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DIMERIZATION IN FINKELSTEIN[1] CYCLIZATIONS[2,3]

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GENERAL concern with the dimethylenecyclobutene system provided a specific interest in the chemistry of dimethylenebenzocyclobutene (I). Since synthesis of the hydrocarbon I from dimethyl benzocyclobutene-1,2-dicarboxylate (II) would be expected to be straightforward,[6] preparation of II was sought *via* a Finkelstein ring closure of *a*,*a*'-dibromo-*o*-phenylene-bis-(methyl acetate) (III).

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[1] H. Finkelstein, Dissertation, Strasbourg, 1910.

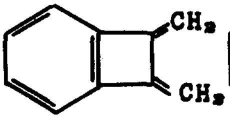
[2] This is the tenth publication concerned with the chemistry of small carbon rings. For the previous paper, see A.T. Blomquist and Y.C. Meinwald, *J. Amer. Chem. Soc.* **82**, 3619 (1960).

[3] This study was supported in part by the National Science Foundation, Grant NSF-G 5923.

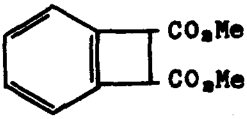
[4] American Viscose Fellow, Summer, 1958; Procter and Gamble Fellow, 1959-1960; National Science Foundation Summer Fellow, 1960.

[5] National Science Foundation Undergraduate Research Assistant, Summer, 1960.

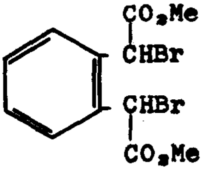
[6] A.T. Blomquist and Y.C. Meinwald, *J. Amer. Chem. Soc.* **82**, 3619 (1960).



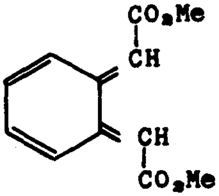
I



II



III



IV

It was observed independently, as established by Cava in the Finkelstein cyclization of α,α,α',α'-tetrabromo-*o*-xylene to 1,2-dibromobenzocyclobutene,[7] that compound III produced a substituted *o*-quinodimethane intermediate, compound IV.

Methanolysis at 0° of the product obtained by refluxing *o*-phenylene-bis-(acetyl chloride)[8] in bromine produced the bromo-ester III (70-80%), m.p. 105.0-106.5°. Reaction of compound III with sodium iodide in dimethylformamide for 48 hr at room temperature gave a 69% yield of a halogen-free tetra-ester, V or VI, m.p. 158.0-158.5°. None of the desired monomeric di-ester II was formed. All of the evidence obtained is in support of structure VI for the tetra-ester, formed by a self Diels - Alder reaction of the *o*-quinodimethane intermediate IV:

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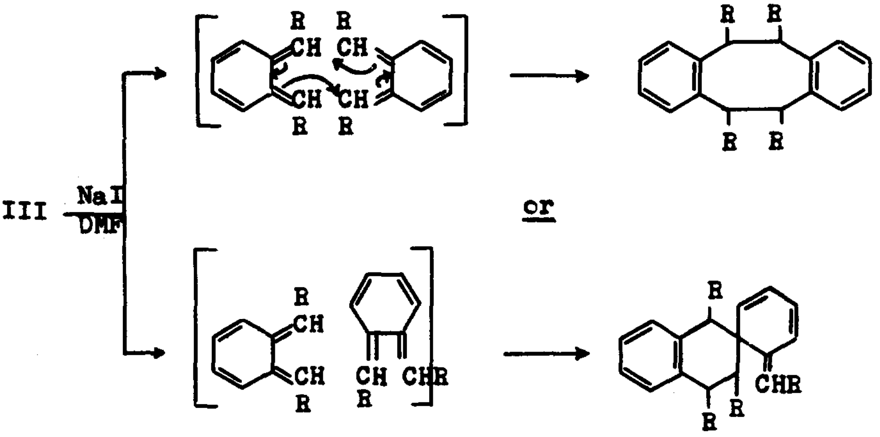
[7] M. P. Cava, A. A. Deana and K. Muth, J. Amer. Chem. Soc. **81**, 6458 (1959).

[8] J. O. Halford and B. Weissman, J. Org. Chem. **17**, 1646 (1952).



V

VI

R = $-CO_2Me$

The compound absorbs 3 molar equivalents of hydrogen upon catalytic reduction, it possesses a maximum in its ultraviolet spectrum at 327 mμ (log ε 3.97),[9] and in the infrared it has a strong absorption band at 6.21 μ.[10]

Finally, the NMR spectrum of this tetra-ester shows the presence of five vinyl-type hydrogens and that the two adjacent hydrogen atoms on the cyclohexane ring are trans to each other.[11]

The formation of the o-quinodimethane intermediate IV was demonstrated by a trapping experiment. Upon carrying out the Finkelstein reaction in methanol and in the presence of N-phenylmaleimide, the adduct VII, m.p. 229-230°, was isolated in quantative yield. Hydrolysis of the adduct VII,

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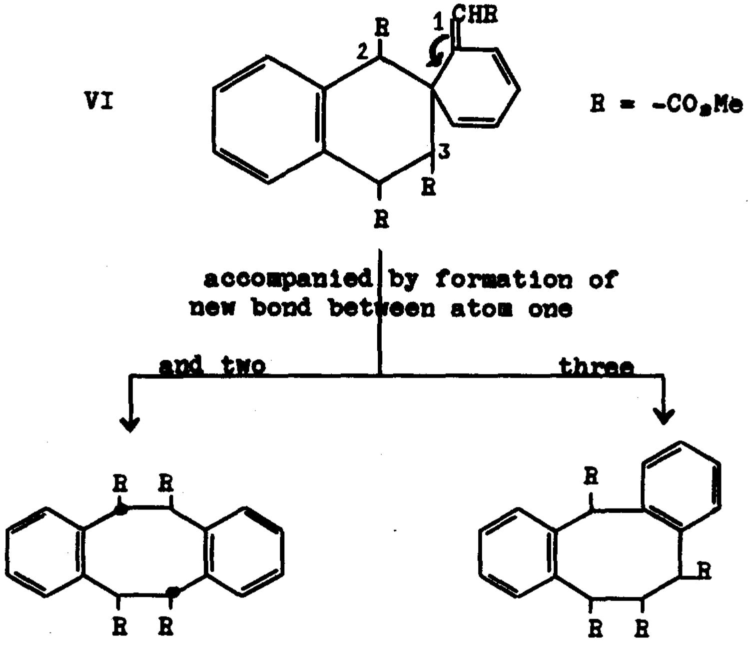
[9] Illustration of a similar chromaphore is "example 20" in L.F. Fieser and M. Fieser, Steroids p. 20. Reinhold, New York (1959).

[10] L.J. Bellamy, The Infra-Red Spectra of Complex Molecules pp. 35-36., John Wiley, New York (1957).

[11] This NMR spectrum together with its interpretation were done by Varian Associates.

followed by decarboxylation and dehydrogenation produced naphthalene.

The tetra-ester VI was unreactive toward the common dienophiles in boiling benzene solution. The compound VI rearranged quantitatively, when heated for 24 hr in boiling xylene, to give an isomeric tetra-ester, m.p. 255.0-255.5°, which had only aromatic unsaturation as shown by its ultraviolet spectrum; λ_{max} 263 mμ, log ε 2.82. The foregoing is consistent with the rearrangement of the "semi-benzene" VI to either of the two dibenzocyclo-öctadienes VIII or IX.[12]



VIII

IX

The NMR spectrum of the rearranged tetra-ester shows three groups of

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[12] Pertinent examples of similar semi-benzene rearrangements are given in [a] M.S. Newman and L.L. Wood, Jr., *J. Amer. Chem. Soc.* **81**, 4300 (1959); [b] K. Auwers and K. Ziegler, *Liebigs Ann.* **425**, 217 (1921).

signal peaks which can be assigned to aromatic, methyl ester, and alicyclic hydrogens. The group assignable to alicyclic hydrogens, center ring in VIII, appear as a pair of doublets, indicative of two different hydrogen species strongly spin-coupled. All of this is in full accord with the trans arrangement indicated in VIII and in the preferred conformation proposed for the dibenzocycloöctadiene system in VIII.[13]

Alkaline permanganate oxidation of the tetra-acid, m.p. 259-260°, obtained by acid hydrolysis of the tetra-ester, gives only *o*-phthalic acid as required by structure VIII.

We have observed the formation dimeric products and also monomeric cyclobutene derivatives in the Finkelstein reaction with *α,α*'-dibromo-*o*-ethylbenzylbenzene and *α,α*'-dibromonaphthalene-2,3-bis-(methyl acetate). Details about these studies will be reported later.

All compounds isolated and described in this report gave correct elemental analyses and molecular weight values.

Acknowledgement - The authors express their gratitude to Mrs. Georgia Fritz for her aid in the determination and interpretation of the NMR spectra of many of the compounds described.

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[13] W. Baker, R. Banks, D. R. Lyon and F. G. Mann, J. Chem. Soc. 27 (1945).