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PYROLYTIC AND ELECTRON IMPACT STUDIES ON 1-BROMO- AND 1,1-DIBROMO-2,3-DIMETHYLCYCLOPROPANES

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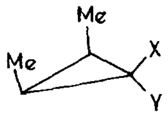
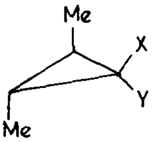
We have previously presented evidence(1) in support of the conclusion that the thermal rearrangement of the epimeric 6-chlorobicyclo[3,1,0]hexanes is subject to the same stereochemical control as the solvolytic rearrangement of the corresponding tosylates(2). Thus both reactions appear to proceed via a similar heterolytic step involving the disrotatory transformation of a cyclopropyl to an allyl cation(3). We now wish to report the results of a study of the thermal rearrangement of the related monocyclic systems, 1-bromo- and 1,1-dibromo-2,3-dimethylcyclopropanes; we have also examined the effect of electron impact on the latter compounds.



I a; X=Br, Y=H
b; X=H, Y=Br
c; X=Y=Br



II a; X=Br, Y=H
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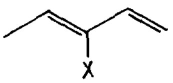

III a; X=H
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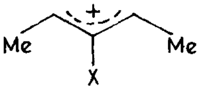

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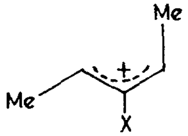

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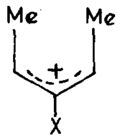

VI a; X=H
b; X=Br

When each of the three isomeric 1-bromo-2,3-dimethylcyclopropanes (Ia, Ib, and IIa) was heated in lepidine solution, trans-penta-1,3-diene (IIIa) was obtained as the sole volatile product, and could be isolated in moderate to good yield (see Table 1). The order of the rates of rearrangement of the three isomers (Ib > IIa > Ia, see table 1) is in accord with the order reported(4) for the solvolysis rates of the 2,3-dimethylcyclopropyl tosylates. It is noteworthy that Ia, which corresponds stereochemically to the reactive endo-isomer of 6-chlorobicyclo[3,1,0]hexane, was the least reactive isomer. This is presumably because steric compression rather than ring-strain is a critical factor in determining the energy of the transition state. Thus the order of the rates of rearrangement of the three isomeric dimethylcyclopropyl bromides correlates with that of the stabilities (from the point of view of steric interaction) of the intermediate allylic cations (IVa, Va and VIa) expected(3) for a concerted disrotatory process.*

Similarly, when either of the isomeric 1,1-dibromo-2,3-dimethylcyclopropanes (Ic and IIb) was heated in lepidine solution, 3-bromopenta-1,3-diene (IIIb or its cis-isomer) was the sole volatile product obtained. The observation that the ease of rearrangement of Ic was greater than that of IIb (see table 1) is again evidence for a concerted disrotatory process as the intermediate cation (IVb) would be expected to be of lower energy than Vb. It is also reasonable that Ic should have rearranged more slowly than Ib as the bromo-substituent would be expected(5) to destabilize the intermediate cation IVb with respect to IVa.

TABLE 1. Action of Heat on 20% (w/w) Solutions of 1-Bromo- and 1,1-Dibromo-2,3-dimethylcyclopropanes in Lepidine.

Compound	Temp (°C)	Time[a] (min)	Yield[b] (%)
Ia	185	165	50
Ib	127	10	66
Ic	185	10	55
IIa	185	10	48
IIb	185	30	16

[a] Time required for complete reaction of starting material, as indicated by g.l.c. [b] Isolated yield of IIIa or IIIb (or its cis-isomer).

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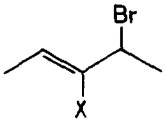
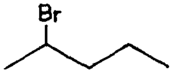
[*] cis-Penta-1,3-diene is the expected product from the concerted rearrangement of Ia in lepidine solution. A possible rationalization of the formation of the trans-diene (IIIa) involves the assumption that the cis,cis-cation (VIa) was formed first, and that it isomerized to Va before proton loss occurred.



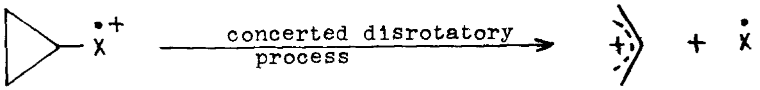
VII a; X=H
b; X=Br



VIII

The results obtained when the substrates were heated in the absence of base were more complicated. When Ib was heated at 165°, no unchanged starting material remained after 15 min, and the expected trans-4-bromopent-2-ene (VIIa) was the sole volatile product. Although, as anticipated, Ia was thermally more stable than Ib, it underwent reaction at 200-205° to give 2-bromopentane (VIII), the dihydro-derivative of VIIa. The third isomer (IIa) rearranged at an intermediate rate to give a mixture of VIIa and VIII. Both the dibromo-compounds (Ic and IIb) rearranged to give a mixture of trans-3,4-dibromopent-2-ene[1] (VIIb) and an unidentified product; as expected, Ic rearranged more readily (165 min at 160°) than IIb.

Scheme 1



We previously noted$^{(1)}$ that the mass spectra of endo- and exo-6-chlorobicyclo[3,1,0]hexanes differed considerably. Although this was possibly due to thermal rearrangement of the endo-isomer in the mass spectrometer, it was conceivable that the loss of a halogen atom from the molecular ion (M^+) was a concerted process (see Scheme 1), and thus subject to the same stereochemical control as the thermal rearrangement reaction. The five bromocyclopropane derivatives considered in this article all give weak molecular ions, but the ratio of the peak heights of $(M-Br)^+$ and M^+ varies widely. It can be seen from table 2 that this ratio increases as the process indicated in Scheme 1 becomes more

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[1] On the basis of chemical and spectroscopic evidence, this product appears to be the trans- and not the cis-isomer as suggested by Duffrey et al. (D. C. Duffrey, J. P. Minyard and R. H. Lane, J. Org. Chem. 31, 3865 (1966)).

favourable. Although the ratios appear to be independent of electron beam energy, it would seem desirable to obtain spectra at a low temperature, with a photo-ionization source, before discussing the significance of the present data further.

TABLE 2. Fragmentation of Molecular Ions of 1-Bromo- and 1,1-Dibromo-2,3-dimethylcyclopropanes.

Compound	$(M-Br)^+/M^+$
Ia	8.3
Ib	63
Ic	13
IIa	29
IIb	4.8

Acknowledgement

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