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STEREOCHEMICAL CONSEQUENCES OF THE REACTION OF MONOHALOCARBENE WITH NORBORNENE (1)

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Recently we reported that reaction of chlorocarbene with norbornene afforded four products which were attributed to <u>exo</u> and <u>endo</u> addition in the <u>syn</u> and <u>anti</u> senses (2). On the basis of further work, we now report that only <u>exo</u> addition in fact took place and that the product composition depends on the provenance of methyllithium used to generate the carbene. However, although two of the original structures are necessarily revised, the substantiation of the Hoffmann-Woodward hypothesis (3) concerning the stereospecificity of the ionic opening of cyclopropane remains firm.

Methyllithium is commonly prepared by the reaction of lithium with either i) methyl chloride or ii) methyl bromide. In the former case only a negligible amount of lithium chloride complexes with methyllithium, whereas in case ii) an equimolar methyllithium-lithium bromide complex is formed

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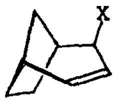
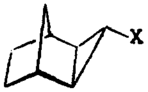
which is soluble in ether (4).

We now find that when pure methyllithium (from i) and methylene chloride are allowed to interact in the presence of norbornene only two products are formed; *exo*-4-chlorobicyclo[3.2.1]octene-2 (I) and *exo*-*anti*-3-chlorotricyclo-[3.2.1.$0^{2,4}$]octane (II). This behaviour contrasts to that observed earlier (2). When methyllithium-lithium bromide complex is used four products are formed. Two of these are compounds I and II, but the two others were found to be their bromo analogues (III and IV) (5).



I X = Cl

III X = Br



II X = Cl

IV X = Br

The tricyclic structures II and IV have very similar nuclear magnetic resonance spectra. The cyclopropyl protons (on C_3) both show distinctly as narrow downfield triplets ($^3J \sim 1.5$ c.p.s.), thereby indicating a *trans* arrangement of the C_3 proton with respect to the protons of the ring junction (6). Either the *anti*-*exo* or the *anti*-*endo*-3-halotricyclo-[3.2.1.$0^{2,4}$]octane structures can satisfy this stereochemistry. Conclusive proof for the *exo* configuration was provided by the reduction of compounds II and IV to *exo*-tricyclo[3.2.1.$0^{2,4}$]-octane identical to that prepared from norbornene by the Simmons-Smith procedure (7,8).

The structures of the exo-4-halobicyclo[3.2.1]octenes-2 (I and III) follow from their hydrolysis to exo-4-hydroxybicyclo[3.2.1]octene-2 (V) (9). Further, photohalogenation of bicyclo[3.2.1]octene-2 using N-bromosuccinimide and t-butyl hypochlorite afforded exo-4-bromo and exo-4-chlorobicyclo-[3.2.1]octene-2 which were identical to compounds III and I (10).

The addition and rearrangement processes can be summarised as follows. Depending on the source of methyllithium, monochlorocarbene is generated separately or together with monobromocarbene. The steric course of the carbene addition is exclusively exo, with a preference for products of anti configuration. The remarkable stability of the exo-anti adducts (II and IV), the non-appearance of the exo-syn adducts, but the presence instead of their stereospecifically rearranged products (I and III), constitute a striking exemplification of the predictions of Hoffmann and Woodward (3,11 and 12).

Acknowledgements

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References

(1) Part X, "The Stereochemistry of the Bicyclo[3.2.1]octane System". Ref.2 is to be regarded as Part IX. Presented at the Autumn Meeting of the Chemical Society, 21-22 Sept. 1966, Brighton, Sussex, England.

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(3) R.Hoffmann and R.B.Woodward, *J.Amer.Chem.Soc.*, **87**, 345 (1965); H.C.Longuet-Higgins and E.W.Abrahamson, ibid, **87**, 2045 (1965).

(4) Typical analyses (expressed as percentages by weight) of methyllithium in ethyl ether, formed by the two methods are:

	MeCl	LiBr	LiCl	Et_2O
i)	5.0	-	0.4	94.6%
ii)	5.0	19.8	-	75.2%

Data furnished by Foote Mineral Company, U.S.A.

(5) Separation was effected as described in ref. 2. Compounds II and IV gave acceptable elemental analyses. A typical reaction would involve 0.32, 0.25 and 0.25 M of norbornene, methyllithium and methylene chloride. Yields were about 14%. Product ratios were variable; with pure methyllithium, I and II were formed in a ratio of 1:6; with the complex, I,II,III and IV were formed in ratios of 5:10:2:5.

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(10) C.W.Jefford and E.Huang Yen, Tetrahedron Letters, No.37, 4477 (1966).

(11) Compounds II and IV were quite stable to aqueous silver ion and heat. Compound II, for example, remained unchanged after being heated in a sealed tube at 188-194° for 16 hours.

(12) Several examples of the selective cationic reactivity of cyclopropyl derivatives have been described recently. (cf. P.v R.Schleyer, G.W.Van Dine, U.Schollkopf and J.Paust, J.Amer.Chem.Soc., **88**, 2869 (1966) and references cited therein). An interesting parallel to the present work is provided by a study of the addition of monochlorocarbene to 7-oxanorbornene. The stereochemical course of the addition and rearrangement is the same as that reported here (private communication from L.Ghosez, University of Louvain, Belgium).