

STEREOCHEMISTRY OF THE CYCLOPROPYL-ALLYL REARRANGEMENTS.

II. THERMAL RING OPENING OF THE CHLOROFLUOROCARBENE-NORBORNENE ADDUCTS.

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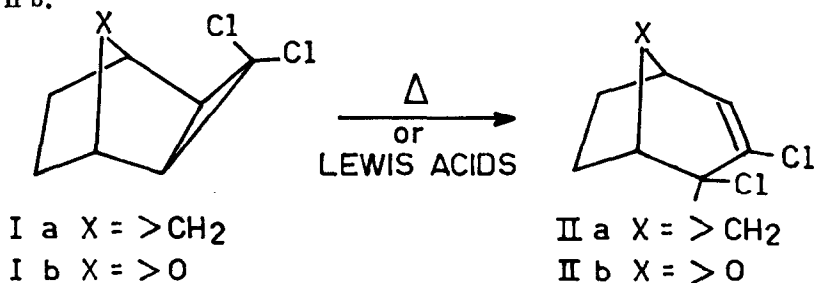
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The adducts I of dichlorocarbene to norbornene or 7-oxanorbornene have been shown⁽²⁾ to rearrange thermally or in the presence of Lewis acids to yield stereospecifically exo-3,4-dichlorobicyclo [3.2.1.] octene-2, IIa, or the corresponding 8-oxa derivative II b.



Previous studies^(2,3) of these rearrangements indicated a cationic mechanism involving simultaneous ionization and ring opening. In agreement with the Woodward - Hoffmann predictions⁽⁴⁾, the electrocyclic ring opening was shown to be a disrotatory process accompanied by the selective departure of the syn chlorine atom. The present study includes new data which demonstrate the importance of stereoelectronic factors on the thermal rearrangements of the chlorofluorocarbene-norbornene adducts.

The reaction of sym. difluorotetrachloroacetone with sodium methoxide⁽⁵⁾ in the presence of an excess norbornene in pentane (Fig. 1) gave a 12 % yield of two isomeric adducts $\text{C}_8\text{H}_{10}\text{ClF}$ in the ratio 1.1:1 (g.l.c. analysis on a 90 cm column packed with S.E. 30 on chromosorb W). Both isomers were obtained in pure form⁽⁶⁾ by fractionation through a 60 cm spinning band column. Structure III was assigned to the major component, n_D^{25} 1.4800, on the basis of its spectral properties. The infra-red spectrum showed the absence of unsaturation (no band in the 1600 cm^{-1} region) but exhibited absorption bands at 3040 cm^{-1} and 1015 cm^{-1} indicative of a cyclopropane ring: the proposed structure was confirmed by the comparison of the n.m.r. spectra⁽⁷⁾ of III and Ia: the signal of H_8 anti

in III appeared as a broad doublet at 9.17 τ (as the A part of an AB system, $J_{\text{gem}} = 10$ cps, the same proton in Ia absorbing at 9.24 τ with $J_{\text{gem}} = 11$ cps. Moreover the high field shift experienced by the syn H-8 proton in III (ca 8.45 τ as compared with Ia, 7.86 τ) indicated a different spatial environment (fluorine instead of chlorine).

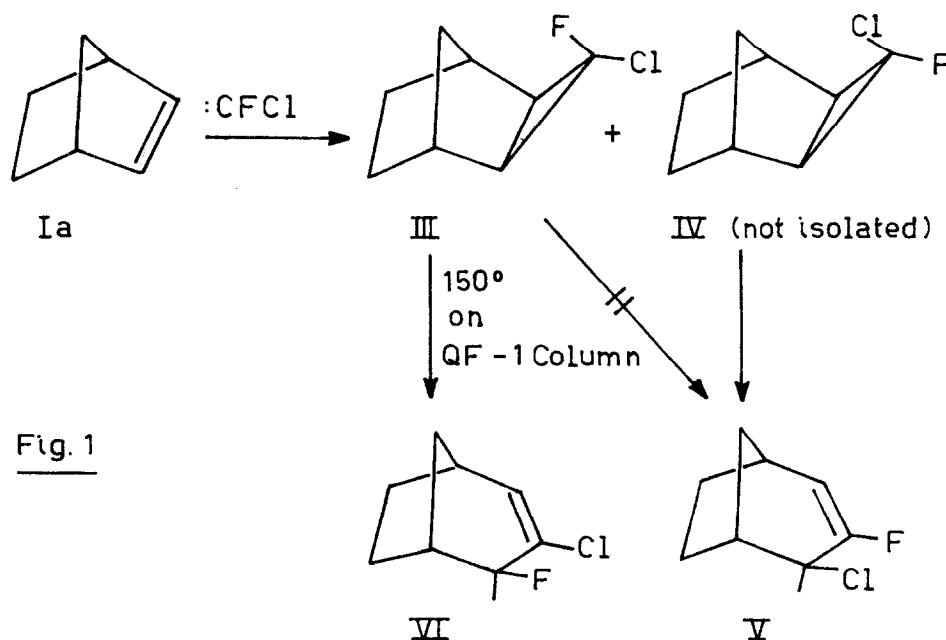
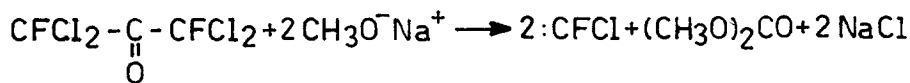


Fig. 1

The second component, $n_{\text{D}}^{25} 1.4962$, showed an absorption band at 1683 cm^{-1} attributable to a carbon-carbon double bond bearing a fluorine substituent. As expected for structure V, four groups of signals were observed in the n.m.r. spectrum: a complex absorption (6 methylene protons) between 7.65 τ and 8.95 τ ; a broad unresolved band (2 bridgehead H) of 17 cps half-height width centered at about 7.4 τ ; a doublet of doublets at 5.85 τ (1 allylic H) appearing nearly as a triplet ($J_{\text{H}_4\text{F}} = 3.4$ cps, $J_{\text{H}_4\text{H}_5} = 3$ cps, a value indicating an endo allylic proton^(2a, b)); two pairs of signals equal in intensities and further split by about 0.8 cps at 4.48 τ corresponding to one olefinic proton ($J_{\text{H}_2\text{F}} = 12.6$ cps, $J_{\text{H}_2\text{H}_1} = 7$ cps).

III could be excluded as possible precursor of V on the basis of the following data:

1) it remained unchanged under the experimental conditions used in its synthesis and iso-

lation;

2) its thermal decomposition in solution (e. g. 150° in nitrobenzene) lead only to tarry materials. However, when passed at 150°C through a 6 m column packed with QF-1 on chromosorb W, it did not rearrange to V but instead yielded a new isomer whose spectral properties indicated structure VI: absorption band at 1632 cm^{-1} in the infra-red; doublet at 3.75 τ (1 olefinic H, $J_{1,2} = 7$ cps); doublet of doublets at 5.65 τ assigned to an endo allylic H coupled to the fluorine atom ($J_{\text{H}_4\text{F}} = 50$ cps) and further coupled to the bridgehead H at C-5 ($J_{1,5} = 3$ cps); two multiplets corresponding respectively to the bridgehead (2 H at ca 7.33 τ) and methylene protons (6 H between 7.8 and 9 τ).

The other tricyclic isomer IV seems thus the logical precursor of V. The striking difference of thermal stability between III and IV is best explained in terms of stereoelectronic factors. A concerted disrotatory process leading to the cis allylic configuration must involve the migration of the syn halogen⁽⁴⁾. Thus it is obvious that IV, having the best leaving group in the appropriate configuration, should rearrange much more readily than III. It is noteworthy that the rearrangement of III involves the heterolytic breaking of C-F bond instead of a C-Cl bond. This result can be taken as a confirmatory evidence for a concerted ring opening with inward rotation of the two C-C bonds: breaking the C-Cl bond would require either the outward rotation of the C-C bonds which is here impossible for steric reasons, or the formation of a highly strained classical cyclopropyl cation followed then by the inward rotation of the C-C bonds.

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