

CYCLOPROPANE RING CLEAVAGE WITH  
N-BROMOSUCCINIMIDE

M. Gaitonde, P.A. Vatakencherry\* and Sukh Dev  
National Chemical Laboratory, Poona (India)

(Received 8 June 1964)

In analogy with the well-established allylic brominations with N-bromosuccinimide (NBS), the action of this reagent on some cyclopropane derivatives has been investigated in an effort to detect any substitution on a carbon  $\alpha$  to the three-membered ring. However, in the case investigated only products resulting from the cleavage of the cyclopropane ring could be isolated (1). These findings are summarised below.

Tricyclene and NBS

A chloroform solution of tricyclene and NBS, on being refluxed and illuminated for 24 hr, yielded as the major product, a bromide,  $C_{10}H_{15}Br$  (b.p.  $84^{\circ}/7$  mm,  $n_D^{30}$  1.5122,  $d_4^{30}$  1.2168) in a yield of 50-60%. That the product

---

\*Department of Organic Chemistry, Indian Institute of Science, Bangalore. Preliminary work on this problem was carried out at Bangalore (P.A. Vatakencherry, Ph.D thesis, Bombay University, 1958) when the senior author (SD) was located there.

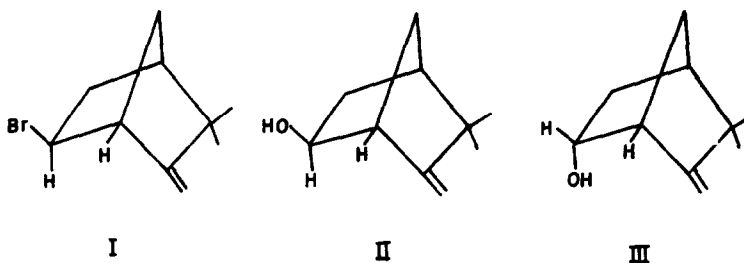
must be represented by I was clear from its spectral characteristics: IR,  $\nu_{\text{C}=\text{CH}_2}$  (3030, 1770, 1650 and  $890\text{ cm}^{-1}$ ), gem-dimethyl ( $1360$  and  $1389\text{ cm}^{-1}$ ); PMR<sup>+</sup>, only two methyls (both quaternary, sharp singlets at 62 and 65 cps), two vinyl protons (singlets at 280 and 296 cps), one proton on a carbon linked to Br (quartet centred at 232 cps; X part of ABX spectrum,  $J_{\text{AX}} = 8$  cps,  $J_{\text{BX}} = 4$  cps), one allylic tertiary proton (singlet at 176 cps, half-band width = 4 cps); since the signal for the allylic tertiary proton is unsplit, it would mean that this proton and the hydrogen on the carbon carrying bromine must make a dihedral angle close to  $90^\circ$  and consequently the bromine must have the exo-configuration as shown in I. This is borne out from the NMR data for the two epimeric alcohols obtainable from I. Hydrolysis of the bromide in aq. dioxane in the presence of  $\text{Li}_2\text{CO}_3$  yielded a single alcohol<sup>\*</sup>,  $\text{C}_{10}\text{H}_{16}\text{O}$ , (m.p.  $54-55^\circ$ ; 3,5-dinitrobenzoate, m.p.  $103-104^\circ$ ), the PMR spectrum of which again showed the allylic tertiary proton (at 155 cps) as essentially unsplit (half-band width = 4 cps) and hence must be the exo-isomer (II). The alcohol (II), on oxidation with pyridine-chromic acid, yielded the corresponding ketone<sup>\*</sup> (m.p.  $75-76^\circ$ ,  $\nu_{\text{C}=\text{O}}$

---

<sup>+</sup>The spectra were taken on 10-20% solutions in  $\text{CCl}_4$  on a Varian A-60 spectrometer; the signals are recorded in cps from tetramethylsilane as zero.

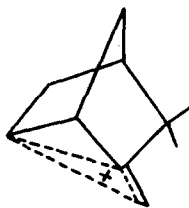
<sup>\*</sup>These compounds have been described in the literature (2). The present work confirms these structures and establishes the configuration of the alcohol.

1754  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}^{\text{EtOH}}$  294  $\text{m}\mu$ ,  $\epsilon = 291$ ; semicarbazone, m.p.



205-206° dec.; 2,4-dinitrophenylhydrazone, m.p. 195-197°), which on reduction with tri-*ter*-butoxy lithium aluminium hydride yielded the epimeric alcohol (III), m.p. 100-101°, which, as expected, showed in the PMR, the allylic tertiary proton (centred at 160 cps) as a doublet ( $J = 5$  cps).

The facile hydrolysis of the bromide (I) to yield alcohol (II) with retention of configuration is clearly due to the participation of the suitably located olefinic



IV

linkage (3,4,5,6) leading to the formation of the homoallylic cation (IV)<sup>2+</sup>

#### Carane and NBS

Carane (V), on being treated with NBS and benzoyl peroxide in  $\text{CHCl}_3$  at reflux and under illumination, yielded a complex mixture of products (Chart 1) in which olefins (VI) and (VII) and m- and p-cymene could be identified. The bromide fraction (b.p.  $81^\circ/3$  mm,  $n_D^{30}$  1.4970) which analysed for  $\text{C}_{10}\text{H}_{15}\text{Br}$ , though showing a single peak on several gas-liquid chromatography columns, was clearly a mixture as revealed by its NMR spectrum; the latter was consistent with its being a mixture of VIII and IX, in which one component exceeded the other by a factor of two. The bromide mixture reacted quantitatively with

---

\* For a detailed discussion of homoallylic and bicyclobutenium ions see: S. Winstein and E.M. Kosower, J. Amer. Chem. Soc. **81**, 4399 (1959).

† The importance of the non-classical ion (A) in this reaction can be assessed from a study of the hydrolysis



of the optically active bromide (I) or a similar reaction. The alcohols (II and III), together with their dihydro derivatives form an interesting series for a study of homoallylic participation in solvolytic reactions.

alcoholic  $\text{AgNO}_3$ , but failed to react appreciably with  $\text{Li}_2\text{CO}_3$  in aq. dioxane at  $\sim 100^\circ$ .

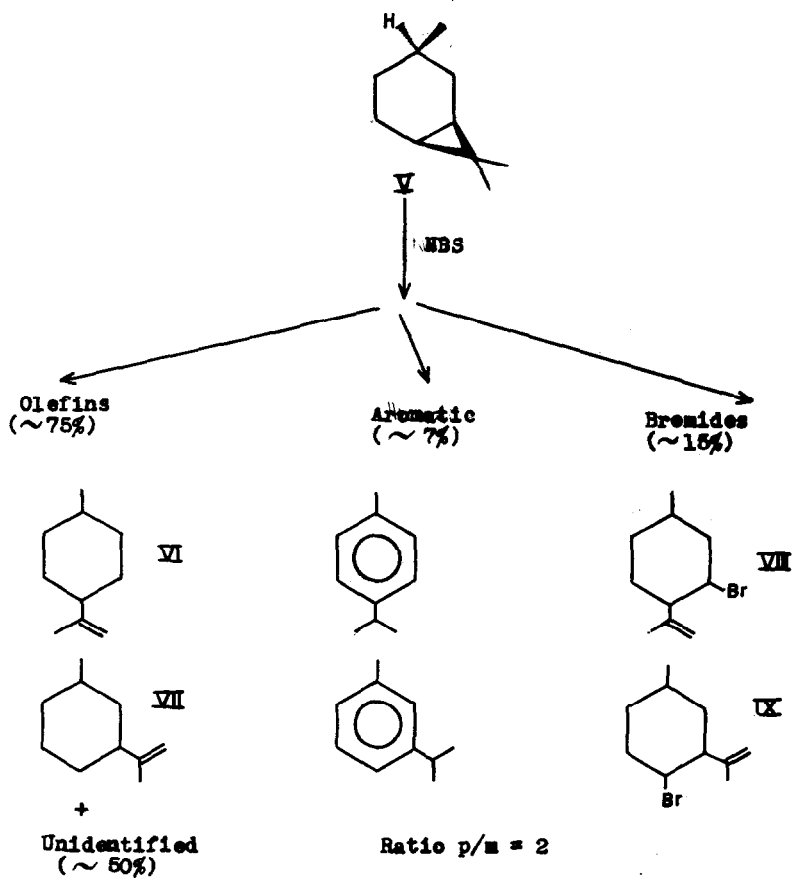


CHART 1

The mechanistic implications of this cleavage reaction (by NBS) will be discussed elsewhere.

#### REFERENCES

1. cf. H.G. Klivila, S.C. Gaywood, W.F. Boyce and F.L. Langwin, J. Amer. Chem. Soc. 77, 5175 (1955).
2. P. Lipp, Chem. Ber. 80, 165 (1947).
3. S. Winstein, M. Shatavsky, C.J. Norton, and R.B. Woodward, J. Amer. Chem. Soc. 77, 4183 (1955).
4. W.G. Woods, R.A. Carboni and J.D. Roberts, J. Amer. Chem. Soc. 78, 5653 (1956).
5. E.E. van Tanelen and C.I. Judd, J. Amer. Chem. Soc. 80, 6305 (1958).
6. C.H. dePuy, I.A. Ogawa and J.C. McDaniels, J. Amer. Chem. Soc. 82, 2397 (1960).