$[\alpha]^{25}$D +14.55°, 15.1% optical purity, prepared by dilution of bromide with $[\alpha[^{25}$D +72.5°), NBS (1.50 g., dried over phosphorus pentoxide at 20° (15 mm.) for 5 days) and carbon tetrachloride (7.0 ml., distilled from phosphorus pentoxide) were heated under reflux for 25 min. The mixture was cooled in an ice-bath, filtered, the carbon tetrachloride removed under reduced pressure, and the residue distilled to give (+)-phenylmethylcarbinyl bromide (0.61 g., α^{25}D +19.44° (1 dm., neat) or $[\alpha]^{25}$D +14.31°, 14.8% optical purity) with less than 2% racemization.

(B). (+)-Phenylmethylcarbinyl bromide (0.61 g., 0.0033 mole, α^{25}D +19.44° (1 dm., neat), $[\alpha]^{25}$D +14.31°, 14.8% optical purity), NBS (1.81 g., 0.010 mole, dried as in A), ethylbenzene (1.17 g., 0.011 mole), benzoyl peroxide (0.024 g., 0.0001 mole) and carbon tetrachloride (65 ml., dried as in A) were heated under reflux until reaction was complete (35–45 min.). The mixture was cooled, filtered, the carbon tetrachloride removed under reduced pressure, and the residue distilled to give (+)-phenylmethylcarbinyl bromide (1.37 g., b.p. 90–91° (19 mm.), n^{25}D 1.5580, α^{25}D +6.10° (1 dm., neat) or $[\alpha]^{25}$D +4.49°, 4.66% optical purity). From the amount of bromide isolated and its optical rotation the limits of a maximum of 72% benzylic substitution with no racemization or a minimum of 41% substitution with 30% racemization were estimated as follows: amount of bromide formed in the reaction = 1.37 − 0.61 = 0.76 g. or 41% yield (lower limit); maximum possible rotation for isolated bromide = 19.44 (0.61/1.37) = 8.65°; amount of racemization = [(8.65 − 6.10)/8.65] 100 = 30% (lower limit); assume no racemization and let x = amount of bromide formed in the reaction, then from 19.44 [0.61/(0.61 − x)] = 6.10, x = 1.33 g. or 72% yield (upper limit).

Bromination of (−)-α-Deuterioethylbenzene by NBS.—(−)-α-Deuterioethylbenzene (9.00 g., 0.084 mole, α^{23}D −0.51° (2 dm., neat), $[\alpha]^{23}$D −0.293° (1 dm., neat)), NBS (13.9 g., 0.077 mole based on 98.5% active bromine, dried over phosphorus pentoxide at 20° (15 mm.) for 5 days), benzoyl peroxide (0.19 g., 0.00077 mole) and carbon tetrachloride (50 ml., distilled from phosphorus pentoxide) were heated under reflux until the bromination reaction was complete (<10 min.). The mixture was cooled, filtered, and carbon tetrachloride removed under reduced pressure from the filtrate. Distillation of the residue gave the following fractions: (1) 0.13 g., b.p. to 91° (16 mm.), n^{25}D 1.5530; (2) 3.88 g., b.p. 91–92° (16 mm.), n^{25}D 1.5582, α^{24}D −0.07 ± 0.02° (2 dm., neat); (3) 4.57 g., b.p. 92° (16 mm.), n^{25}D 1.5591, α^{24}D −0.07 ± 0.03° (2 dm., neat); (4) 3.24 g., b.p. 92–91° (16 mm.), n^{25}D 1.5596, α^{24}D − 0.02 ± 0.03° (2 dm., neat); yield of bromo product (fractions 2–4) 11.69 g. (82.0% yield); weighted average for same fractions, α^{24}D −0.056 ± 0.026° (2 dm., neat) or using $d^{24}{}_4$ 1.3677 (includes correction of +0.0084 for the deuterium content, assumed same as that for introduction of α-deuterium into ethylbenzene), $[\alpha]^{24}$D −0.020 ± 0.01° (1 dm., neat). The isotope effect, k_H/k_D, for the reaction of NBS with this sample of α-deuterioethylbenzene in refluxing carbon tetrachloride with benzoyl peroxide or ultraviolet light initiation was 2.67 ± 0.04.[22,23] With the reasonable assumption that phenylmethylcarbinyl bromide and its α-deuterio analog have the same specific rotations ($[\alpha]^{20}$D 96.4°), it follows that substitution for hydrogen and for deuterium on (−)-α-deuterioethylbenzene will give enantiomorphic bromide products. Then, using k_H/k_D = 2.67, the maximum specific rotations of the bromide products from the reaction of NBS with this sample of α-deuterioethylbenzene (41.6% optical purity) would be given by

$$[\alpha]^{24}\text{D (max.)} = (0.416)(96.4)\left[\pm\frac{2.67}{2.67-1.00}\pm\frac{1.00}{2.67-1.00}\right] = \pm 18.3^\circ$$

or −18.3° for complete retention, and +18.3° for complete inversion. Therefore, the bromide product obtained was no more than 0.11% optically pure, and the NBS reaction has occurred with at least 100 − (0.11/41.6) = 99.7% racemization.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. VII. Diels–Alder Adducts of Benzocyclobutadiene

BY M. P. CAVA AND M. J. MITCHELL

RECEIVED APRIL 14, 1959

Adducts of benzocyclobutadiene with two dienes, cyclopentadiene and furan, have been obtained. The structure of the cyclopentadiene adduct, as reported independently by Nenitzescu, has been confirmed by additional transformations. The reaction of benzocyclobutadiene with a typical dienophile, N-phenylmaleimide, has been achieved: a derivative of 1,2-dihydronaphthalene is formed.

Reactions which would be expected to generate benzocyclobutadiene (I)[1–3] produce, instead of the monomer I, the crystalline dimer II, shown[1,2] to be 6a,10a-dihydrobenzo[*a*]biphenylene. The formation of II from two moles of benzocyclobutadiene has been envisaged[2] in its primary stage as a Diels–Alder reaction in which benzocyclobutadiene acts as both diene and dienophile. The results of some attempts to trap the elusive benzocyclobutadiene by reaction with other dienes and dienophiles are now reported.

During the course of this investigation, a report[4] appeared describing the trapping of benzocyclobutadiene[5] by an active diene, cyclopentadiene. A liquid hydrocarbon, $C_{13}H_{12}$, was obtained which formed a crystalline phenyl azide adduct and which absorbed only *one* mole of hydrogen in the presence of a palladium catalyst.[6] Largely on this basis the adduct was assigned structure III. The less likely structure IV, which might be expected if the cyclopentadiene had acted as a dienophile instead of a diene, was not compatible with the hydrogenation data.

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[1] M. P. Cava and D. R. Napier, THIS JOURNAL, **78**, 500 (1956).

[2] M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957).

[3] M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

[4] C. D. Nenitzescu, M. Avram and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957).

[5] The benzocyclobutadiene was generated from 1,2-dibromobenzocyclobutene and lithium amalgam in ether. For a recent report on the preparation of the *linear* dimer of benzocyclobutadiene, 3:4–7:8-dibenzo-tricyclo[4.2.0.0^{2,5}]octadiene, see M. Avram, D. Dinu and C. D. Nenitzescu, *Chemistry & Industry*, 257 (1959).

[6] Reference 4, p. 2542: "Die katalytische Hydrierung zwecks Feststellung der Zahl der Doppelbindungen kam nach Aufnahme von *einem* Mol. Wasserstoff zum Stillstand" (italics supplied).

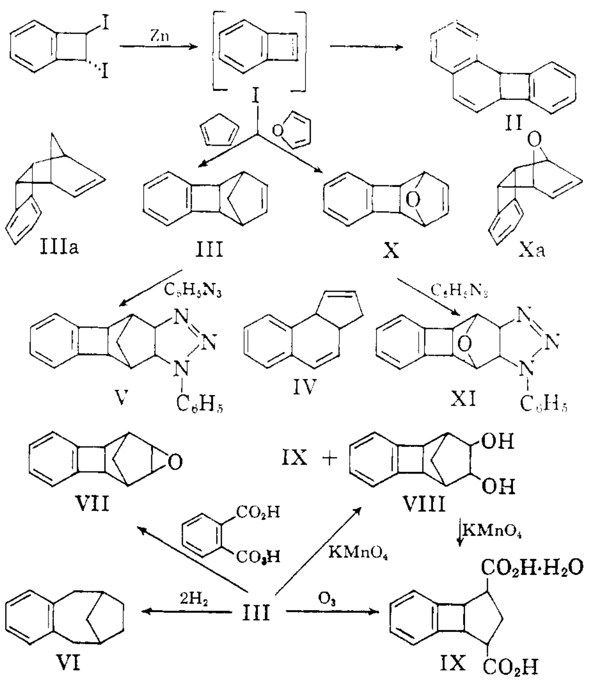
In our investigation, benzocyclobutadiene generated from 1,2-diiodobenzocyclobutene and zinc in ethanol was readily trapped by cyclopentadiene to give a hydrocarbon (III), $C_{13}H_{12}$, m.p. 7–8°, in 65% yield. This substance formed a phenyl azide adduct (V), m.p. 132–133°, identical with the derivative obtained by the Romanians.[4] However, hydrogenation of our hydrocarbon III resulted in the uptake of *two* moles of hydrogen and gave a homogeneous tetrahydro derivative (VI), $C_{13}H_{16}$. On the other hand, III reacted with only *one* mole of monoperphthalic acid to give a crystalline monoepoxide (VII), $C_{13}H_{12}O$. Oxidation of III by potassium permanganate gave, in addition to a diol (VIII), a saturated dicarboxylic acid (IX), $C_{13}H_{12}O_4$. This same acid IX was also obtained by ozonolysis of III, and by further oxidation of diol VIII. These oxidation results are compatible with structure III, but not with structure IV. Consequently, the unusual hydrogenation behavior of III must be attributed to a hydrogenolysis of the cyclobutane ring which is probably exceptionally strained in III by the fused bicyclo[2,2,1]heptene ring system.

It has been reported[4] that benzocyclobutadiene can be trapped by furan, but that the resulting crude adduct, m.p. 155–160°, is polymerized rapidly to amorphous and insoluble products. Our own investigation of this reaction in ethanolic medium led to quite different results. In a rather extensive series of experiments in which benzocyclobutadiene was generated in ethanol at various temperatures and concentrations in the presence of a large excess of furan, the major product isolated was always benzocyclobutadiene dimer II. Apparently, benzocyclobutadiene is far more prone to dimerize than to attack furan. This is understandable, since furan is certainly a much less reactive diene than is cyclopentadiene. Under optimum conditions, however, a *stable* adduct (X) of benzocyclobutadiene and furan, m.p. 58.5–59°, can be isolated in about 5% yield. This substance readily adds phenyl azide to give the triazole derivative XI, m.p. 188–190°, analogous to the phenyl azide derivative V of adduct III.

Butadiene appears to be even less effective than furan as a trapping agent for benzocyclobutadiene, and we could isolate only benzocyclobutadiene dimer under the conditions employed successfully with cyclopentadiene or furan in ethanol. Similar negative results with butadiene in ethereal solution have been reported by the Romanian group.[4]

No rigorous proof of the stereochemistry of the adducts III and X is available at this time. However, the usual rule of maximum accumulation of double bonds[7] should be operative, suggesting the *endo* structures IIIa and Xa for the adducts III and X, respectively.

In an attempt to observe a reaction in which benzocyclobutadiene would behave as a diene rather than as a dienophile in the Diels–Alder reaction, benzocyclobutadiene was generated in alcoholic solution in the presence of N-phenylmaleimide, an active dienophile. Rather surprisingly, the major product isolated was benzocyclobutadiene dimer II, indicating that I is relatively unreactive as a diene. There was produced, however, in 5% yield an adduct (XII) of benzocyclobutadiene and N-phenylmaleimide, m.p. 137–138°. If the adduct XII is formed by a process mechanistically similar to that proposed[2] for the formation of dimer II, it should have the structure of N-phenyl-1,2-dihydro-*cis*-1,2-naphthalimide. The ultraviolet absorption spectrum of XII is consistent with this formulation, being essentially identical with the addition curve of the spectra of 1,2-dihydronaphthalene and N-phenylsuccinimide. Furthermore, XII was dehydrogenated readily to give the fully aromatic compound N-phenyl-1,2-naphthalimide (XIII), identical with comparison material synthesized from 1,2-naphthalic acid and aniline. Indeed, a small amount of the aromatic imide XIII was subsequently isolated from the original Diels–Alder reaction mixture. Its exact mode of formation is uncertain, but it undoubtedly arises from XII by an oxidation–reduction process, probably involving N-phenylmaleimide.



Finally, in the hope of obtaining the adduct XII under somewhat different conditions, N-phenylmaleimide and *cis*-1,2-diiodobenzocyclobutene[8,9] were melted together at 190°. It was expected that at this temperature the *cis*-diiodide might lose iodine readily to form benzocyclobutadiene which would then be trapped by the imide to give adduct XII. Subsequently, XII could be dehydrogenated by the liberated iodine to form N-phenyl-1,2-naphthalimide (XIII). A vigorous reaction was in fact observed at 190°, but the only reaction product isolated was not XII or XIII, but rather N-phenyl-2,3-naphthalimide (XIV), which was obtained in

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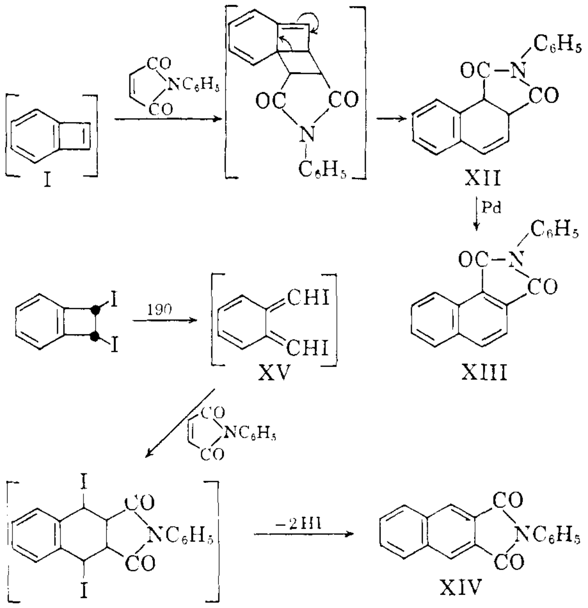
[7] K. Alder, *et al.*, *Ann.*, **514**, 1 (1934); R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[8] F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 869 (1958).

[9] This substance was originally isolated by us, but was erroneously assigned the composition of a "triiodide," $C_{16}H_{12}BrI_3$, on the basis of an analysis of a sample of material which contained 1,2-dibromobenzocyclobutene (*cf.* ref. 2).

reasonably good yield (35%). This product probably arises by a thermal decomposition of the *cis*-diiodide to give an intermediary quinodimethane (XV) which goes on to react with N-phenylmaleimide and to lose hydrogen iodide to give XIV. This sequence of steps finds very close analogy in the formation of XIV from sodium iodide, N-phenylmaleimide and $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-*o*-xylene.[10]

Further work on the hydrogenation and hydrogenolysis products of hydrocarbon III is now in progress and will be reported in a later paper.



Acknowledgment.—We wish to thank the Research Corporation for a grant supporting this work. We are indebted to Dr. L. T. Capell and to Mr. J. H. Stone of The "Chemical Abstracts" Service for the systematic nomenclature used in the Experimental section, and to Mr. A. A. Deana of this department for several of the ultraviolet determinations.

Experimental[11]

Adduct of Benzocyclobutadiene and Cyclopentadiene (III).—Benzocyclobutadiene was generated *in situ* in the reaction mixture by adding a solution of 17.8 g. (0.050 mole) of *trans*-1,2-diiodobenzocyclobutene[2,8] in 300 ml. of ethanol to a stirred suspension of 50 g. of activated zinc dust[12] in 500 ml. of ethanol containing 50 ml. of cyclopentadiene. The temperature of the ethanol suspension was held at 30°, and a slow stream of nitrogen was passed through the reaction flask. When half of the diiodide solution had been added, a further portion (25 ml.) of cyclopentadiene was poured into the flask. When the addition of the diiodide solution was complete (4.5 hr.), the reaction mixture was filtered to remove the excess zinc dust, and the filtrate was concentrated to 100 ml. by vacuum distillation. The residual solution was poured into 150 ml. of water, and the resulting suspension was extracted three times with 100-ml. portions of petroleum ether (Skellysolve F). The extracts were combined, washed once with 50 ml. of water, and dried over sodium sulfate. Distillation of the dried solution gave 5.44 g. (64.9%, based on diiodide) of cyclopentadiene adduct, 1,4,4a,8b-tetrahydro-1,4-methanocyclobutadibenzene (III), b.p. 68–70° (1–2 mm.), m.p. 7–8°, n^{25} 1.5739; reported[4] b.p. 82–84° (2 mm.), n^{20} 1.57317.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.80; H, 7.19. Found: C, 92.73; H, 7.52.

Epoxide VII.—The cyclopentadiene adduct III (157 mg., 0.935 millimole, m*M*) was dissolved in 10 ml. of 1.6 *N* ethereal monoperphthalic acid solution. After standing for three days at room temperature, the solution was washed with excess saturated aqueous sodium thiosulfate solution, then with water, and finally with 10% aqueous sodium bicarbonate solution. The ether layer was dried over sodium sulfate and evaporated to dryness. The residue was sublimed and resublimed at 89° (1–2 mm.) to give 134 mg. (78%) of 2,3-epoxy-1,2,3,4,4a,8b-hexahydro-1,4-methanocyclobutadibenzene (VII), m.p. 56–57°.

Anal. Calcd. for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.77; H, 6.33.

Phenyl Azide Derivative V.—A solution of 457 mg. (2.72 m*M*) of adduct III and 411 mg. (3.45 m*M*) of phenyl azide in 5 ml. of Skellysolve F, allowed to stand for 6 hr. at room temperature, deposited 348 mg. (44.5%) of phenyl azide derivative V. Recrystallization from 1:10 benzene–Skellysolve F gave the analytical sample as white needles, m.p. 132–133°; reported[4] m.p. 132–133°.

Anal. Calcd. for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.46; H, 5.81; N, 14.48.

Hydrogenation of III.—In a series of quantitative hydrogenations with platinum oxide or palladium–charcoal catalysts at atmospheric pressure, the adduct III was found to absorb one mole of hydrogen rapidly and a second mole more slowly. Under pressure, the adduct readily absorbed two moles of hydrogen. Thus, 3.05 g. (0.018 mole) of adduct III in 25 ml. of glacial acetic acid was hydrogenated for 2 hr. under 33 p.s.i. initial hydrogen pressure in the presence of 100 mg. of 10% palladium–charcoal catalyst. After neutralization of the acetic acid with dilute aqueous sodium hydroxide solution, extraction with petroleum ether, and removal of the organic solvent by fractional distillation, 2.78 g. (89%) of a colorless residual oil was obtained.

Vapor phase chromatography of the oil on a fire-brick column at 160° showed that it contained two components only. The smaller of these was approximately 5% of the total material and showed the same elution time as the starting material III. The other component was the tetrahydro compound VI. The analytical sample of VI, b.p. 65–68° (1–2 mm.), was obtained by treating the residual oil from the hydrogenation of III with dilute aqueous potassium permanganate solution, followed by drying and fractional distillation.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.52; H, 9.14.

Preparation of Diacid IX. A. By Ozonolysis of III.—A solution of 1.168 g. (6.95 m*M*) of the cyclopentadiene adduct III in 10 ml. of ethyl acetate was treated at −30° with a stream of ozone–oxygen gas until ozone was no longer absorbed (*ca.* 0.5 hr.). The reaction mixture was warmed to room temperature, 10 ml. of glacial acetic acid was added, and the ethyl acetate was removed by evaporation under an air jet. The residual solution was warmed on the steam-bath and poured into 10 ml. of water to give, after filtration and drying, 1.303 g. (88%) of amorphous ozonide. The ozonide (500 mg., 2.3 m*M*), 250 mg. of 30% hydrogen peroxide solution and 7 ml. of 91% formic acid were heated together at 110° for 4 hr. The reaction mixture, after standing at room temperature overnight, deposited 147 mg. (26%) of the diacid IX, 2,3,3a,7b-tetrahydro-1*H*-cyclopenta[3,4]-cyclobuta[1,2]benzene-1,3-dicarboxylic acid, as the monohydrate, m.p. 240–241°.

B. **Permanganate Oxidation of III.**—A solution of 5.764 g. (0.0342 mole) of the cyclopentadiene adduct III in 100 ml. of acetone was treated dropwise at room temperature with a solution of 14.8 g. (0.937 mole) of potassium permanganate in 800 ml. of acetone. When all of the permanganate solution had been added (30 min.), the reaction mixture was concentrated to 300 ml. by evaporation and diluted with 300 ml. of aqueous 1% sodium bisulfite. The resulting turbid suspension was acidified to *p*H 2 with dilute sulfuric acid and was extracted ten times with 75-ml. portions of 1:20 ben-

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(10) M. P. Cava, A. A. Deana and K. Muth, THIS JOURNAL, **81**, in press (1959), part VIII of this series.

(11) Melting points are uncorrected. Analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(12) The zinc dust was activated by 10% aqueous ammonium chloride and was subsequently washed six times each with water and ethanol, in that order.

zene–ether. The organic extracts were combined, washed once with 10 ml. of water and dried over sodium sulfate. Evaporation of the solvent *in vacuo* left a solid residue which was shaken with a mixture of 100 ml. of 1% aqueous sodium hydroxide solution and 100 ml. of ether. The aqueous layer was separated and acidified with 18 *N* sulfuric acid, chilled to 0°, and filtered to give the crude diacid IX as the monohydrate. The ether layer was reserved for the recovery of neutral oxidation products (see Diol VIII, below). Recrystallization of the crude diacid from 1:10 tetrahydrofuran-benzene gave the diacid monohydrate (3.13 g., 36%) as fluffy white needles, m.p. 239–240°. The anhydrous acid IX was obtained by drying the monohydrate *in vacuo* for 12 hr. at 100°, or by subliming the monohydrate at 180° (1–2 mm.).

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.20; neut. equiv., 116. Found: C, 67.08; H, 5.47; neut. equiv., 118. Monohydrate: Calcd. for $C_{13}H_{14}O_5$: neut. equiv., 125. Found: neut. equiv., 127.

Diamide of IX.—A solution of 100 mg. (0.4 m*M*) of the diacid IX monohydrate and 250 mg. of phosphorus pentachloride in 15 ml. of anhydrous ether was allowed to stand for four days at room temperature. The solvent and the phosphorus oxychloride produced in the reaction were removed by evaporation *in vacuo,* and the oily acid halide residue was extracted once with 15 ml. of warm Skellysolve B. The extract was added dropwise to 25 ml. of ether through which a steady stream of dry ammonia gas was bubbled. The diamide, obtained by filtration of the reaction mixture, was crystallized once from 1:5 ethanol–water to give in two crops 81 mg. (88%) of 2,3,3a,7b-tetrahydro-1*H*-cyclopenta-[3,4]cyclobuta[1,2]benzene-1,3-dicarboxamide, m.p. 300–305°. The analytical sample was obtained by sublimation of the crude diamide at 300° (755 mm.).

Anal. Calcd. for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.46; H, 6.09; N, 11.92.

Diol VIII.—The acid-free ether layer from the permanganate oxidation of adduct III (see Preparation of Diacid IX, above) was evaporated to dryness *in vacuo* to give a neutral oily residue which was chromatographed on a column of Grade III neutral alumina (2.5 × 10 cm.). The first eluate fraction (400 ml. of benzene) gave a few milligrams of a yellow, pungent oil which was not investigated further. The second eluate fraction (300 ml. of benzene) gave no residue. The third fraction (300 ml. of ether) gave a solid residue which, after crystallization from benzene, afforded 0.418 g. (0.6%, based on adduct III) of diol VIII, 1,2,3,4,4a,8b-hexahydro-1,4-methanocyclobutadibenzene-2,3-diol, m.p. 106–108°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 75.72; H, 7.13.

Diacetate of VIII.—A solution of diol VIII (150 mg., 0.74 m*M*) and a trace of sodium acetate in 2–3 ml. of acetic anhydride was refluxed for 1 hr., then allowed to stand for 5 hr. at room temperature. Water was added dropwise to the reaction mixture over a period of 1.5 hr. until a good crop of crystalline product was obtained. After chilling, the mixture was filtered to give 194 mg. (91%) of the diacetate of VIII as shiny white flakes, m.p. 132–134°, after recrystallization from ethanol–water.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.57; H, 6.18.

Oxidation of Diol VIII.—A solution of diol VIII (28 mg., 0.14 m*M*) in 1 ml. of acetone was treated with an excess of potassium permanganate solution (100 mg. of potassium permanganate in 10 ml. of acetone). After standing at room temperature overnight, the reaction mixture was worked up with aqueous sodium bisulfite, dilute sulfuric acid, and ether (see Preparation of Diacid IX, above) to give 30 mg. (86%) of diacid IX monohydrate, identical in melting point and infrared spectrum with the sample prepared by ozonolysis of III.

Adduct of Benzocyclobutadiene and Furan (X).—A solution of 10 g. (0.0281 mole) of *trans*-1,2-diiodobenzocyclobutene in 300 ml. of ethanol was added dropwise to a stirred suspension of 50 g. of activated zinc dust[12] in 500 ml. of ethanol containing 50 ml. of furan. The temperature of the suspension was kept at 30°, and a slow stream of nitrogen was passed through the reaction flask. When all of the diiodide solution had been added (4 hr.), the reaction mixture was filtered and poured into 2.5 l. of water. The resulting suspension was extracted ten times with 100-ml. portions of Skellysolve F. The extracts were combined, washed once with water, dried over sodium sulfate and evaporated to dryness *in vacuo.* The residue was taken up in a few milliliters of Skellysolve F and chromatographed on a column of ordinary basic Fisher adsorption alumina (2 × 8 cm.). Development of the column with 100 ml. of Skellysolve F gave 1.841 g. (64%, based on diiodide) of benzocyclobutadiene dimer II, m.p. 73–74°, obtained by evaporation of the petroleum ether. Further development of the column with 2:3 benzene–ether afforded an oil which was sublimed and resublimed at 38° (1 mm.) to give 0.266 g. (5.6%) of the furan adduct, 1,4,4a,8b-tetrahydro-1,4-oxidocyclobutadibenzene (X), as moist white crystals, m.p. 51.5–53.5°. Pressing the crystals between filter paper in a hydraulic press at 1200 p.s.i. gave the dry, analytically pure sample, m.p. 58.5–59°.

Anal. Calcd. for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.78; H, 5.98.

Phenyl Azide Derivative XI.—A solution of 45 mg. (0.26 m*M*) of the furan adduct X and 100 mg. (0.84 m*M*) of phenyl azide in 1 ml. of Skellysolve F, allowed to stand for 24 hr., gave 74 mg. (97%) of the phenyl azide derivative XI. Recrystallization from 1:10 benzene–Skellysolve F gave the analytical sample, white needles, m.p. 188.5–190°.

Anal. Calcd. for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.23; N, 14.53. Found: C, 74.76; H, 5.16; N, 14.44.

Adduct of Benzocyclobutadiene and N-Phenylmaleimide (XII).—A solution of 10 g. (0.0281 mole) of *trans*-1,2-diiodobenzocyclobutene in 400 ml. of absolute ethanol was added dropwise under nitrogen to a stirred, refluxing suspension of 50 g. of *unactivated* zinc dust in 500 ml. of absolute ethanol containing 10 g. of N-phenylmaleimide and 1 mg. of hydroquinone. When half of the diiodide solution had been added (8 hr.), an additional 5-g. portion of N-phenylmaleimide was added to the reaction mixture. When all of the diiodide solution had been added (16 hr., total addition time), the reaction mixture was refluxed for an additional hour, then filtered through Celite. The filtrate was concentrated to 250 ml. by distillation *in vacuo,* and then poured into 1 l. of water. Extraction with four 100-ml. portions of 1:20 benzene–ether, followed by drying and evaporation in the usual way, gave a yellow oil which was chromatographed on a column of Grade IV neutral alumina (5 × 20 cm.) to give fractions: (A) 200 ml. of 1:1 benzene–Skellysolve F, the residue of which was 1.36 g. (47.5%) of benzocyclobutadiene dimer II, identical in melting point and infrared spectrum with known material; and (B) and (C), each of 200 ml. of 1:1 benzene–Skellysolve F, the residues of which consisted of a mixture of N-phenyl-2,3-naphthalimide (XIII) and N-phenyl-1,2-dihydro-*cis*-1,2-naphthalimide (XII). Fractional crystallization from 1:5 benzene–Skellysolve F of the combined residues of B and C gave 0.403 g. (5.2%) of adduct XII, m.p. 137–138°, in two crops, and 0.100 g. (1.3%) of the fully aromatic compound, XIII, m.p. 162–163°, in the third crop (see also Dehydrogenation of XII, below). The analytical sample of adduct XII, m.p. 139.5°, was obtained by recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.47; H, 4.70; N, 5.08.

The experimentally determined absorption spectrum of XII ($\lambda_{\max}^{n\text{-hexane}}$ 261 mμ, $\log \epsilon$ 3.94; $\lambda_{\max}^{n\text{-hexane}}$ 272 mμ, $\log \epsilon$ 3.92; $\lambda_{\max}^{n\text{-hexane}}$ 296 mμ, $\log \epsilon$ 2.56) was quite similar to that predicted for this compound. The hypothetical curve was obtained by adding together the absorption curves of 1,2-dihydronaphthalene ($\lambda_{\max}^{n\text{-hexane}}$ 262 mμ, $\log \epsilon$ 4.01; $\lambda_{\text{infl.}}^{n\text{-hexane}}$ 273 mμ; $\lambda_{\max}^{n\text{-hexane}}$ 296 mμ, $\log \epsilon$ 2.68)[13] and N-phenylsuccinimide (no maxima, $\lambda_{\max}^{n\text{-hexane}}$ 262 mμ, $\log \epsilon$ 2.90; $\lambda_{\max}^{n\text{-hexane}}$ 273 mμ, $\log \epsilon$ 1.97).

Dehydrogenation of Adduct XII.—The adduct, N-phenyl-1,2-dihydro-*cis*-1,2-naphthalimide, (66 mg., 0.24 m*M*) was refluxed for 2 hr. in benzene with 175 mg. of 10% palladium–charcoal to give 28 mg. (42%) of the aromatized product, N-phenyl-1,2-naphthalimide (XIII), m.p. 162–163°, identical in melting point and infrared spectrum with the material isolated from the benzocyclobutadiene and N-phenylmaleimide reaction above, and also identical with a sample prepared by independent synthesis from naphthalic acid and aniline. Thus, 1.0 g. (4.8 m*M*) of 1,2-naphthalic acid and 6 ml. of aniline refluxed 20 min. with stirring, the reaction

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(13) R. A. Morton and J. A. de Gouveia, *J. Chem. Soc.*, 916 (1934).

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.

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[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

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RECEIVED JANUARY 13, 1959

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).