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STEREOCHEMICAL CONSEQUENCES OF THE ADDITION OF CHLOROCARBENOID TO SOME BRIDGED BICYCLIC OLEFINS(1)

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Chlorocarbenoid undergoes addition to bicyclo[2.2.2]octene-2, norbornene, 1-methyl- and 2-methylnorbornene with preferential anti stereoselectivity. The present report deals with the stereochemistry of the rearrangement of the adducts which were obtained.(2) The results are novel in that they provide further information concerning the electrocyclic transformation of cyclopropyl compounds to allylic derivatives.(3)

1-Methylnorbornene displayed similar reactivity to that of norbornene,(4) no syn adduct (I) was isolated, only the products of its rearrangement, viz. exo-1-methyl-4-chlorobicyclo[3.2.1]octene-2 (II) and exo-1-methyl-2-chlorobicyclo[3.2.1]octene-3 (III) in a ratio of 1.6:1.0. II and III proved impossible to separate in a pure state; however, their hydrolysis with aqueous silver nitrate afforded the isomeric hydroxy derivatives IV and V which were separated by column chromatography.(5) The anti-chlorotricyclic adduct (VI) was stable to heat and aqueous silver ion, despite the bridgehead methyl substituent, which formally, at least, could facilitate ionic rearrangement.(6)

A mixture of three products was formed from bicyclo[2.2.2]octene-2; the syn and anti adducts (VII and VIII) and the ring enlarged product IX. On heating the mixture, the syn adduct (VII) underwent ready rearrangement to

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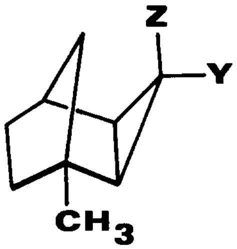
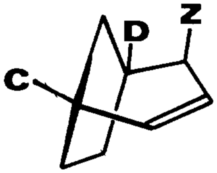


I Y = H, Z = Cl

VI Y = Cl, Z = H

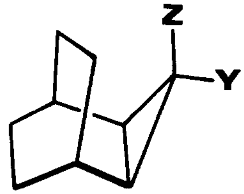


II C = CH_3, D = H, Z = Cl

IV C = CH_3, D = H, Z = OH

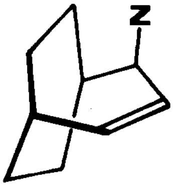
III C = H, D = CH_3, Z = Cl

V C = H, D = CH_3, Z = OH



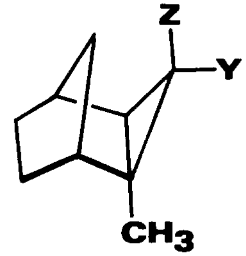
VII Y = H, Z = Cl

VIII Y = Cl, Z = H



IX Z = Cl

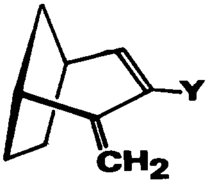
X Z = OH



XI Y = Cl, Z = H

XV Y = Z = Br

XIII Y = H, Z = Cl



XII Y = H

XIV Y = Br

2-chlorobicyclo[3.2.2]nonene-3 (IX), thereby providing the analogy for the presumed transposition of I to II and III.(7) Treatment of the mixture (VII, VIII and IX) with aqueous silver nitrate left the anti adduct VIII unchanged, but converted VII and IX to 2-hydroxybicyclo[3.2.2]nonene-3 (X). In a separate experiment, VIII was found to be stable to aqueous silver ion for 24 hours.

The treatment of 2-methylnorbornene with methyllithium and methylene chloride followed by aqueous work-up gave particularly interesting results. Just two products were obtained. The major product, 2-methyl-anti-3-chloro-exo-tricyclo[3.2.1.$0^{2,4}$]octane (XI) was easy to isolate and obtain pure on account of its exceptional stability both to heat and aqueous silver ion. Unfortunately, it proved impossible to obtain the minor product in a greater state of purity than 85% as it decomposed readily on attempted separation. However, by inspection of its n.m.r. and i.r. spectra, it was obviously the conjugated diene XII derived from the syn adduct XIII.(8) A related reaction is the formation of 2-methylene-3-bromobicyclo[3.2.1]octene-3 (XIV) from the addition of dibromocarbene to 2-methylnorbornene.(9) XIV must have arisen from the intermediate adduct XV by elimination of hydrogen halide. The present evidence indicates that the eliminative process is contingent on prior electrocyclic rearrangement of the cyclopropyl portion of the tricyclic precursors (XV and XIII), to their derived allylic cations, which then lose a proton.

All the foregoing additions were carried out with methyllithium prepared from methyl chloride. It was noticed that if methyl bromide was used as the source of methyllithium, then the bromo analogues were obtained in smaller yield,(10) along with the chloro products. However, no methylated products were isolated. These results are compatible with the intermediate formation of dichloromethyllithium which undergoes exchange with bromide ion to eventually yield both chloro-and bromocarbene. However, no exchange of halogen with the methyl of methyllithium apparently occurs.(11)

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References

1. Part XIV of a series entitled "The Stereochemistry of Bicyclo[3.2.1]-octane". Part XIII, C.W. Jefford and W. Wojnarowski, preceding paper.
2. Chlorocarbene or its chlorocarbenoid progenitor was prepared by the Closs procedure, (see ref. 5 of previous paper). In all cases a 25% excess of olefin was used. Yields were based on methylene chloride; 1-methylnorbornene and bicyclo[2.2.2]octene-2 gave yields of 6.7 and 5.5%. 2-Methylnorbornene (1.0 M) gave 14.6 g of crude product from 0.75 M of methylene chloride.
3. a) R. Hoffmann and R.B. Woodward, J. Am. Chem. Soc., **87**, 345 (1965);
   b) H.C. Longuet-Higgins and E.W. Abrahamson, ibid., **87**, 2045 (1965).
4. a) C.W. Jefford, E. Huang Yen and R.T. Medary, Tetrahedron Letters, No. **51**, 6187 (1966).
   b) C.W. Jefford and R.T. Medary, Tetrahedron, **23**, 4123 (1967).
5. Compounds IV, V, VI, VIII, X and XI all gave acceptable elemental analyses. Compounds II, III, VII and IX were not isolable. However their n.m.r. signals were sufficiently distinct to enable their structures to be established.
6. The structures of VI, X and XI were rigorously established by double n.m.r. experiments (C.W. Jefford and K.C. Ramey, unpublished results).
7. cf. L. Ghosez, P. Laroche and G. Slinckx, Tetrahedron Letters, No. **29**, 2767 (1967); and L. Ghosez, G. Slinckx, M. Glineur, P. Hoet and P. Laroche, ibid., No. **29**, 2773 (1967).
8. The infrared absorption spectrum of compound XII (neat) showed characteristic maxima at 878, 1605 and 1639 cm^{-1}. The n.m.r. spectrum showed resonances centered at 6.0 (2H) and 4.5 ppm (2H).
9. C.W. Jefford, S.N. Mahajan, J. Waslyn and B. Waegell, J. Am. Chem. Soc., **87**, 2183 (1965).
10. Yields of bromo compounds were no more than 50% of those of the analogous bromo compounds.
11. cf. R.M. Magid and J.G. Welch, Tetrahedron Letters, No. **27**, 2619 (1967).