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DEHYDROCHLORINATION OF <u>ENDO</u>-2-CHLORONORBORNANE-<u>EXO</u>-2,3-d_2

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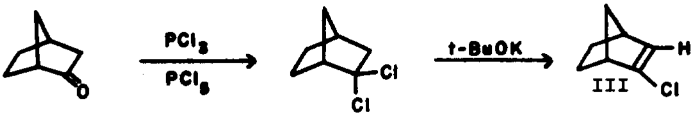
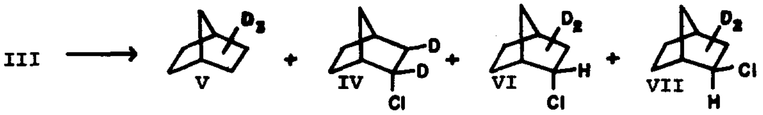
Bimolecular *cis* elimination reactions usually are only observed in cyclic systems because the rotation of the leaving group about the carbon atom is restricted (2a). In the norbornyl system a perfect *trans* elimination is impossible due to the lack of coplanarity (ca. 120° dihedral angle) of the leaving groups. In the light of this evidence, it was recently postulated (2b) that the product obtained from the reaction of *endo*-2-bromonorbornane-*exo*-3-d_1 (I) with *t*-hexoxide in *t*-hexanol would be 2-deuterionorbornene (II). This prediction

was based both on the presumed preference for *cis* elimination in the norbornyl system, and the added re-enforcement of a primary deuterium isotope effect which would be expected to outweigh the abstraction of the *exo*-proton. We felt therefore, that it would be of interest to determine whether *cis* elimination would indeed occur over *trans* elimination by preparing *endo*-2-chloronorbornane-*exo*-2,3-d_2 (IV) and performing the base elimination with *t*-hexoxide in *t*-hexanol. This question is significant since both *cis* (3) and *trans* (4) elimination mechanisms have been invoked to elucidate the mode of addition of ionic reagents to various cyclic olefins.

The model compound IV was prepared from norcamphor by known methods (5,6). The addition of deuterium to the double bond of norbornene in the presence of a heterogeneous catalyst is known to add *exo*-*cis* (7,8). Moreover, whether one or two substituents are attached to the double bond of norbornene, hydrogenation occurs *exo*-*cis* (9,10).

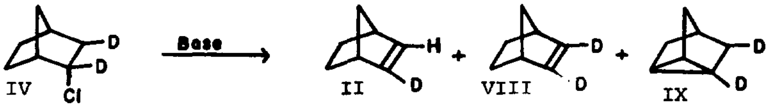


The addition of deuterium (11) to 2-chloronorbornene (III) forming IV, in an ether solvent with or without added sodium acetate, or other solvents, is accompanied by deuteriumolysis resulting in the formation of norbornane-d_3 (V), the major product, as well as rearranged chlorides



(VI and VII). The sample of norbornyl chloride employed for the elimination reaction contained 84% IV, 6% VI, and 10% VII as determined by integration of the n.m.r. spectra.

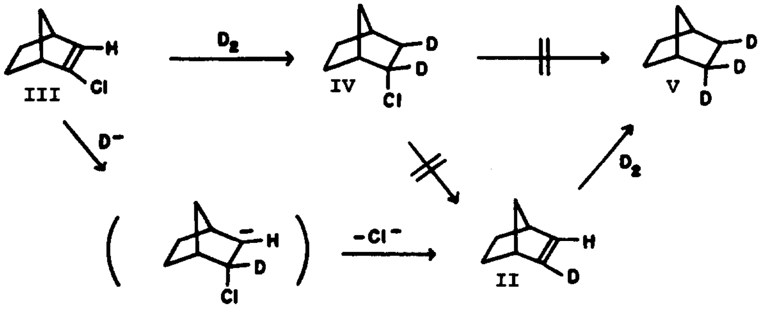
Dehydrochlorination of the mixture of IV, VI, and VII with t-hexoxide in t-hexanol (3) yielded a norbornene to nortricyclene ratio of 89:11 as determined by v.p.c. analysis. It is known (12) that under the same conditions, exo-2-chloronorbornane affords only norbornene;



thus the nortricyclene must only be forming from the endo-chloride.

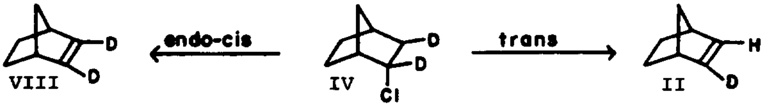
By a series of calculations (13) the percentages of II, and VIII were found to be 86:14, respectively. Thus trans elimination is favored over endo-cis by a factor of about 6.0.

The formation of V during deuteration can be rationalized by the following sequence of reactions. That V is not formed



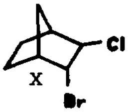
from IV either by an elimination of deuterium chloride to give II followed by deuteration or by deuteriumolysis of IV was demonstrated by the fact that IV was found to be unreactive under the reaction conditions.

Even though the primary deuterium isotope effect ($k_H/k_D \simeq 7.5$) favors the removal of the endo-2-proton by base from IV, steric considerations tend to make this mode of attack less likely. Of primary importance in the E-2 elimination reaction is the ease of removal of the

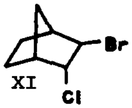


exo-3-deuterium atom and thus trans elimination is forced.

This result was not unexpected in light of recent work (14) on various 2,3-dihalonorbornanes. Even though it is well known that bromide is a better leaving group than chloride, it was found that dehydrohalogenation of X and XI gave 2-bromonorbornene and 2-chloronorbornene respectively.



X



XI

These results, previously rationalized by the favored *cis* elimination geometry, can also be explained by the preferential removal of an *exo* proton.

Examination (15,16) of the relative rates of elimination of 2,3-halonorbornanes by base to form 2-halonorbornenes showed that *exo*-*cis* elimination was faster than *trans*. From our results it is evident that the dehydrohalogenation of halonorbornanes would fall in the order *exo*-*cis* > *trans* > *endo*-*cis*.

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(11) V.p.c. analyses on different runs indicated that the ratio of *endo*- to *exo*-2-chloronorbornane was 92.1-95.8% in ether.

(12) Unpublished result.

(13) Detailed calculations are given in the dissertation of F. M. Sonnenberg, University of Iowa, 1966. Integration of the areas in the n.m.r. spectra of the olefinic and bridgehead protons with appropriate corrections for IX, and the contamination of IV with chlorides VI and VII--which would also afford norbornenes--provided the data necessary to obtain the ratio of II to VIII.

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