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THE STEREOCHEMICAL CONSEQUENCES OF THE ADDITION OF CHLOROCARBENE TO NORBORNENE

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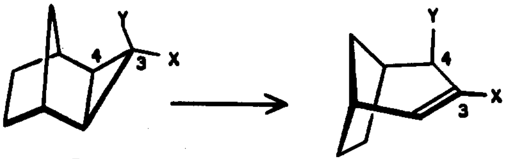
The addition of dihalocarbenes to norbornene proceeds stereospecifically to form the _exo_-cyclopropane adduct (I) which can undergo thermal rearrangement to _exo_-3,4-dihalobicyclo (3.2.1) octene-2 (II) [1].



I II

Y = X = Cl, Br

Whatever the nature of the intermediate or transition state in the rearrangement, it is clear that during the conversion of I to II, C_3 moves in the _endo_ direction and Y migrates to the _exo_ C_4 position.

The observations are in accord with a recent hypothesis concerning the transformation of cyclopropyl to allylic systems[2]. However, it seemed to us that a better test of the hypothesis should be available from a study of the addition of chlorocarbene to norbornene and the propensity of rearrangement of the adducts so obtained.

Consequently, chlorocarbene and norbornene were allowed to interact according to the procedure of Closs[3]. The addition afforded a mixture of four products. The chief features of the nuclear magnetic resonance spectrum[4] of the mixture were a multiplet between 5.32 - 6.18 ppm, characteristic of a pair of vicinal vinyl protons[5], and two triplets at 4.50 and 4.22 ppm (both 6.5 cps wide, $^3J_{large}$ = 4.0 and $^3J_{small}$ = 2.5 cps indicative of two different allylic protons. Furthermore, at 2.83 and 2.75 ppm there appeared two narrow triplets (both 3.0 cps wide) due to two different deshielded cyclopropyl protons.

By preparative vapour phase chromatography [6] two of the products were obtained pure with no difficulty[7]. From a consideration of their nmr spectra (Table) their structures were assigned as <u>exo</u>-<u>anti</u> and <u>endo</u>-<u>syn</u>-3-chlorotricyclo(3.2.1.0^{2,4})octanes (III and IV). The same small coupling constant (^3J = 1.5 cps) exhibited by the cyclopropyl proton on C_3 in both III and IV requires that the cyclopropyl protons at the ring junction must be <u>trans</u> to the proton at C_3 [9]. The rest of the data in the table are perfectly compatible with the tricyclo(3.2.1.0^{2,4})-octane skeleton [10].

Unfortunately, the other two components of the mixture decomposed during column and vapour phase chromatography. Accordingly, the initial mixture was gently heated with silver nitrate in aqueous acetone. The product of the reaction was submitted to chromatography over neutral alumina. Elution with pentane resulted in the separation of compounds III and IV as a mixture. Subsequent elution with ether afforded a colourless solid which was shown to be identical with exo-3-hydroxybicyclo(3.2.1)octene-2 (same nmr and infrared spectra and undepressed mixed mp).

The findings may be rationalized as follows. Initially chlorocarbene adds to norbornene to form all four possible adducts(III - VI)[11]. However, two of these cyclopropane adducts (V and VI) possess the critical molecular geometry for facile thermal rearrangement in a disrotatory process to generate their corresponding exo-and endo allylic derivatives (VII and VIII). The presence of exo-and endo-3-chlorobicyclo(3.2.1)octenes-2 (VII and VIII) accounts for the allylic triplets at 4.22 and 4.50 ppm respectively. Both VII and VIII on treatment with silver ion undoubtedly afford the same allylic carbonium ion IX, which has been shown previously to afford exo-3-hydroxybicyclo(3.2.1)octene-2 on hydrolysis[1,12].

The two other cyclopropyl chlorides, III and IV remain intact even at 150° (chromatography conditions) and in the presence of silver ion, thereby completely substantiating the Hoffman Woodward hypothesis.

Acknowledgements

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TABLE

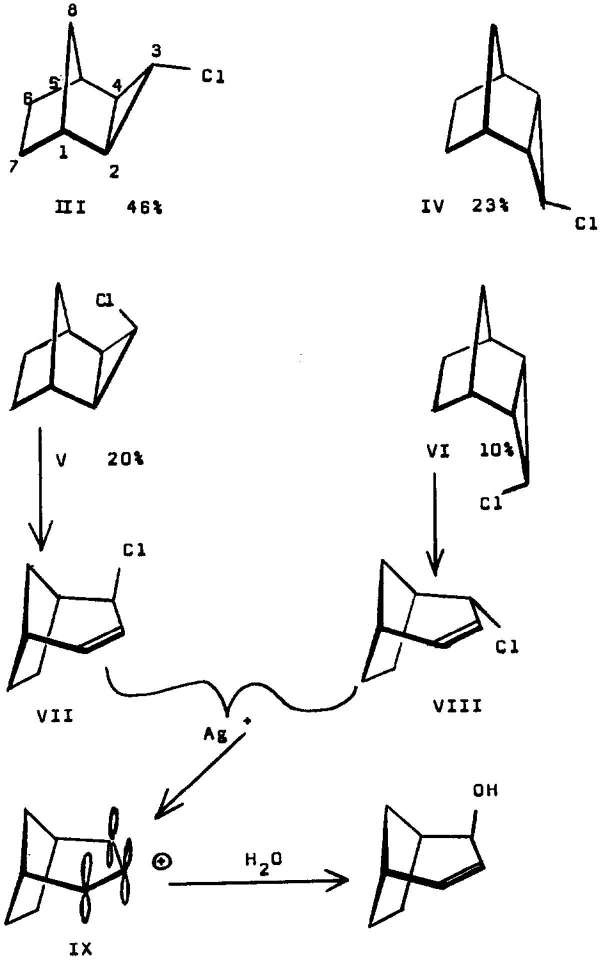
nmr Spectral Data of exo-anti and endo-syn-3-chlorotricyclo $(3.2.1.0^{2,4})$octane (III and IV)

Major Isomer (1)	Minor Isomer (2)	Intensity	Assignment
T at 2.83 ppm ($^3J \sim 1.5$ cps)	T at 2.75 ppm ($^3J \sim 1.5$ cps)	1 H	C_3
S at 2.41 ppm	S at 2.43 ppm	2 H	C_1, C_5
S at 1.36 ppm	S at 1.38 ppm	4 H	C_6, C_7
S at 1.08 ppm	S at 1.17 ppm	2 H	C_2, C_4
D at 0.91 ppm ($^2J \sim 10.5$ cps)	D at 0.94 ppm ($^2J \sim 10.5$ cps)	1 H	C_8
D at 0.66 ppm ($^2J \sim 10.5$ cps)	D at 0.82 ppm ($^2J \sim 10.5$ cps)	1 H	C_8

(1) Shorter chromatographic retention time, C-Cl band at 782 cm^{-1} in the infrared spectrum.

(2) Longer chromatographic retention time, C-Cl band at 712 cm^{-1} in the infrared spectrum.

T = Triplet S = Singlet D = Doublet


8
3
Cl
5
4
6
7
1
2
III 46%
IV 23%
Cl
Cl
V 20%
VI 10%
Cl
Cl
Cl
VII
VIII
Ag+
⊕
H2O
OH
IX

References

1 - C.W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, J. Amer. Chem. Soc., 87, 2183 (1965) and references cited therein.

2 - R. Hoffman and R.B. Woodward, J. Amer. Chem. Soc., 87, 395 (1965).

3 - G.L. Closs and L.E. Closs, J. Amer. Chem. Soc., 82, 5723 (1960).

4 - Spectra were determined on a Varian Associates A-60 nmr spectrometer at 60 Mcps in carbon tetrachloride solution containing tetramethylsilane (TMS) as a standard (TMS = 0.00 ppm).

5 - The multiplet consisted of a doublet of doublets at 6.02 ppm ($^3J_{large}$ ∿ 10.0 cps; $^3J_{medium}$ ∿ 6.5 cps) and a doublet of doubled doublets centred at 5.50 ppm ($^3J_{large}$ ∿10.0 cps, $^3J_{medium}$ ∿ 4.0 cps and J_{small} 1.5 cps).

6 - A column of 25 % cyano-silicone 1150 on "Chromosorb W" was used at 150° with helium flowing at a rate of 30 cc/min.

7 - Both products gave acceptable elemental analysis for $C_8H_{11}Cl$.

8 - Exo designates the side of the molecule which bears the methylene bridge (C_8). Syn and anti designate the orientation of the chlorine atom on C_3 with respect to C_8.

9 - a) J.D. Graham and M.T. Rogers, J. Amer. Chem. Soc., 84, 2249 (1962); G.L. Closs, R.A. Moss and J.J. Coyle, ibid., 84, 4985 (1962).

b) Although the chemical shifts for the protons on C_2, C_3, C_4 are distinctly different, the two 60 Mc spectra are sufficiently similar as to make differentiation between III and IV difficult. However, while waiting for the results of a complete spectral analysis, we have assumed that the major component was the exo anti structure (III).

10. - Cf. R.C. DeSelms and C.M. Comb, J. Org. Chem., **28**, 2206 (1963).

11. - The product composition was estimated from the chromatographic and nmr data and represents the average of several addition experiments.

12. - C.W. Jefford, S. Mahajan, J. Gunsher and B. Waegell, Tetrahedron Letters, Nº 28, 2333 (1965).