A mixture of 16.2 g. (0.05 mole) of the diene III, 50 ml. of absolute ethanol and 0.2 g. of PtO_2/carbon catalyst was placed in a Parr apparatus at 28 lb. gauge pressure of hydrogen. Reduction occurred rapidly within 15 min., two moles of hydrogen was absorbed and no further reduction appeared to take place. The reaction mixture was filtered, the alcohol removed under reduced pressure and the crystalline residue recrystallized from methanol to give 10 g. (61%) of colorless needles, m.p. 92–93°.

Anal. Calcd. for $C_9H_8Cl_6$: Cl, 64.7. Found: Cl, 65.0.

Bromination of 1,4,5,6,7,7-Hexachloro-2,3-bis-(methylene)-bicyclo[2.2.1]heptene-5.—A solution of 6 g. (0.02 mole) of the diene III in 20 ml. of carbon tetrachloride was treated with 2.96 g. (0.02 mole) of bromine at 25°. After several seconds of shaking an exothermic reaction took place

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(14) The chlorine analyses were carried out in the Hooker Laboratories under the supervision of R. H. Kimball. The authors are also indebted to L. E. Tufts and A. Davis of the Hooker Laboratories for aid in interpreting the infrared and ultraviolet spectra. Infrared spectra were run on a Beckman model IR-4 and the ultraviolet spectra on a Cary model 14 in methanol. Melting points are uncorrected.

(15) A preparation for this compound appears in a German patent (ref. 8), which reports a higher melting point for the solid adduct (104–106°), and which implies that the liquid products are stereoisomers.

(16) Prepared by a procedure outlined by W. Reppe, *et al.*, *Ann.*, **596**, 1 (1955).

and the bromine color disappeared in 2–3 min. The solvent was allowed to evaporate and a light yellow crystalline solid was obtained; recrystallization of this from methanol with Norite decolorization gave 6 g. (67%) of product, m.p. 124.5–125°.

Anal. Calcd. for $C_9H_4Cl_6Br_2$: Cl, 43.89; Br, 32.9. Found: Cl, 44.10; Br, 32.75.

Reaction of 1,4,5,6,7,7-Hexachloro-2,3-bis-(bromomethyl)-bicyclo[2.2.1]heptadiene-2,5 (X) with Sodium Acetate and Acetic Acid.—A solution of 8 g. (0.016 mole) of compound X in glacial acetic acid (50 ml.) was treated with 2.7 g. (0.033 mole) of anhydrous sodium acetate. The solution was stirred at reflux for 2 hr. then poured into water. A dark semi-solid was isolated. It was saturated with water and taken up in hot *n*-hexane; the hexane solution was dried over anhydrous magnesium sulfate and after removing the drying agent the hexane solution was cooled to −10°. A crystalline solid separated that melted at 48–51°. A sample, m.p. 54–55°, was obtained by recrystallization from hexane. A mixed m.p. with a known sample of the diacetate showed no depression. The infrared spectra of this material and the known diacetate were identical.

Addition of Chlorine to 1,4,5,6,7,7-Hexachloro-2,3-bis-(methylene)-bicyclo[2.2.1]heptene-5.—A solution of 6 g. (0.018 mole) of III in 20 ml. of carbon tetrachloride in a test-tube was cooled and 1.4 g. (0.019 mole) of chlorine gas was added. The contents of the test-tube were permitted to rise to 40° with vigorous shaking. The tube was irradiated with ultraviolet light from a General Electric H 100-A4 lamp placed at 6-8″. After 5 min. the chlorine color disappeared. The carbon tetrachloride was permitted to evaporate and the solid recrystallized from methanol, m.p. 106–107°. A mixed melting point of this material with the product obtained from the adduct of 1,4-dichlorobutyne-2 and hexachlorocyclopentadiene showed no depression. The infrared spectra of both materials were identical.

Preparation of 1,4,5,6,7,7-Hexachloro-2-ethynylbicyclo-[2.2.1]heptene-5 (IV).—A solution of 84.6 g. (0.51 mole) of potassium hydroxide (85%) in 200 ml. of ethanol was warmed with stirring to 55°; to this was added 79.8 g. (0.20 mole) of the liquid dichloride compound II during 35 min. The reaction was exothermic; the temperature was permitted to rise to 55–60°. The dark suspension was stirred an additional 1.5 hr. and then poured into 1 l. of water. The organic material was extracted with methylene chloride. The organic layer was washed with water several times and dried over anhydrous magnesium sulfate. The drying agent was filtered and the solvent removed under diminished pressure. The residual oil was distilled through a 3″ Vigreux column, b.p. 103–106° (1.5 mm.), to give 35.8 g. (55%) of product, $n^{26.5}_{D}$ 1.574, d^{25}_{4} 1.584.

Anal. Calcd. for $C_9H_4Cl_6$: Cl, 65.48. Found: Cl, 65.9.

Hydrogenation of 1,4,5,6,7,7-Hexachloro-2-ethynylbicyclo-[2.2.1]heptene-5.—Compound IV (16 g., 0.049 mole) was subjected to a hydrogenation in a conventional Parr hydrogenator using Adams catalyst at 39 lb. of hydrogen starting pressure. Reduction was very rapid; two moles of hydrogen was absorbed during 10 min. No further reduction occurred. The catalyst was removed by filtration; the alcohol was distilled under reduced pressure, and the residual oil was subjected to a micro-distillation through a 2″ Vigreux column. The distillate was a colorless oil of pleasant camphor-like odor, b.p. 86–87° (0.5 mm.), n^{27}_{D} 1.5408, wt. 10 g. (62%). Its infrared spectra were identical with that of the product obtained below from the Diels–Alder adduct of 1-butene and hexachlorocyclopentadiene.

Anal. Calcd. for $C_9H_8Cl_6$: Cl, 64.8. Found: Cl, 64.3.

Preparation of 1,4,5,6,7,7-Hexachloro-2-vinylbicyclo-[2.2.1]heptene-5 (V).[17]—Hexachlorocyclopentadiene (273 g., 1.0 mole) was stirred and warmed to 175°. Into this liquid was introduced at 1 g./min. a stream of 1,3-butadiene for 2.5 hr. At this point the reaction mixture was cooled. A solid formed during the addition was filtered from the solution. The filtrate was subjected to a distillation under reduced pressure to give 27 g. of crude product; this was redistilled through a 6″ Vigreux column to give 15 g. (4.6%) product, b.p. 116–117° (1.5 mm.), n^{25}_{D} 1.5521. It was the monoadduct of one mole of butadiene and one mole of hexachlorocyclopentadiene. The solid isolated is the adduct of two moles of hexachlorocyclopentadiene with one mole of butadiene. It was recrystallized from toluene, m.p. 238–240°.

Anal. Calcd. for $C_9H_6Cl_6$ (liquid): Cl, 65.2. Found: Cl., 65.4. Calcd. for $C_{14}H_6Cl_{12}$ (solid): Cl, 71.1. Found: Cl, 71.2.

Chlorination of 1,4,5,6,7,7-Hexachloro-2-vinylbicyclo[2.-2.1]heptene-5 (Compound IV).—The liquid monoadduct of butadiene and hexachlorocyclopentadiene (16.35 g., 0.05 mole) was chlorinated at 35–40° in the presence of ultraviolet irradiation supplied by a General Electric H-I lamp. The reaction was exothermic and the theoretical amount of chlorine was absorbed. The product was fractionated at diminished pressure through a 6″ Vigreux column, b.p. 140–145° (0.1 mm.). A sample submitted to infrared analysis indicated it to be identical with compound II.

Preparation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(acetoxymethyl)-bicyclo[2.2.1]heptadiene-2,5 (VIII).[18]—To 430 g. (2.54 moles) of well stirred 1,4-diacetoxybutyne-2[16] containing 11 g. of epichlorohydrin heated to 160° was added dropwise 694 g. (2.54 mole) of hexachlorocyclopentadiene during 12 hr. at an internal temperature of 167°. The dark reaction mixture was stirred at 165–167° for 2 hr. after addition was complete, and contents of the flask were submitted to a vacuum distillation. After removal of a forerun of hexachlorocyclopentadiene and the diacetates, 98–120° (2 mm.) (306 g.), the main product, 614 g. (54%), was distilled using a modified Claisen flask, b.p. 193–198° (2 mm.). The product crystallized on standing and was recrystallized from hexane, m.p. 54-55°.

Anal. Calcd. for $C_{13}H_{10}Cl_6O_4$: Cl, 48.08. Found: Cl, 48.12.

Preparation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(chloromethyl)-bicyclo[2.2.1]heptadiene-2,5 (VII).—A solution containing 369 g. (3 moles) of 1,4-dichlorobutyne-2[19] and 819 g. (3 moles) of hexachlorocyclopentadiene with 250 ml. of *o*-dichlorobenzene was stirred and heated to 140–150° for a total of 72 hr. The mixture was cooled and treated with 200 ml. of *n*-hexane. A crystalline product formed weighing, after drying in air, 583 g. (49%). The filtrate was evaporated to one-half its volume and another 198 g. of solid was obtained; total yield 66%. A small amount of the solid was recrystallized and decolorized several times from methanol to give a solid, m.p. 106–107°.

Anal. Calcd. for $C_9H_4Cl_8$: Cl, 71.7. Found: Cl, 71.4.

Preparation of 1,4,5,6,7,-Hexachloro-2,3-bis-(acetoxymethyl)-bicyclo[2.2.1]heptadiene-2,5 (VIII).—The proceurde used was identical with that used in treating the dibromo compound (X) above. A yield of 79.6% was realized. The melting point and the infrared spectrum of the product were identical with those of the product from the Diels–Alder reaction of 1,4-diacetoxybutyne-2 and hexachlorocyclopentadiene.

Preparation of 1,4,5,6,7,7-Hexachloro-2,3-bis-(hydroxymethyl)-bicyclo[2.2.1]heptadiene-2,5 (IX).—A solution containing 103 g. (0.24 mole) of 1,4,5,6,7,7-hexachloro-2,3-bis-(acetoxymethyl)-bicyclo[2.2.1]heptadiene-2,5, 300 ml. of methanol and 15 ml. of concentrated hydrochloric acid was stirred at reflux for 40 hr. The methanol was distilled under vacuum, and the solid residue recrystallized from chlorobenzene after treatment with activated charcoal. The product, a white solid, (dense prisms) weighed 56.4 g. (75%), m.p. 155–156°.

Anal. Calcd. for $C_9H_6Cl_6O_2$: Cl, 59.3. Found: Cl, 59.1.

Preparation of 1,4,5,6,7,7-Hexachloro-2-ethylbicyclo-[2.2.1]heptene-5 (VI).—Into 273 g. (1 mole) of hexachloro-

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(17) The Diels–Alder addition products of butadiene and hexachlorocyclopentadiene are mentioned in a British Patent 614,931 (Dec. 20, 1948). The reactions were carried out in sealed tubes. No physical data are given for the monoadduct. A melting point of 230–233° is reported for the bis-adduct.

(18) The preparation of this diacetate and the corresponding diol are described in a German patent application F 14487 IVb/120 (1956). We found the reaction somewhat prone to tar formation and unpredictable. Several different procedures were attempted before any product was obtained. The purity of the 1,4-diacetoxybutyne-2 is critical. The addition of epichlorohydrin as a hydrogen chloride scavenger appeared to reduce tar formation. The melting point of the diacetate adduct in the patent is 56°, and that of the diol 155–156°.

(19) Prepared by procedure described by A. Johnson, *J. Chem. Soc.*, 1009 (1946).

cyclopentadiene heated with good stirring to 170° gaseous 1-butene (Mathieson) was passed for a total of 10 hr. at approximately 1–2 g./min. At the end of this time the contents of the flask distilled; a forerun of (232 g.) hexachlorocyclopentadiene, b.p. 94–97° (2.5 mm.), was obtained, and the product, b.p. 129–130° (5. mm.), was a colorless oil, 68 g. (21%), n^{24}_D 1.5409, d^{25}_4 1.522. The infrared spectrum of this compound was identical with that of the compound obtained by reduction of IV.

Reaction of 2-Butene with Hexachlorocyclopentadiene.—Into 273 g. (1 mole) of hexachlorocyclopentadiene stirred and warmed to 160–170° was passed a stream of normal butenes (Phillips Petroleum butene-2, vapor phase chromatographic analysis indicated 47% *trans*- and 51% *cis*-butene-2) for 14 hr.; a weight gain of approximately 30 g. was realized in this time. The reaction mixture was submitted to a vacuum distillation to give recovered hexachlorocyclopentadiene, b.p. 125–158° (15–18 mm.), and a solid residue. This was treated with hot methanol; part of the solid was not soluble in methanol and was recrystallized from toluene. The methanol-soluble material melted at 200–202°.

Anal. Calcd. for $C_9H_8Cl_6$: Cl, 64.7. Found: Cl, 65.0.

The toluene-soluble material, m.p. 238–241°, was identified as the bis-adduct of butadiene and hexachlorocyclopentadiene compound by infrared analysis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Bridged Polycyclic Compounds. IX. 3-Phenylbicyclo[2,2,1]-hepta-2,5-diene-2-carboxylic Acid[1,2]

BY STANLEY J. CRISTOL AND ROBERT T. LALONDE

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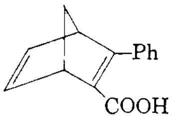
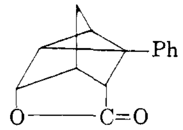
Cyclopentadiene and phenylpropiolic acid reacted in a steel autoclave at 120° to give a substance which was not the anticipated 3-phenylbicyclo(2,2,1)hepta-2,5-diene-2-carboxylic acid (I) but instead was the γ-lactone of 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-carboxylic acid (II). The same reactants at 185° in glass again failed to give the desired diene. However phenylpropiolyl chloride and methyl phenylpropiolate reacted with cyclopentadiene to give Diels–Alder products which when hydrolyzed gave I. Isomerization of I with a strong acid gave II.

In earlier publications[3] the photoisomerization of bicyclo(2,2,1)hepta-2,5-diene-2,3-dicarboxylic acid to quadricyclo(2,2,1,$0^{2,6}$,$0^{3,5}$)heptane - 2,3-dicarboxylic acid was described. As part of a program in the study of this photoisomerization of derivatives of bicyclo(2,2,1)hepta-2,5-diene, we wished to prepare 3-phenylbicyclo(2,2,1)hepta-2,5-diene-2-carboxylic acid (I).



I



II

An attempt to prepare I by a Diels–Alder reaction in a steel autoclave at about 120° from cyclopentadiene and phenylpropiolic acid gave a solid which had a satisfactory analysis and neutralization equivalent but did not decolorize either bromine in carbon tetrachloride or an aqueous solution of potassium permanganate. These negative unsaturation tests demonstrated that this material was not the desired product.

The γ-lactone of 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)-heptane-*endo*-3-carboxylic acid (II) has the same empirical formula as I. Evidence from the infrared absorption spectrum suggested, by analogy, that the structure of this solid was that of the nortricyclenic γ-lactone.[3-8]

Treatment of the solid with phenylhydrazine gave a phenylhydrazide. The infrared absorption spectrum of this phenylhydrazide exhibited the characteristic nortricyclenic absorption[4-6] and the characteristic absorption[9] of the amide carbonyl. This phenylhydrazide reacted readily with acetyl chloride, and is undoubtedly 2-phenyl-*endo*-5-hydroxytricyclo(2,2,1,$0^{2,6}$)heptane-*endo*-3-N-phenylcarboxhydrazide.

The data given above are consistent with the formulation of the product as the γ-lactone II, and this was confirmed when II was prepared from I.

In another attempt to prepare I, phenylpropiolic acid and cyclopentadiene, in benzene solution, were heated in a sealed glass tube at 185°. This led to products (not I) that were not identified.

Phenylpropiolyl chloride and methyl phenylpropiolate reacted with cyclopentadiene to give Diels–Alder products. These were not isolated in a pure form. However, subsequent hydrolysis of the reaction products gave I, m.p. 136°. This acid readily decolorized an aqueous solution of potassium permanganate and had a satisfactory analysis and neutralization equivalent weight.

In the infrared absorption spectrum were found broad bands characteristic of the carbon–oxygen and carbon–carbon double bonds.[10] The presence of the absorption bands at 6.39 and 14.2μ is good evidence for the presence of the norbornene ring.[11]

The ultraviolet absorption spectrum of the 136° acid in ethanol showed an absorption maximum at

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[1] Previous paper in series: S. J. Cristol and R. T. LaLonde, THIS JOURNAL, **81**, 1655 (1959).

[2] This paper was presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

[3] (a) S. J. Cristol and R. L. Snell, THIS JOURNAL, **76**, 5000 (1954); (b) **80**, 1950 (1958).

[4] (a) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950); (b) E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

[5] C. D. Ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

[6] S. J. Cristol and R. T. LaLonde, *ibid.*, **80**, 4355 (1958).

[7] J. A. Berson, *ibid.*, **76**, 4975 (1954).

[8] P. Wilder, Jr., and A. Winston, *ibid.*, **77**, 5598 (1955).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 180.

[10] L. J. Bellamy, *ibid.*, p. 111.

[11] P. R. Schleyer, THIS JOURNAL, **80**, 1700 (1958).