The Addition of Deuterium Chloride to Norbornene and Nortricyclene; a 220 MHz Nuclear Magnetic Resonance Study

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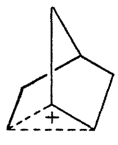
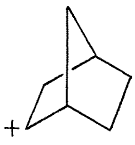
FOR the structure of the norbornyl cation in solution,[1] three possibilities have been suggested: Winstein's[2] bridged structure (I), Brown's[3] localised classical structure (II), and edge-protonated nortricyclene (III) postulated by Olah[4] on the basis of Raman spectral studies. Three approaches have been made: solvolysis of *exo*-2-norbornyl derivatives, electrophilic addition to norbornenes,[5] and direct observation of the carbonium ion in strongly acidic media.[6] Some experiments have involved addition of DCl to norbornene,[5] addition of HCl to 2,3-dideuterionorbornene, and n.m.r. study of the site of deuteriation in the product, *exo*-2-norbornyl chloride (IV). Such studies have been hampered by the impossibility of complete analysis of the eleven-spin system of (IV) at 60 or 100 MHz. Nevertheless, with the help of analysis on norbornene produced by *E*2 *cis*-elimination from (IV), Brown suggested that in nonpolar solvents at −78°, the deuterium distribution in (IV) was 60% at 3-*exo*, 35% at 7-*syn*, and 5% at 5-*exo*, a result claimed to be incompatible with (I) as the sole product-forming intermediate.

We have found that addition of norbornene in chloroform to a saturated DCl solution of chloroform at −78°, and freeze pumping after 120 sec. gave pure *exo*-2-norbornyl chloride (g.l.c.), 93% monodeuteriated (mass spectrometry), which had the n.m.r. spectrum shown (Figure, a). The assignments agree with the literature.[7] A spin-decoupling experiment was carried out to define H-3-*endo*, and show complete internal consistency. Even at 220 MHz., resolution, is incomplete, with overlap between 3-*exo*- and 7-*syn*-, between 5-*exo*- and 6-*exo*, and between 5-*endo*- and 6-*endo*-hydrogens. From careful integration (the mean weight of six tracings on each peak) one can say that all the deuterium is at 3-*exo* or 7-*syn*, with none (< 2%) at 5-*exo*, in contrast to the report of Brown and Liu.[5] Relative amounts of 3-*exo* and 7-*syn* deuteriation can be determined by application of the Gaussian line-shape simulator routine of Dr. J. Royston (University of Warwick) to the 7-*anti*-hydrogen. Appropriate correction for remaining protium shows that 3-*exo*: 7-*syn* = 55:45 ± 3%.

Under identical conditions tricyclene gave rise to pure *exo*-norbornyl chloride (94% deuteriated) with 50 ± 3%


(I)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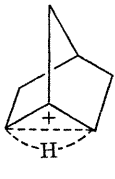
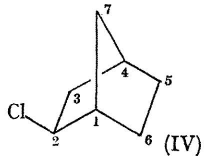

(III)



(IV)

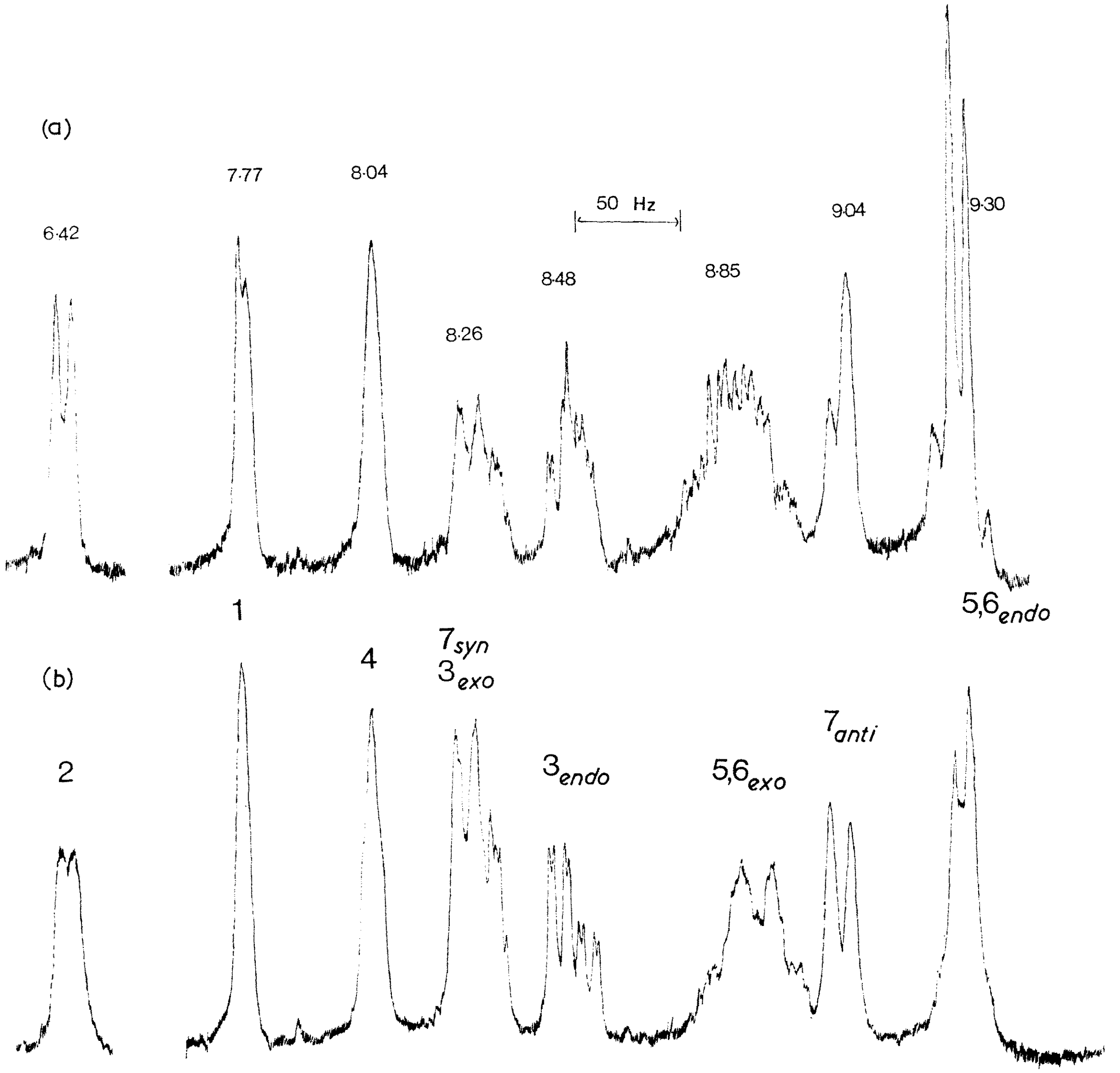


FIGURE. 220 MHz. *spectra of deuteriated norbornyl chloride* (a) *from the addition of* DCl *to norbornene*; (b) *from the addition of* DCl *to nortricyclene. Spectra were taken for* 10% *benzene solutions at* 500 Hz *sweep width*; τ *values are relative to* Me_4Si *and taken from similar spectra at* 2500 Hz *sweep width.*

deuterium at 5-*endo* or (as is assumed) 6-*endo*, 43 ± 3% at 6-*exo*, and apparently 6% in the 7-*anti*-position.†

The mechanism of deuterium incorporation at 7-*anti* is not obvious but its reality is reinforced by the observation of deuterium (15%) at 3-*endo* in isobornyl chloride produced by addition of DCl to tricyclene in chloroform, where the *initial* product is >95% camphene hydrochloride, which later isomerises. In the nortricyclene case our experiments show nearly all the deuterium is at C-6, and unequally distributed in favour of the *endo*-position.

We feel that these results reflect the kinetic product of DCl addition and no ionisation-induced scrambling of deuterium in the initial addition product occurs before work-up. Thus camphene hydrochloride is about 10^8 times more readily ionised than (IV), is thermodynamically unstable with respect to isobornyl chloride, and is only isomerised to isobornyl chloride relatively slowly at −78° in chloroform saturated with HCl. Mass spectra show that only one deuterium atom is incorporated, and thus protonation is essentially irreversible. The results also show that norbornene and nortricyclene do not interconvert under the reaction conditions, and thus their addition products may be considered separately.

The results from norbornene addition are not conducive to a unique mechanistic explanation. A bridged ion (I) cannot be the *only* product-forming ion, but if it is suggested[3] that a rapidly equilibrating localised classical ion (II) is *solely* responsible for these results, then it is necessary to postulate that 1,2-shifts are very much faster than attack of chloride ion in this nonpolar medium. If, in chloroform solution, the most stable ion were the protonated nortricyclene (III), and scrambling around the cyclopropane ring were slow compared with product formation, then addition of DCl to nortricyclene would give *endo*-6-deuterio-*exo*-2-norbornyl chloride. That (III) is the most stable ion in this system is suggested by calculations.[8] Since (III) is almost certainly[9] the initial product, it is apparent that most (III) has leaked to (I) or (II), with subsequent rapid equilibration, prior to product formation. This leakage is *irreversible* since no deuterium is observed at positions 1 and 2. We suggest that these results favour (but do not require) a greater stability for (I) than for (II) or (III). Bicyclo[2,1,1]hexene, which is stereoelectronically less likely to produce a bridged ion, reacts[10] with DCl to give the "classical" product of 1,2-addition.

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† It is possible to distinguish 5-*exo* from 6-*exo* by running the spectrum in carbon tetrachloride, on the assumption that the more strongly coupled high-field group of lines is due to 5-*exo*, which has an additional long-range coupling (to 3-*exo*).

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