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ON THE MECHANISM OF THE DEHYDROBROMINATION OF $\alpha,\alpha,\alpha',\alpha'$-TETRABROMO-o-XYLENE

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It was reported recently[1] that $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-o-xylene(I) reacts with excess potassium t-butoxide to yield a mixture of 5,10-dibromobenzo[b] biphenylene(II) and 1,2,5,6-tetrabromo-3,4:7,8-dibenzotricyclo[4,2,0,$0^{2,5}$] octadiene(III). In interpreting this remarkable transformation, the reasonable suggestion was made that II and III arise via 1,2-dibromobenzocyclobutadiene(IV), the dehydrobromination product of 1,1,2-tribromobenzocyclobutene (V). The unknown tribromide V was not isolated in this reaction but its formation from tetrabromide I certainly could be postulated, via the intermediary production of the quinoid tribromide VI. Evidence now has been gathered that neither tribromide V nor the cyclobutadiene IV is involved in the conversion of I to II and III.

The bromination of trans-1,2-dibromobenzocyclobutene(VII) by N-bromosuccinimide (NBS) gave, after two days, 1,1,2,2-tetrabromobenzocyclobutene (VIII), m.p. 117-118°, in 65% yield.[2] By fractional distillation and crystallization of an incompletely brominated reaction mixture, a small amount of 1,1,2-tribromobenzocyclobutene(V), m.p. 40-41°, was obtained.

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[1] F. R. Jensen and W. E. Coleman, Tetrahedron Letters No. 20, pp. 7-11, 1959.

[2] All new compounds gave satisfactory analyses for the formulae assigned.

Tribromide V was produced also rapidly and in good yield (72%) by treatment of cis-1,2-dibromobenzocyclobutene[3] (IX), m.p. 101-101.5°, with one equivalent of NBS. The structure of tetrabromide VIII was proven by its reaction with silver trifluoroacetate to give benzocyclobutenedione[4] (X) in 41% yield. The dehydrobromination of tribromide V with potassium t-butoxide gave none of compounds II and III, but rather an 85% yield of the orange 5,6-dibromobenzo[a]biphenylene (XI), m.p. 149-150°. The biphenylene derivative XI was obtained as well, in 41% yield, by sodium iodide treatment of 1,1,2,2,tetrabromobenzocyclobutene (VIII). The intermediary 1,2-dibromobenzocyclobutadiene (IV) thus undergoes not linear dimerization, but the previously observed type of angular dimerization.[5,6] The postulated immediate precursor of XI, the tetrabromide XII, could be synthesized in 68% yield as colorless crystals, m.p. 155-155.5°, by addition of bromine to XI. As predicted, XII lost bromine rapidly under the influence of potassium t-butoxide to regenerate the orange bromide XI.[7]

As a result of the above observations, we suggest tentatively that tetrabromo-o-xylene is dehydrobrominated by strong base to the quinoid bromide VI; instead of undergoing intramolecular cyclization to a benzocyclobutene, VI dimerizes to the dibenzocyclooctadiene derivative XIII.

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[3] F. R. Jensen and W. E. Coleman, American Chemical Society Meeting, April, 1958. Abstracts of Papers, p. 79 N.

[4] M. P. Cava and D. R. Napier, J. Am. Chem. Soc. 79, 3606 (1957).

[5] M. P. Cava and D. R. Napier, J. Am. Chem. Soc. 79, 1701 (1957).

[6] M. P. Cava and J. F. Stucker, J. Am. Chem. Soc. 79, 1706 (1957).

[7] The confirmation of the structure of compound XI by direct synthesis from a derivative of benzo[a]biphenylene will be described in the full publication. This work is omitted here for the sake of brevity.

Reasonable paths can be envisaged from XIII to Jensen and Coleman's compounds II and III. Attempts to confirm this mechanism are in progress.

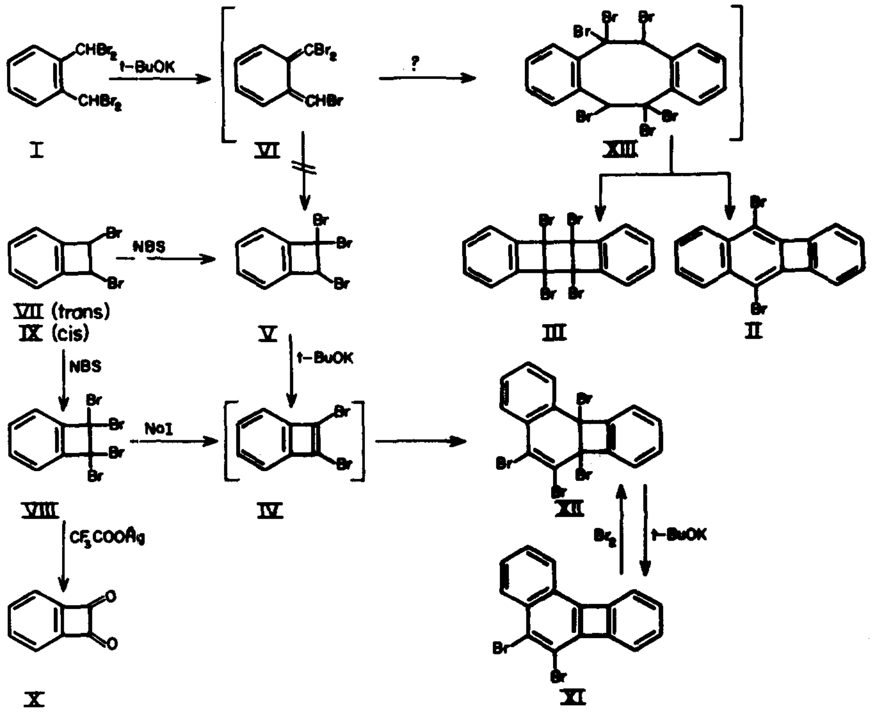

Chart 1

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