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ALLYLIC REARRANGEMENT OF EXO-1-METHYL-3,4-DIBROMO-BICYCLO[3.2.1]OCTENE-2.(1)

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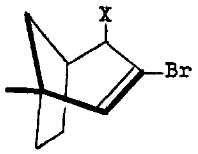
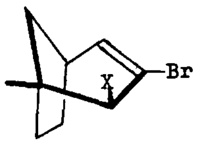
In the course of a study concerned with the addition of dihalocarbenes to bicyclic olefins, we found that the interaction of dibromocarbene and 1-methylnorbornene afforded the isomeric allylic bromides I and II. Furthermore, the joint reduction of I and II, followed by acid hydrolysis of the reduced products, furnished one product, 1-methylbicyclo-[3.2.1]octanone-3.(3)

We now wish to report our findings on the stereochemical outcome of the metal hydride reduction of I.



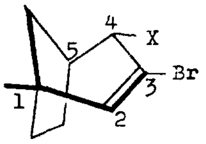
I X = Br
VII X = OH



II X = Br
VIII X = OH

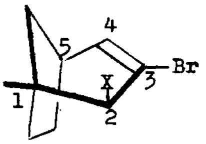
<u>Exo</u>-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 (I) possesses features of geometry which make it a model cyclohexenyl substrate.(4) The bridgehead methyl group marks the position of the double bond and the ethane bridge holds the attached cyclohexenyl moiety in a rigid half-chair-like conformation.

The treatment of I with powdered lithium aluminum hydride in boiling ether for twelve hours gave an oil of empirical formula $C_9H_{13}Br$. The n.m.r. spectrum(5) of the product showed a widely spaced doublet at 370 c.p.s. and a finely split singlet at 355 c.p.s. which are ascribed to two kinds of vinyl proton (see Table). These findings accord with the formation of the two vinyl bromides III and IV. In III the signal of the vinyl proton on C_2 (which has no vicinal protons) displays a finely spaced doublet which is due to interaction with a remote proton.(6) On the other hand, in IV, the signal of the vinyl proton (on C_4) exhibits a wide doublet due to interaction with the proton on C_5.



III X = H

V X = D



IV X = H

VI X = D

Integration of the respective vinyl signals due to III and IV in the product afforded the isomeric composition. Several reductions of I with lithium aluminum hydride showed that reductive debromination occurred consistently with only 84% allylic rearrangement.

Furthermore, reduction of I with lithium aluminum deuteride gave 4-deuterio-1-methylbicyclo[3.2.1]octene-2 (V) and 2-deuterio-1-methylbicyclo[3.2.1]octene-3 (VI).(7) Similarly, the isomeric composition was determined by integration of the clearly distinct vinyl signals of V and VI (see Table). The whole product consisted of 84% of VI and 16% of V.

TABLE

N.m.r. Spectral Data(5) of 1-Methylbicyclo[3.2.1]octene Derivatives

Compound	Signal (in c.p.s. from TMS) due to the	
	Allylic	Vinyl Protons
I	266 d w $^3J = 2.8$	363 d $^4J = 1.4$
III	-	355 s w
IV	-	370 d w $^3J = 7.0$
V	-	356 s w
VI	-	371 d w $^3J = 7.0$
VII	232 d w $^3J = 3.0$	371 s w
VIII	217 s w	386 d w $^3J = 7.0$

s = singlet, d = doublet, w = broadened due to long range coupling.(6) Coupling constants (J) are in c.p.s.

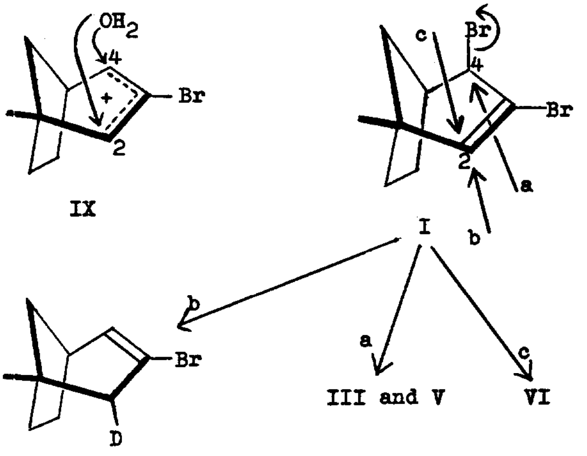
The infrared absorption spectra(8) of the V - VI mixture exhibited two sets of maxima at 2184, 2169 cm.$^{-1}$ (weak) and 2132 (strong), 2101 cm.$^{-1}$ (weak), due to C-D stretching frequencies. The major component, VI, was obtained pure by preparative vapor phase chromatography and exhibited maxima at 2132 (strong) and 2101 cm.$^{-1}$ (weak). The stereochemistry of the deuterium substituents in V and VI, endo at C_4 and exo at C_2 respectively, was assigned by deduction and accordingly with reservation (see below).

In comparison with the above results, the behavior of exo-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 (I) under mild conditions for carbonium ion development was quite different. Treatment of I at 25° with silver nitrate in aqueous acetone or with alumina in moist ether produced, after five minutes and one week respectively, a white solid of empirical formula $C_9H_{13}OBr$. The n.m.r. spectrum showed a finely split singlet at 371 c.p.s. and a broad doublet at 386 c.p.s. characteristic of two kinds of vinyl protons. A doublet and a singlet appeared at 232 and 217 c.p.s. respectively indicative of two kinds of allylic protons (see Table). These findings accord with a mixture of exo-1-methyl-3-bromo-4-hydroxybicyclo[3.2.1]octene-2 (VII) and exo-1-methyl-2-hydroxy-3-bromo-bicyclo[3.2.1]octene-3 (VIII).(9) VII and VIII were formed consistently in equal amounts in several different experiments. The isomeric composition was assessed from the n.m.r. spectrum of the mixture and corroborated by quantitative chromatographic separation.(10)

The ionic reactions of I under mild conditions clearly involve the stable symmetrical allylic cation IX. Hydroxyl anion can annihilate the charge of IX by attack at C_2 or C_4. The formation of only the exo derivatives may be due to steric hindrance or the operation of some stereoelectronic factor.

On the other hand, the product composition indicates that the reductive debromination of I by metal hydrides does not involve an ion such as IX. The formation of the minor products III and IV, (no allylic rearrangement), necessitates attack from the endo side by hydride or deuteride ion at C_4 of I (see Fig. 1, arrow a). The reduction with allylic rearrangement can proceed by hydride or deuteride ion attack at C_2 from the endo or exo directions (Fig.1, arrows b and c), to give X and VI. However, the formation of X can be ruled out by a consideration of the infrared data of the mixture of reduced products,and the separate allylically rearranged product which contain deuterium (see above). Accordingly, the mechanism for the reduction of I proceeds mainly via an SN2' or SNi' process and to a smaller extent via an SN2 or SNi process.

Finally, it should be pointed out that the foregoing results are consonant with the qualitative findings of Stork and Clarke,(11) who studied the lithium aluminum hydride reduction of a system similar to I, viz., the α- and β-halocodides.



X Figure 1. Reduction of I.

A detailed discussion of allylic rearrangements in the bicyclo[3.2.1]octene-2 skeleton and related structures will be undertaken in the full paper.

Acknowledgements

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References

(1) To be regarded as Part V of a series entitled "The Stereochemistry of the Bicyclo[3.2.1]octane System". For Part IV see ref. 6.

(2) Visiting Lecturer for the Summer Session, 1964; on leave from the Institut de Chimie, Strasbourg, France.

(3) C. W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, J. Amer. Chem. Soc., **87**, 2183 (1965).

(4) *Exo* designates the side of the molecule which bears the methylene bridge.

(5) N.m.r. spectra were determined at 60 Mc. on a Varian Associates A-60 spectrometer. All compounds were investigated as approximately 10% solutions in carbon tetrachloride with tetramethylsilane (TMS) as internal standard.

(6) For an account of long range coupling in derivatives of bicyclo[3.2.1]octene-2, see C. W. Jefford, B. Waegell and K. Ramey, J. Amer. Chem. Soc., **87**, 2191 (1965).

(7) All new compounds cited gave acceptable elemental analyses.

(8) Infrared spectra were determined in carbon tetrachloride solution on a Beckman I.R. 9 spectrometer.

(9) The *exo* stereochemistry was arrived at by consideration of the chemical shifts and coupling constants of the allylic protons. A pertinent discussion concerning the assignment of allylic stereochemistry

of the epimeric 3-bromo-4-hydroxybicyclo[3.2.1]oct-2-enes will be found in ref. 3. See also footnote 17 of ref. 6.

(10) VII and VIII had m.p.'s of 60° and 74-75° respectively.

(11) The α-chloro- (**i**) and β-halocodides (**ii**), (which contain cyclohexenyl moieties most probably constrained in half-boat and half-chair conformations respectively (T. Rüll, *Bull. Soc. chim. France*, 586 (1963)), have been treated with lithium aluminum hydride. Although the total product was not examined, it was stated that **i** produced only Δ^6-desoxycodeine and that from **ii** only Δ^7-desoxycodeine could be isolated, (G. Stork and F. H. Clarke, *J. Amer. Chem. Soc.*, **78**, 4620 (1956)).