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STUDIES IN THE CYCLOPROPARENE SERIES: 2-HALOCYCLOPROPABENZENES[1]

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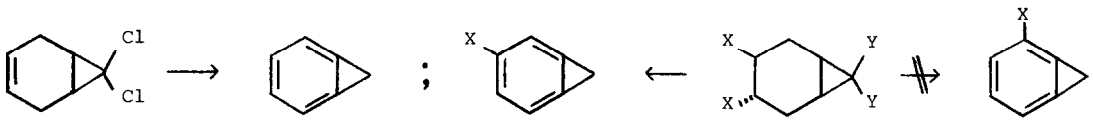
Summary: *Labelling studies show that dehydrohalogenation of the tetrahalobicycloheptanes (8b,c) yields the title compounds (5a,b) both with and without skeletal rearrangement. 2-Chlorocyclopropabenzene (5b) is the major product and the expected 2-bromo derivative (5a) the minor product of reaction from the 'mixed' tetrahalide (8c).*

Of the routes available for the synthesis of the cycloproparenes, e.g. (2), that involving the bis-dehydrohalogenation of a 7,7-dihalobicyclo[4.1.0]heptene, e.g. (1), has proved to be of general significance.[2] Furthermore, it has been shown that the olefinic linkage of the bicycloheptene is not necessary provided that appropriate functionality is present to allow for the generation of the π-framework under the conditions of elimination.[3-5] Thus the tetrahalobicycloheptanes (3a,b) have proved to be viable synthons for the corresponding halocyclopropabenzenes. Originally assigned as the 2-halo derivatives (5a,b),[3] the structures of these products have been re-assigned as 3-halocyclopropabenzenes (4a,b) primarily from their spectroscopic data.[4,5] We now provide further evidence to substantiate the assignment of structure (4) to the dehydrohalogenation products from compound (3), and present results which unambiguously establish the presence of competing pathways in the synthesis of the hitherto unknown 2-halocyclopropabenzenes (5a,b).



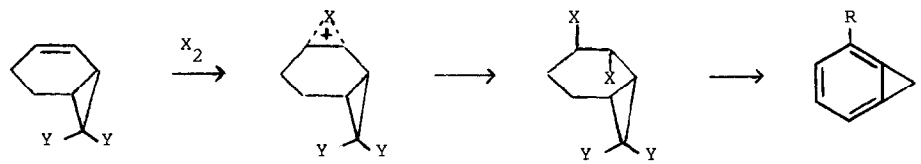
(1) (2) (4a) X=Br (4b) X=Cl (3a) X=Y=Br (3b) X=Y=Cl (3c) X=Br; Y=Cl (5a) X=Br (5b) X=Cl

In their original report, Devaprabhakara and co-workers[3] proposed that the dehydrohalogenation product of compound (3) was the rearranged 2-halocyclopropabenzene (5). A complex pathway involving halocycloheptatriene intermediates was proposed,[3] one corollary of which is that the dibromodichloro precursor (3c) would, of necessity, deliver both bromo- and chloro-cyclopropabenzenes. Because of our interest in the mechanistic aspects of cycloproparene formation,[6] we have examined the behaviour of compound (3c)[7] (prepared by bromination of 7,7-dichlorobicyclo[4.1.0]hept-3-ene[6,8] employing the method of Paquette and Barrett[9]) with potassium t-butoxide under a variety of conditions.[10] In each case, a mass spectral analysis of the crude reaction product shows bromine-containing material compatible with a bromocyclopropabenzene (m/z 168,170; 1:1) but *no* chlorine-containing material (see below). The carbon-13 spectrum of the

purified product exhibits seven resonances compatible only with a single compound which is confidently assigned[11] as 3-bromocyclopropabenzene (4a) (30-40%)[4,5] from a comparison of these data with those of the 2-bromo isomer (5a) (see below and Table). Furthermore, the tetrachloride (3b)[8] labelled with carbon-13 at C-7 yields (4b) (37%) with the label at C-1 only. Thus we conclude that the conversion (3) → (4) proceeds without measureable skeletal rearrangement as has been determined by Gunther[12] for the dehydrochlorination of compound (1).

On the basis of the foregoing observations, it can be argued that the isomeric 2,3,7,7-tetrahalobicycloheptanes (8a-c) should suffer analogous tris-dehydrohalogenation to deliver the hitherto unknown 2-halocyclopropabenzenes (5a,b). In particular, the C-2 halogen atom is *trans*-disposed to the halogen at C-3 and cannot participate in antiperiplanar elimination irrespective of the specific configuration of the molecule. Furthermore, the operation of any *syn*-elimination mechanism should favour abstraction of the more acidic homoallylic proton at C-2 and likewise leave the C-2 halogen substituent in place during the conversion into product.

In order to test this hypothesis, the tetrahalide (8c) was prepared by bromination of 7,7-dichlorobicyclo[4.1.0]hept-2-ene (6b).[10] A dibromo addition product[7] is obtained in 72% yield which exhibits a sharp melting point (102.5-103°). While this and the spectroscopic data argue for the production of a single diastereoisomer, they do not allow for differentiation between the proposed structure (8c) and its isomer in which the configuration of the two bromine substituents is reversed. However, crystallographic analysis[13] confirms the product as that depicted by (8c)[14] and this is believed to result from nucleophilic capture of the cis-transoid-cis bromonium ion (7c) at the more cationic cyclopropylcarbinyl centre thereby accounting for the high stereoselectivity of the process.



(6a) Y=Br
(6b) Y=Cl

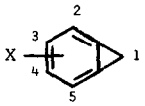
(7)

(8a) X=Y=Br
(8b) X=Y=Cl
(8c) X=Br; Y=Cl

(5a) R=Br
(5b) R=Cl

Subjection of the 'mixed' tetrahalide (8c) to the action of potassium t-butoxide in tetrahydrofuran results in the characteristic foul odour of the volatile cyclopropabenzenes. Mass spectral analysis of the crude product mixture surprisingly reveals the presence of *both* bromine- (m/z 168,170; 1:1) and chlorine- (m/z 124,126; 3:1) containing materials compatible with cyclopropabenzene structures. Although the 60MHz H-1 n.m.r. spectrum shows only a broadened singlet (δ 3.29, CH_2), the C-13 spectrum reveals thirteen lines consistent with the presence of 2-bromo- and 2-chloro-cyclopropabenzene (5a,b) (~20%) from a comparison with the expected[15] chemical shifts. Confirmation of the proposed structures stems from separate dehydrohalogenation of the tetrabromide (8a) and the tetrachloride (8c) which provide compounds (5a) (17%) and (5b) (15%) respectively.[7] The assignment of these compounds as 2-halocyclopropa-

Table: ^{13}C N.M.R. Data of the Halocyclopropabenzenes[a]

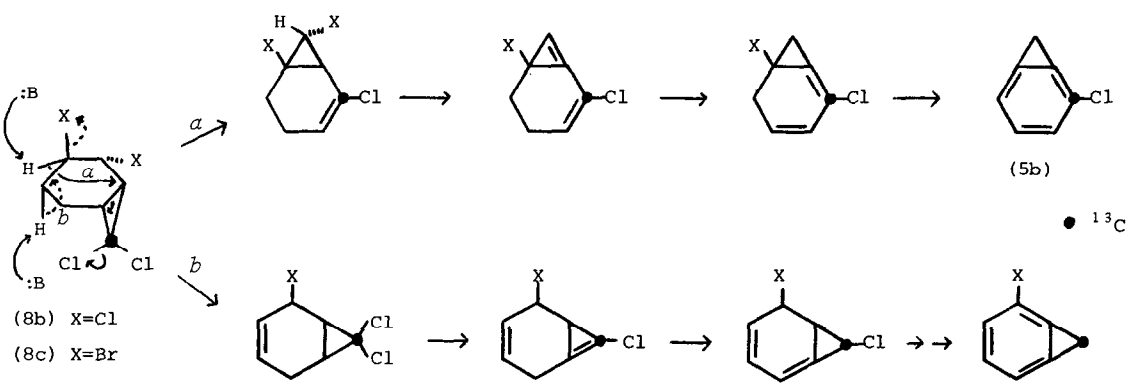


	C-1	C-1a	C-2	C-3	C-4	C-5	C-5a
X = H[b]	18.4	125.4	114.7	128.8	128.8	114.7	125.4
X = 2-Br	21.9	126.0	110.1	132.5[c]	132.1[c]	113.4	130.4
X = 2-Cl	21.4	122.6	123.1	129.8	132.1	112.9	130.2
X = 3-Br	21.2	128.8	118.3	122.0	132.0	117.6	125.0
X = 3-Cl[d]	21.4	128.3	117.2	133.8	129.2	115.8	124.1

[a]Spectra were recorded for $CDCl_3$ solutions with Me_4Si as internal standard and chemical shifts are ±0.1ppm. [b]Data taken from ref. 11. [c]Assignments could be reversed. [d]See also ref. 4.

benzenes is fully compatible with the appearance of a low field singlet for C-2 (δ 110.1) and a doublet for C-5 (δ 113.4) from (5a) while chloride (5b) shows only C-5 of the aromatic carbon atoms at low field (δ 112.9) as anticipated (Table).[11,15] The precise ratio of the (5a/b) mixture from the dibromodichloro compound (8c) is not easy to determine,[16] but the distinct C-1 n.m.r. signals (δ 21.9, 21.4) indicate a value approaching 2:3, *i.e. the major product of reaction results from skeletal rearrangement.*

In order to provide some insight into the pathway by which the rearranged product (5b) is formed from compound (8c), compounds (8b) and (8c) labelled at C-1 with carbon-13 were examined. The 2-chlorocyclopropabenzene thus obtained from (8b) shows enhancement of *both* C-1 (δ 21.4) and C-2 (δ 123.1)[17] while the (5a/b) mixture resulting from labelled (8c) exhibits one enhanced signal in each component - C-1 of (5a) at δ 21.9 and C-2 of (5b) at δ 123.1. We conclude therefore that the route by which the major product, 2-chlorocyclopropabenzene (5b), is formed from



Scheme

(8c) involves the formation of a new three-membered ring with retention of one C7-Cl moiety and that the same pathway operates in the formation of (5b) from tetrachloride (8b) to approximately the same extent.[18] Analagous competition in the conversion (8a) → (5a) is probable.

The route to the product (5) labelled at C-1 is presumed to involve bicyclo[4.1.0]-heptene and -heptadiene intermediates and subsequent dehydrohalogenation by the accepted pathway.[12] On the other hand, the mechanism of rearrangement is yet to be established but could proceed as indicated in the Scheme.

The mechanistic aspects of the rearrangement and the potential of the 2-halocyclopropabenzenes to act as progenitors for 2,3-dehydrocyclopropabenzene are the subjects of continuing study.

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References and Footnotes:

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13. Robinson, W.T. private communication. Full details of the X-ray analysis will be published in a subsequent paper.
14. Compound (8c) is (1α,2α,3β,6α)-2,3-dibromo-7,7-dichlorobicyclo[4.1.0]heptane.
15. The observed chemical shifts are in excellent agreement with those calculated from the data for the parent hydrocarbon (see ref. 11) and C-13 halogen substituent effects.
16. Attempted g.l.c. separation of the mixture resulted in decomposition under a variety of conditions.
17. Methanolysis of the three-membered ring leads to 1-chloro-2- and 1-chloro-3-methoxymethylbenzene. Enhanced carbon-13 signals are recorded only for the characteristic C-1 resonances at 132.9 and 133.4 ppm respectively, thereby confirming the assignment of C-2 at 123.1 ppm in 2-chlorocyclopropabenzene (5b).
18. Based on the degree of signal enhancement from spectra recorded under the same conditions.

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