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REACTION OF TETRACYCLO[3.3.0.$0^{2,4}$.$0^{3,6}$]OCT-7-ENE WITH HCL AND DCL; SUCCESSIVE FORMATION OF *EDGE*- AND *CORNER*-PROTONATED CYCLOPROPANES

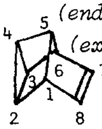
I.D.C. Rood and G.W. Klumpp*
Scheikundig Laboratorium der Vrije Universiteit, Amsterdam, The Netherlands

Abstract The title compound (I) is protonated at C(4). Product ratios depend on the solvent and are interpreted in terms of the opened, *edge*-protonated and *corner*-protonated forms, respectively, of the protonated cyclopropane ring of I. One of the *corner*-protonated forms is credited with laticyclic participation of the double bond.

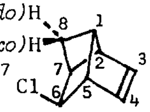
Many cations $[(CH)_7CH_2]^{\oplus}$ are known.[1,2] Some of them have played landmark roles in the definition of new concepts of bonding and neighbouring group participation.[3] Protonation of tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct-7-ene (I)[4] provides a new entry into this family of valence isomers. We were especially interested in the way in which the cyclopropane ring of the highly strained olefin I might be involved therein. Following our earlier work on the unimolecular thermal[5] and photochemical[6] rearrangements of I we therefore undertook to study its reaction with HCl and DCl. Reaction with HCl gave II-VI as the products of kinetic control. Results obtained with DCl are given in Table 1.

Protonation of I takes place at C(4) exclusively and II-VI result from breaking of a peripheral bond of the cyclopropane ring. UV photoelectron spectroscopy and Hartree-Fock-Slater calculations have shown the e_A Walsh orbital of the cyclopropane ring of I to be of exceptionally high energy and to have its maximum amplitude at C(4).[7] Thus, the formation of II-VI and the absence of products derived from protonation at C(2)[C(3)] might indicate FMO controlled protonation. An additional factor favouring cleavage of the C(2)C(4)[C(3)C(4)] bond may be that more strain is relieved by this process than by cleavage of the bond between C(2) and C(3).[8] Protonation of deltacyclane (VIII) opens both kinds of cyclopropane ring bonds with equal ease.[9] In VIII the Walsh orbitals e_A and e_S are nearly degenerate[7] and there is little difference in strain release upon breaking the two kinds of cyclopropane ring bonds. Preferential protonation of the cyclopropane ring in molecules containing also a strained double bond has precedent.[10]

Insight into the various modes of cleavage of the cyclopropane ring can be gained from the influence of the solvent on both, the product distribution and the stereoselectivity of deuteration (see Table 1 and Scheme 1). Whereas, in electrophilic cyclopropane opening, the carbon atom attacked by the electrophile can be subjected to retention as well as to inversion of configuration, inversion of configuration usually predominates by a wide margin at the carbon atom to which the nucleophile becomes attached.[11] The main product from I and DCl in diethyl ether, *exo-8-d*-II is at variance with this guide-line. The *cis* addition by which *exo*-8-*d*-II is formed is highly reminescent of *cis* additions of acids to alkenes observed in nonpolar media.[12] Like the latter it may occur through the very rapid collapse of a tight ion pair (IX, Scheme 1) formed itself *via* one-step ring opening by $D^{\oplus}$ with retention. The small amount of *endo*-8-*d*-II could have resulted from the epimer of IX(X) produced by one-step ring opening with inversion. Direct, one-step ring opening is considered the more favoured the greater the driving force for ring opening.[11] In the case of I the latter is provided by the much larger than normal amount of strain released by cleavage of C(2)-C(4)[C(3)-C(4)].[8] Furthermore, under conditions where stabilization of $Cl^{\ominus}$ by solvent is weak a high degree of C-D bond making is necessary to balance ionization. *Exo*-8-*d*-III is the product expected from *edge*-deuterated I (XI) whereas *endo*-8-*d*-III together with an equal amount of *exo*-8-*d*-III could be furnished by symmetrical *corner*-deuterated I (XII). Type-IV products have been associated before with the intermediacy of XIII,[13] which embodies the yet seldom encountered mode of laticyclic interaction of three ribbons of orbitals. Since the difference between structures XII and XIII is small the nature of XII as a discrete energy minimum might be questioned. Unsymmetrical *corner*-deuterated I (XIV) could be an alternative precursor of *endo*-8-*d*-III and XIII, respectively.[14]



I



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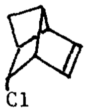

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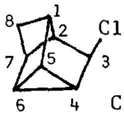

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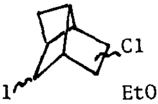

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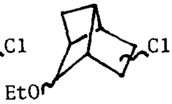

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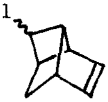


VII


VIII

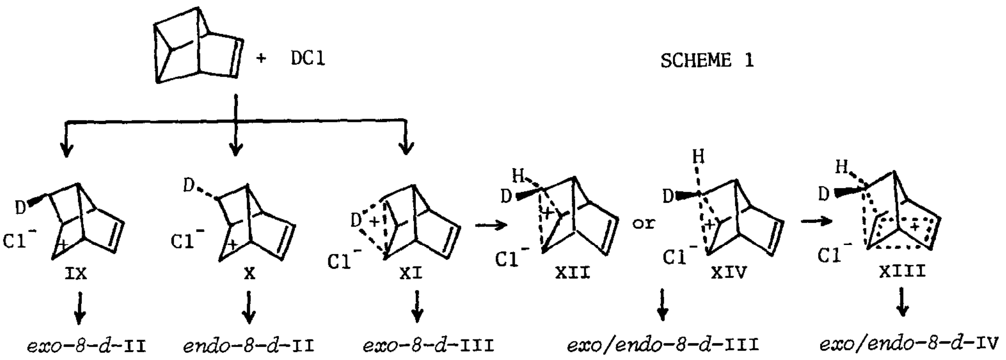
Table 1. Composition (%) of product mixture obtained from I with DCl[a]

Medium	*exo*-8-*d*-II	*endo*-8-*d*-II	*exo*-8-*d*-III	*endo*-8-*d*-III	*exo/endo*-8-*d*-IV[b]
Diethyl ether	75	8.5	13	3	1.5
Ethanol-*O*-*d*	43	5	32	17.5	2
D_2O	8	3	36	30	22.5

[a] Total yield ca. 60%. Yields of V-d_2 and VI-d_2[c] were 3-4% and 1-2%, respectively. On prolonged exposure to the reaction conditions II-*d* and III-*d* slowly gave V-d_2. No isomerization was observed.

[b] *Exo*:*endo* ca. 0.53:0.47 in all cases. [c] Obtained in diethyl ether and ethanol-*O*-*d* only.

SCHEME 1



Based on Scheme 1 the product ratios given in Table 1 show that formation of XI and subsequently XII (XIV) and XIII competes the more successfully with formation of IX and X the more the medium is able to stabilize ion pairs (mainly through hydrogen bonding to the chloride anion). Under the conditions of longest ion pair life time (D_2O) 88% of product is derived from XII (XIV) and XIII. In their very thorough study of the opening of *cis*-1,2,3-trimethylcyclopropane by $D^{\oplus}$ DePuy and coworkers have observed unchanged stereochemistry throughout a wide range of media. Unsymmetrically *corner*-deuterated cyclopropane (*cf.* XIV) could explain the products but *edge*-deuterated cyclopropane was assumed to be formed in the rate determining step. In their view a deuteron added to an edge of *cis*-1,2,3-trimethylcyclopropane must move to a corner within even the shortest ion pair lifetime obtaining in their systems (see also ref. 15). In the case of deuterated I the rigidity of the cage structure seems to slow down the rates of conformational changes so much that both, *edge*- and *corner*-deuterated states, respectively, materialize in different ion pairs (XI, XII (XIV) and XIII). Within a span of time controlled by the anion stabilizing properties of the medium these ion pairs either collapse to characteristic product(s) or rearrange to more stable species.[15] According to Scheme 1 *exo/endo-8-d*-IV arises last from the cascade of ion pairs implied. This is in line with the notion that its precursor is more stable than those of type-II and type-III products laticyclic interaction as indicated in XIII likely being the cause.

Assignment of structures: Catalytic hydrogenation of II and III followed by reduction with Li/*t*-BuOH yielded tricyclo[3.3.0.$0^{2,7}$]octane. Structures VII that might have resulted from protonation at C(2) [C(3)] could be excluded by reacting I-*4-d* with HCl, which did not furnish products carrying deuterium at the chlorine bearing carbon atom. ^1H chemical shifts and couplings of II[16] and III[16] comply with the rules that apply to *exo/endo* isomeric norbornenes.[17] *Exo/endo* assignment of deuterium was greatly facilitated by the absence of couplings of H(8-*exo*) with nongeminal hydrogens.[18] IV was identified by comparison of its ^1H-nmr and IR-spectra with those reported in the literature.[19] The ^1H-nmr spectra of V and VI were very similar to those of II and III.

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