the mixture filtered. The organic solution was separated and the aqueous layer extracted with ether. The combined organic solution was dried with anhydrous sodium sulfate and distilled. The remaining brown thick oil was treated in various ways, but none of the desired compound could be isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. XI. Benzo[1,2:4,5]dicyclobutene

BY M. P. CAVA, A. A. DEANA AND K. MUTH

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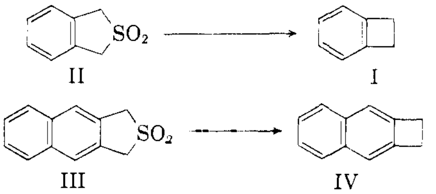
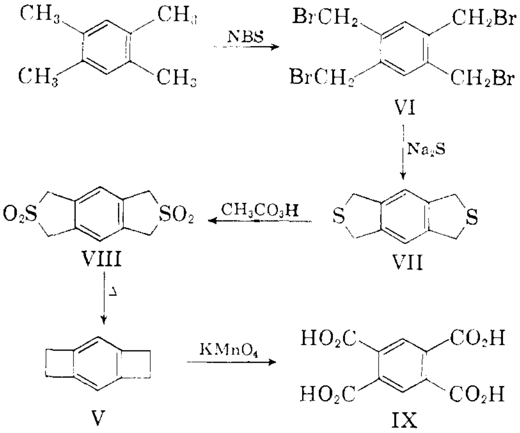
Benzo[1,2:4,5]dicyclobutene (V) has been synthesized from α,α',α'',α'''-tetrabromodurene *via* the intermediary disulfone VIII. The hydrocarbon V is the first example of a system containing more than one cyclobutane ring fused to a single aromatic nucleus.

A novel synthesis of benzocyclobutene (I) consists of the thermal extrusion of sulfur dioxide from the cyclic sulfone 1,3-dihydroisothianaphthene-2,2-dioxide (II).[1] A subsequent application of this reaction was found in the pyrolysis of sulfone III to naphtho[b]cyclobutene (IV).[2] The use of the sulfone pyrolysis method has now been extended to the synthesis of benzo[1,2:4,5]dicyclobutene(V), the first known system containing an aromatic nucleus condensed to two cyclobutane rings.



α,α',α'',α'''-Tetrabromodurene(VI), prepared by treatment of durene with N-bromosuccinimide,[3] reacted with sodium sulfide to give, in 48% yield 1,3,5,7-tetrahydrobenzo[1,2-c:4,5-c']dithiophene(VII), m.p. 213–217°. Peracetic acid oxidation of the disulfide VII afforded the corresponding disulfone, tetrahydrobenzo[1,2-c:4,5-c']dithiophene-2,-2,6,6-tetroxide(VIII). The white crystalline disulfone VIII possessed no definite melting point below 400°, but slowly decomposed to a black powder on strong heating. However, when small samples of the disulfone, diluted with copper powder, were heated at 320° in a low pressure nitrogen atmosphere a volatile hydrocarbon $C_{10}H_{10}$ sublimed out in 20% yield. Passage of the pyrolysate vapors through a Nichrome coil heated to dull red heat[1] increased the yield to 40%. This substance, m.p. 101°, which crystallized in white prisms from methanol, was ascribed the structure benzo[1,2:4,5]dicyclobutene (V). In accord with this formulation, oxidation of V with potassium permanganate yielded pyromellitic acid (IX), isolated as the dianhydride.

A striking manifestation of the extraordinary strain present in benzo[1,2:4,5]dicyclobutene was found in its ultraviolet absorption spectrum. A comparison of the ultraviolet spectrum of V with that of durene (Fig. 1) shows a very appreciable bathochromic shift on going from durene to V. In addition, the extinction coefficients of the maxima of V in the 270–290 mμ region are almost ten times greater than the corresponding maxima of durene. Clearly the distortion effect caused by two fused four-membered rings upon the ultraviolet absorbtion of an aromatic nucleus is considerably more pronounced than the corresponding effect of a single fused cyclobutane ring.[2,4]



An investigation of the chemistry of benzo[1,2:4,5]dicyclobutene is in progress in our laboratory, and the results will be discussed in a subsequent paper of this series.

Acknowledgments.—We should like to thank the National Science Foundation for a grant in support of this work. We are grateful also to Mr. John Stone of "Chemical Abstracts" for suggestions concerning nomenclature.

Experimental[5]

1,3,5,7-Tetrahydrobenzo[1,2-c:4,5-c']dithiophene(VII).—α,α',α'',α'''-Tetrabromodurene[3] (9.0 g., 0.02 mole) was added to a mixture of sodium sulfide monohydrate (10 g.,

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[1] M. P. Cava and A. A. Deana, THIS JOURNAL, **81**, 4266 (1959).

[2] M. P. Cava and R. L. Shirley, *ibid.*, **82**, 654 (1960).

[3] W. Ried and H. Bodem, *Chem. Ber.*, **89**, 2328 (1956).

[4] M. P. Cava and D. R. Napier, THIS JOURNAL, **80**, 2255 (1958).

[5] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected unless stated otherwise.

0.042 mole), ethyl alcohol (100 ml.) and water (10 ml.). The reaction mixture was refluxed on a steam-bath for 36 hours, concentrated, and then poured into cold water (50 ml.). Filtration afforded a brown residue, which was dried and extracted with methylene chloride. The red extract was concentrated and adsorbed on alumina. Elution of the column with methylene chloride and concentration of the eluate gave pale yellow prisms (1.80 g., m.p. 207–210°), which were satisfactory for direct oxidation to the bis-sulfone. Further concentration of the eluate gave an additional crop of yellow sulfide, which was recrystallized from methylene chloride–ethanol, after treatment with charcoal, to yield 0.08 g. of pure VII as small white prisms, m.p. 213–217° dec. The total yield (1.88 g.) was 48%.

Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.00. Found: C, 61.61; H, 5.10; S, 32.81.

1,3,5,7-Tetrahydro[1,2-c:4,5-c′-dithiophene-2,2,6,6-tetroxide(VIII).—The bis-sulfide (1.74 g., 0.009 mole) was cautiously added over a period of 20 minutes to peracetic acid (60 ml.) which was cooled externally by means of an ice–water-bath. After the addition was complete, stirring was continued for 3 days at room temperature. The reaction mixture was diluted with cold water (100 ml.); the white crystalline product was removed by filtration and dried (2.1 g., 90%). Purification was accomplished by dissolving a small quantity of the product in warm dimethylformamide, adsorption on alumina, and continued elution of the column with warm dimethylformamide. Concentration of the eluate *in vacuo*, and addition of a small amount of water afforded the bis-sulfone as small white needles having no observable melting point below 400° dec.

Anal. Calcd. for $C_{10}H_{10}S_2O_4$: C, 46.50; H, 3.90; S, 24.83. Found: C, 46.38; H, 3.80; S, 24.94.

Benzo[1,2:4,5]dicyclobutene (V).—An intimate mixture of disulfone VIII (0.750 g.) and copper powder (0.350 g. was heated to 320° (salt-bath temperature) under a low pressure atmosphere of nitrogen (1 mm.) for two hours, the evolved vapors being passed through a glowing Nichrome coil (~600°) before being condensed on a cold finger.[6] The solid sublimate was washed off the condenser with ether and the ether solution was filtered and evaporated. The residue was extracted with a small amount of petroleum ether (40–70°) and the extract placed on a column (12 × 0.8 cm.) of Woelm neutral alumina. Elution of the column with ether afforded 0.150 g. (40%) of hydrocarbon V, m.p. 98–100°. The analytical sample, m.p. 101° (cor.), formed small white prisms after recrystallization from methanol.

An identical pyrolysis of sulfone–copper mixture gave only a 20% yield of V when the heating spiral was omitted; pyrolysis of the sulfone, undiluted by copper, gave also a 20% yield of V even though the spiral was employed; ultraviolet maxima (in ethanol): 276 mμ (log E 3.66), 280 mμ (log E 3.71), 286 mμ (log E 3.59).

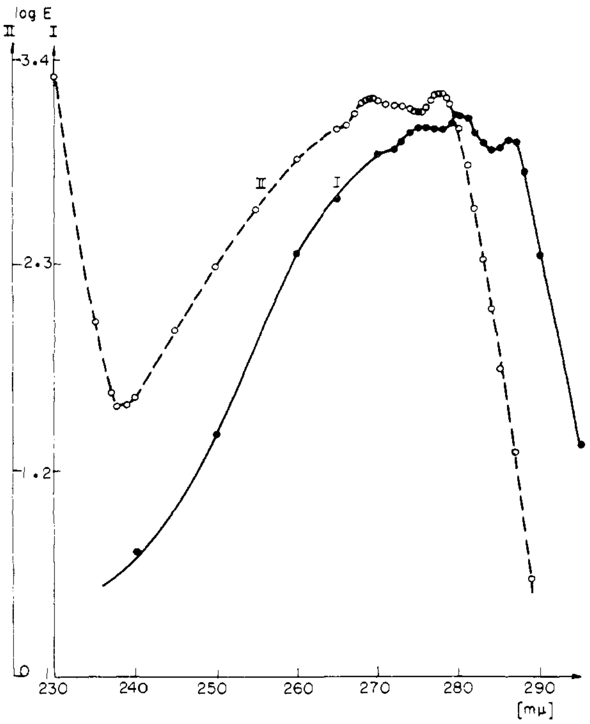

Fig. 1.—Spectra in 95% ethanol: I, benzo[1,2:4,5]dicyclobutene; II, 1,2,4,5-tetramethylbenzene (durene). (Solvent, 95% ethanol).

The maxima observed for durene in ethanol were: 269 mμ (log E 2.80), 278 mμ (log E 2.82).

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74; mol. wt., 130. Found: C, 92.30; H, 7.66; mol. wt. (Rast), 101.

Oxidation of Benzo[1,2:4,5]dicyclobutene(V).—A mixture of hydrocarbon V (0.024 g.), potassium permanganate (0.250 g.) and water (1.5 ml.) was shaken in a sealed tube at 100° for 18 hours. The brown precipitate of manganese dioxide was removed by filtration and the colorless filtrate was passed through a column (10 × 0.8 cm.) of Amberlite IR 120 resin (acid phase). Evaporation of the aqueous acidic eluate gave pyromellitic acid (IX) as white needles, converted by heating into the dianhydride. The sublimed anhydride weighed 0.017 g. (31%) and it was identical in melting point (283–285°) and infrared spectrum (KBr pellet) with material prepared from authentic pyromellitic acid

COLUMBUS 10, OHIO

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[6] The apparatus used was identical with that described previously in ref. 1.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

Sodium Borohydride Reduction of Nitroso Groups and Furoxan Rings[1]

BY J. H. BOYER AND S. E. ELLZEY, JR.

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Sodium borohydride reduces both nitrosobenzene and β-phenylhydroxylamine to azoxybenzene, but transforms *p*-nitrosophenol into *p*-aminophenol. Both *o*- and *p*-dinitrosoaromatic derivatives and furoxans react with this reagent to give corresponding dioximes or their anhydrides, the furazans. Cyclohexanone oxime is reduced by sodium borohydride with lithium bromide to cyclohexylamine.

Nitrobenzene at 90–100°[2] and now nitrosobenzene below 45° are each reduced by sodium borohydride to azoxybenzene. An unexpected transformation, below 45°, of β-phenylhydroxylamine to azoxybenzene using sodium borohydride requires initial air oxidation to nitrosobenzene insofar as the probable transformation of each of these three staritng materials to azoxybenzene includes a condensation between nitrosobenzene and β-phenylhydroxylamine. Dismutation of β-phenylhy-

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[1] Financial support by the Office of Ordnance Research, United States Army, under contracts No. DA-01-009-ORD-428 and DA-01-009-ORD-699 is gratefully acknowledged.

[2] C. E. Weill and G. S. Panson, *J. Org. Chem.*, **21**, 803 (1956).