

REACTION MECHANISMS OF DEHYDROBROMINATION OF 1,1,2-TRIBROMOBENZOCYCLOBUTENE AND TETRAHALO-*o*-XYLENE AND THAT OF DEBROMINATION OF 1,1,2,2-TETRABROMOBENZOCYCLOBUTENE

Tanweer Ahmed Chaudhri, Abdul Rauf Aziz and Mukhtar A. Akhtar

PCSIR Laboratories, Lahore 16

(Received February 16, 1980; revised April 24, 1980)

The dehydrobromination of 1,1,2-tribromobenzocyclobutene and debromination of 1,1,2,2-tetrabromobenzocyclobutene leads to the formation of 5,6-dibromobenzo-(a)-biphenylene, together with smaller amounts of 5,10-dibromobenzo-(b)-biphenylene and 3,4,7,8-tetrabromobenzocyclooctatetraene. The mechanisms of the above-mentioned two reactions and that of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene is discussed in the light of these observations and Woodward-Hoffman orbital symmetry rule.

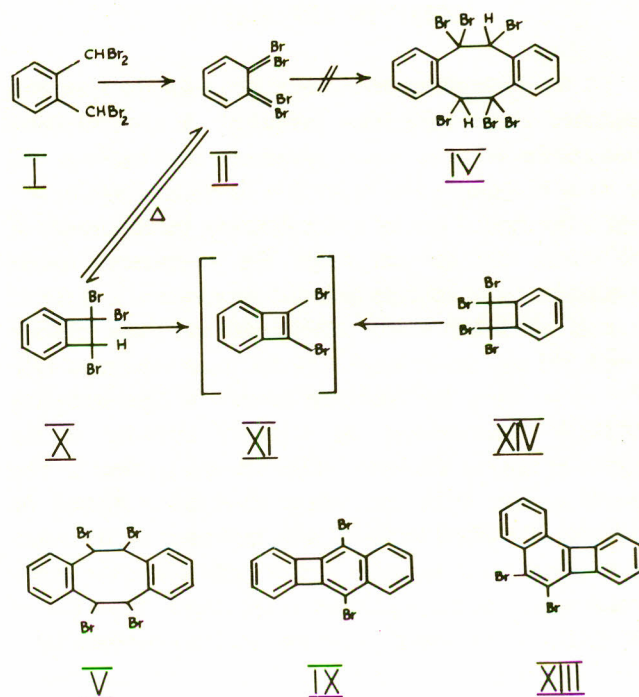
INTRODUCTION

The dehydrobromination of 1,1,2-tribromobenzocyclobutene (X) with potassium-*t*-butoxide affords 5,6-dibromobenzo-(a)-biphenylene (XIII) [1-3]. In this case 1,2-dibromobenzocyclobutadiene (XI) is formed, and the intermediate dimer, 5,6,6a, 10b-tetrabromo-6a-10b-dihydrobenzo-(a)-biphenylene (XII) undergoes debromination to give the final product 5,6-dibromobenzo-(a)-biphenylene (XIII). Similar results are reported, when 1,2-dibromobenzocyclobutadiene (XI) is generated by dehalogenation of 1,1,2,2-tetrabromobenzocyclobutene (XIV) with sodium iodide.

On repetition of this work it was found that there are two more compounds present and the structures assigned to these compounds are 3,4,7,8-tetrabromobenzocyclooctatetraene (V) and 5,10-dibromobenzo-(b)-biphenylene (IX). The structures (V), (IX) and (XIII) are assigned on the basis of IR, NMR, and UV spectra and analysis. The spectra obtained from these compounds are identical to the authentic samples obtained by dehydrobromination of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene.

On the basis of these results and Woodward-Hoffman rule the mechanisms of the reported dehydrobromination of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene by Jensen [3], Cava [1-2] and McOmie [4] can be discussed. According to the Woodward-Hoffman [5] orbital symmetry rule, *o*-quinoid intermediate (II) should not undergo concerted dimerization as the system consists of either $4\pi + 4\pi$ or 8π and is forbidden; as only $(2q + 2s)$ is allowed, but the rule does allow the concerted thermal process of cyclization to (X).

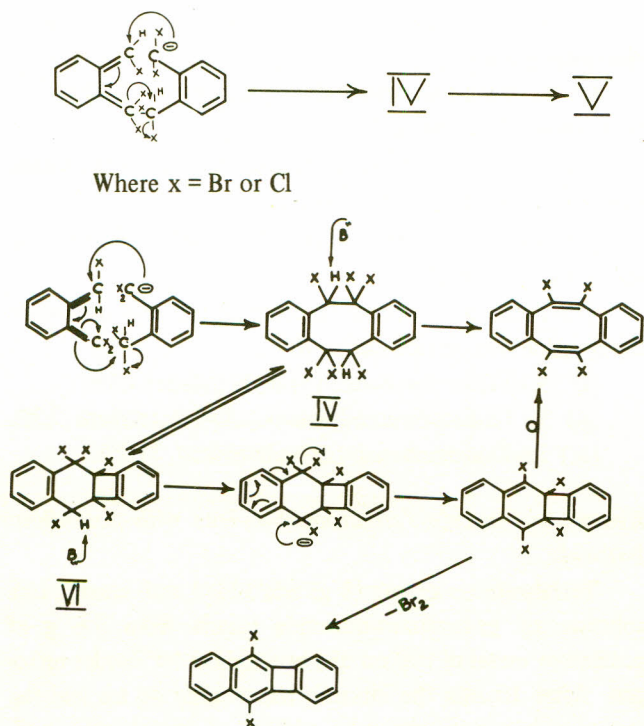
To test the hypothesis put forth by Cava it was attempted to dehydrochlorinate $\alpha,\alpha,\alpha',\alpha'$ -pentachloro-*o*-xylene with potassium-*t*-butoxide, with a hope of getting dibenzocyclooctadiene derivative (IV) or tetrachlorobenzocyclobutene (XIV). But presumably due to the steric reasons the



reaction did not go at all. Dehydrochlorination of $\alpha,\alpha,\alpha',\alpha'$ -tetrachloro-*o*-xylene gave all the three corresponding compounds.

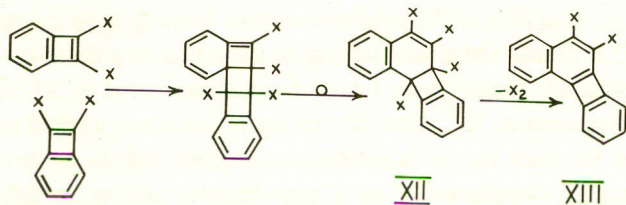
In the light of these results the mechanisms of these three reactions of dehydrobromination of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene, 1,1,2-tribromobenzocyclobutene and debromination of 1,1,2,2-tetrabromobenzocyclobutene could be discussed. Dehydrohalogenation of tetrahalo-*o*-xylene with potassium-*t*-butoxide is 1,4-elimination of hydrogen halide via anion (III) to give quinoid (II) which could react with anion (III) generated by the attack of base on tetrahalo-*o*-xylene to give intermediate (IV), which by dehydrohalogenation gives (V).

Attack of base on (IV) could generate anion (VI)



which could close to benzocyclobutene derivative (VII). Base attack on the hydrogen followed by rearrangement gives intermediate (VIII) which could either rearrange to (V) or undergo dehalogenation to give (IX).

The *o*-quinoid (II) is allowed to undergo the thermal process of cyclization by the Woodward-Hoffman rule to give (X) which undergoes dehydrohalogenation to give diene (XI). The diene (XI) and quinoid (II) could undergo Diels-Alder reaction to give the adduct (VI) which gives (V) or (IX). The diene (XI) could dimerize in angular fashion followed by dehalogenation to give (XIII).

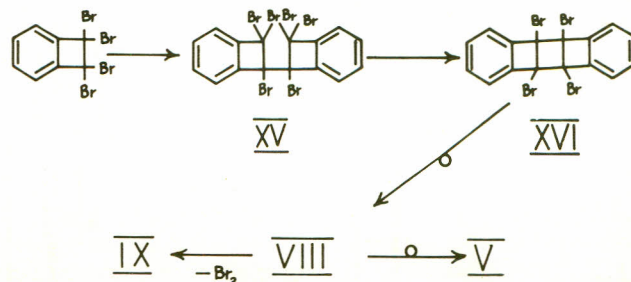


Where x = Br or Cl

The dehydrobromination of 1,1,2-tribromobenzocyclobutene with potassium-*t*-butoxide gives diene (XI) which dimerizes in angular fashion, followed by debromination to give the dimer (XIII). According to Woodward-Hoffman rule (XI) could open thermally to give quinoid (II), which undergoes Diels-Alder reaction with diene (XI) to give (V) and (X).

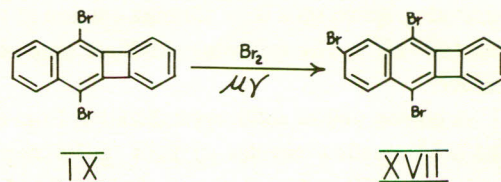
Tetrabromobenzocyclobutene (XIV) with sodium iodide gives benzocyclobutadiene (XI), which dimerises in the angular fashion, followed by debromination to give (XIII). The other two products are formed either via Diels-Alder reaction of quinoid (II) and diene (XI) or by face to face

reaction which according to the orbital symmetry rule could not be concerted but possibly goes via intermediate (XV) to (XVI) which rearranges due to steric reasons to give (V) or rearranges alongwith debromination to give (IV).



The reaction mechanisms are self-explanatory for the low-yields of compounds (V) and (IX) in the reaction of 1,1,2-tribromo- and in 1,1,2,2-tetrabromobenzocyclobutene and that of (X) and (XIV) and that of compound (XIII) in the reaction of tetrabromo-*o*-xylene.

Bromination of 5,10-dibromobenzo-(b)-biphenylene was carried out in carbon tetrachloride under UV light with a little hope to get (V); but instead of addition product a substitution product was formed. On the basis of IR, NMR and UV spectra and analysis the structure (XVII) was assigned to 5,8,10-tribromobenzo-(b)-biphenylene.

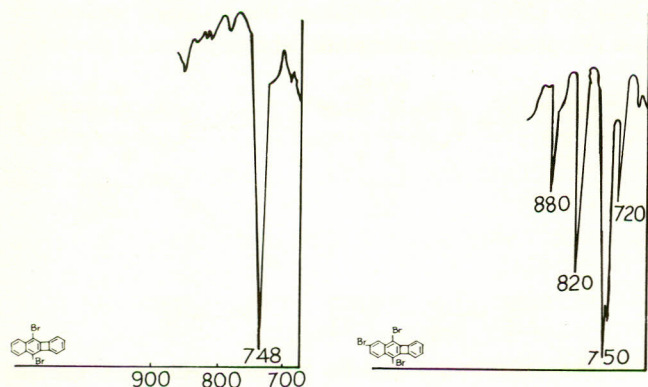


Both the IR and NMR spectra of (XVII) are extremely informative and are in favour of the structure assigned. The IR spectrum is immediately seen to be different from that of dibromide (IX) and tetrabromide (V), strong bands at 750 cm^{-1} show four adjacent hydrogen atoms of benzene ring. In Fig. 2 the intensity of the band at 750 cm^{-1} is somewhat less intense than that in Fig. 1 while there are two more bands, at 820 cm^{-1} (two adjacent hydrogen atoms) and 880 cm^{-1} (one hydrogen atom).

The NMR spectrum is also different from that of dibromide (IX). Aromatic protons of benzene ring having C 6, 8 and 9 consist of AB system. The protons at the C6 position is coupled with that at position C7, while H6 is coupled with H8 and absorption consists of quarter. In the same way H6 and H8 and H7 and H9 are coupled. The absorption of protons in both (IX) and (XVII) is similar.

The protons at 1, 2, 3 and 4 position in compound (IX) are shown as a multiplet at τ 3.03 but in compound (XVII) the spectrum is quite different. The proton at position H3 absorbs as a quartet and the proton at position H4 also comes in the same field but does not disturb the symmetry of the quartet. Proton H1 is at τ 3.14 and is a doublet. This

part of the spectrum is identical to that involving protons 1, 3, 4 in case of 2-bromobiphenylene.



EXPERIMENTAL

Dimerization of 1,2-Dibromobenzocyclobutadiene

From 1,1,2,2-Tetrabromobenzocyclobutene. A mixture of 1,1,2,2-tetrabromobenzocyclobutene (4.0 g), sodium iodide (8.0 g) and dimethylformamide (60 ml) was heated for 20 hr on a steam-bath. The cooled solution was diluted with water (400 ml) and free iodine present was reduced. The suspension was extracted with benzene (200 ml), dried and chromatographed on a large alumina column in petroleum-ether (40–60°). The following products were obtained in the order:

(i) A golden yellow solid, crystallization from ethanol afforded golden yellow needles (0.0634 g; 3%; m.p. 222–223°). IR, UV, NMR and mass spectra showed it to be 5,10-dibromobenzo-(b)-biphenylene (IX). (Found: C 53.12, H 2.17, Br 44.66. $C_{16}H_8Br_2$ requires: C 53.33, H 2.22, Br 44.44%).

(ii) White plates (0.187 g; 6.1%; m.p. 214° decomp). IR, NMR and mass spectra showed it to be 3,4,5,6-tetrabromobenzocyclooctatetraene (V). (Found: C 37.1, H 1.54, Br 61.36. $C_{16}H_8Br_4$ requires: C 36.94, H 1.54, Br 61.52%).

(iii) Orange solid, crystallized from light petroleum (40–60°) afforded orange needles (0.368; 17.3%; m.p. 147–148°). IR, UV and NMR spectra showed it to be 3,4-dibromo-(a)-benzobiphenylene (XIII). (Found: C 53.50, H 2.34, Br 44.39. $C_{16}H_8Br_2$ requires: C 53.33, H 2.22, Br 44.44%).

From 1,1,2-Tribromobenzocyclobutene. A solution of tribromobenzocyclobutene (1.71 g) in t-butanol (5 ml) was added at room temperature to a stirred solution of potassium t-butoxide prepared by dissolving potassium metal (1.45 g) in t-butanol (50 ml). The yellow solution was stirred for additional 1.5 hr, and then diluted with ice-cold water (200 ml). The precipitate was filtered, dried and dissolved in minimum benzene. Benzene solution was absorbed on an alumina column and eluted with petroleum-

ether (40–60°). The following products were obtained in the order given:

(i) 5,10-Dibromobenzo-(b)-biphenylene (0.008 g; 1.1%; m.p. 222–223°).

(ii) 3, 4, 7, 8-Tetrabromodibenzocyclo-octatetraene (0.152 g; 14.4%; m.p. 214° decomp.).

(iii) 5,6-Dibromo-benzo-(a)-biphenylene (0.482 g; 66%; m.p. 147–148°).

The yields of the products were slightly changed when the reaction was carried out at 70°

(i) 5,10-Dibromo-benzo-(b)-biphenylene; 4.5%.

(ii) 3,4,7,8-Tetrabromodibenzocyclo-octatetraene, 7.2%.

(iii) 5,6-Dibromobenzo-(a)-biphenylene, 71.2%.

Reaction of $\alpha,\alpha,\alpha',\alpha'$ -Tetrabromo-o-xylene with potassium-t-butoxide.

Tetrabromo-o-xylene (8 g) was added with stirring to a solution of potassium-t-butoxide (made from 5.6 g of potassium metal in 100 ml of t-butanol) at 70° under nitrogen. After 10 min the mixture was poured on ice and the excess of base neutralized by addition of glacial acetic acid. The product was fractionally crystallized from ethanol; giving (i) 5,10-dibromobenzo-(b)-biphenylene as golden yellow needles (1.79 g. 62.5%, m.p. 222–223°); (ii) white plates and little of yellow needles, which were then crystallized from light petroleum giving 3,4,7,8-tetrabromodibenzocyclo-octatetraene (1.53 g, 31%, m.p. 214° decomp). The mother liquor after chromatography on alumina in light petroleum gave small amount of tetrabromide first and then orange solid, which crystallized as orange needles from light petroleum 5,6-dibromobenzo-(a)-biphenylene (0.14 g; 4%; m.p. 147–148°).

Reaction of Tetrachloro-o-xylene. Tetrachloro-o-xylene (2.0 g) was added with stirring to a solution of potassium-t-butoxide (made from 1.4 g of potassium metal in 27 ml t-butanol) at 70°. After 10 min the reaction was worked up in the same way as in tetrabromo-o-xylene and the product was chromatographed on a large alumina column in light petroleum. The following products were obtained.

(i) 5,10-Dichloro-benzo-(b)-biphenylene as white needles in 10% yield, m.p. 214°.

(ii) 3,4,7,8-Tetrachlorodibenzocyclo-octatetraene as white plates in 35% yield, m.p. 214°. (Found: C 55.90, H 2.31, Cl 41.22. $C_{16}H_8Cl_4$ requires: C 56.14, H 2.34, Cl 41.52%).

(iii) Small amount of light yellow product, m.p. 135°, 5,6-dichlorobenzo-(a)-biphenylene.

Reaction of Pentachloro-o-xylene with Potassium-t-butoxide:

Pentachloro-o-xylene (4 g) was added with stirring to

a solution of potassium-t-butoxide (made from 3.5 g in 65 ml t-butanol) at 70° under nitrogen. After half-an-hour the mixture was poured on ice and excess of base neutralized by glacial acetic acid. The starting material was recovered as such.

Bromination of 5,10-dibromobenzo-(b)-biphenylene. A mixture of benzobiphenylene (0.36 g) and bromine (0.15 g) in carbon tetrachloride (30 ml) was stirred overnight under irradiation. Practically pure yellow compound precipitated out. On the basis of spectra and analysis, it has been found to be, 5,8,10-tribromobenzo-(b)-biphenylene (0.42 g, 96% m.p. 197°). (Found: C 44.44, H 1.61, Br 54.03. C₁₆H₇Br₃ requires: C 43.73, H 1.59, Br 54.67%.) NMR H₆ and H₉ τ 2.20 (q), H₇ and H₈ τ 2.65 (q), H₁ and H₂, τ 2.87, H₄

τ 3.14; $J_{1,2} = 6.00$; $J_{2,4} = 1.5$; $J_{6,7} = J_{8,9} = 6.0$ and $J_{6,8} = J_{7,8} = 2.0$ cps.

REFERENCES

1. M.P. Cava and K. Muth, *Tetrahedron Letters*, 140 (1961).
2. M.P. Cava and K. Muth, *J. Org. Chem.*, **27**, 1561 (1962).
3. F.R. Jensen and W.E. Coleman, *Tetrahedron Letters*, 7 (1959).
4. W. Baker, J.W. Barton, J.F.W. McOmie and R.J.G. Searle, *J. Chem. Soc.*, 2633 (1962).
5. R.B. Woodward and R. Hoffman, *Angew. Chem. Intern. Ed. Engl.*, 781 (1969).