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HYDROCHLORINATION OF 1-CHLORO- AND 2-CHLORONORBORNENE

THE DIRECTIVE EFFECT OF CHLORINE

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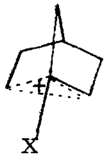
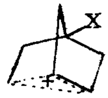
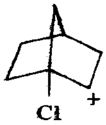
It has been demonstrated that in hydrochlorination of 1-methylnorbornene, protonation takes place unselectively at both ends of the double bond (1, 2). The absence of a directive effect by the 1-methyl substituent in a reaction possessed of carbonium ion character (3) was interpreted as evidence against a significant degree of σ- bridging in the transition state for hydrochlorination of 1-methylnorbornene, since the methyl group could stabilize the bridged transition state corresponding to ion Ia better than that corresponding to ion IIa. We wish to report experiments which argue further against σ- bridging in hydrochlorination of norbornenes and demonstrate the importance of inductive effects in this system.



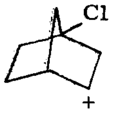
Ia
b



IIa
b



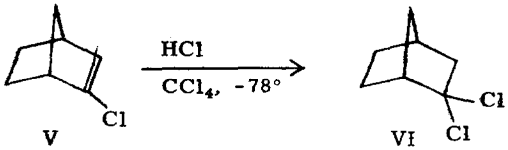
III



IV

(a X = CH_3; b X = Cl)

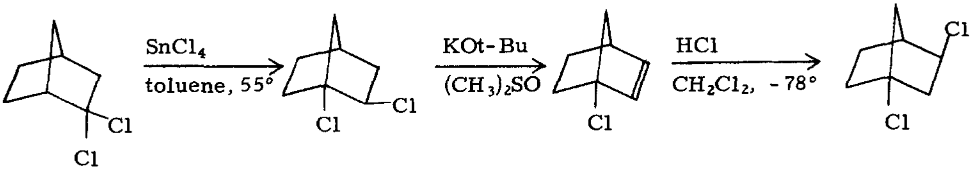
Hydrochlorination of 2-chloronorbornene (V) in CCl_4 at -78°C leads rapidly and quantitatively to 2, 2-dichloronorbornane (VI) (4). This result is consistent with the recognized



V VI

ability of chlorine to stabilize a carbonium ion to which it is directly bonded (5). Since chlorine can exercise a substantial directive effect, hydrochlorination of 1-chloronorbornene (VIII) via bridged intermediates should afford a mixture predominating in products VI and VII derived from bridged ion Ib.

When 1-chloronorbornene (VIII), prepared in the indicated manner,[*] was hydrochlorinated in CH_2Cl_2 at -78°C, the major (>99.5%) product, obtained in 95% yield, was 1,exo-3-dichloronorbornane (IX). Less than 0.5% of the product was 2,2-dichloronorbornane while no (<0.1%) 1,2-dichloronorbornane could be detected.



VI VII VIII IX

Although 1,3-endo-dichloronorbornane has not been prepared, we have assigned the exo position of chlorine on the basis of several reports of exclusive (or nearly so) exo attachment of chlorine in hydrochlorination of norbornenes (1,2,8). Microanalysis and spectral data were consistent with the assigned structure. Confirmation was obtained by dehydrohalogenation of IX to the olefin VIII; and by chromic acid oxidation of the alcohol, prepared by treating IX with aqueous silver nitrate, to the known compound 4-chloronorcamphor (7). The 1,3-dichloride is cleanly separated from VII and VI under our VPC conditions.[**]

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[*] Professor James W. Wilt generously provided an unpublished manuscript (6) describing the conversion of VI to a mixture of VI, VII, and 1,endo-2-dichloronorbornane (X) under the action of $AlCl_3$ in CCl_4, and the preparation of VIII from VII. The treatment of VI with stannic chloride requires a longer reaction time, but is preferred because it affords VII free of VI and X. Dehydrohalogenation of VII with potassium t-butoxide in dimethyl sulfoxide is smooth at room temperature.

[**] Varian Aerograph model 90-P3, using a 18" column packed with 15% Carbowax 20M on Fluoropak 80, operating at 110°.

Although hydrochlorinations give products indicative of carbonium ion character (3), e.g. rearrangements are observed and Markovnikov's rule is obeyed, exact specification of the transition state and subsequent stages is not easy (2, 3). There is good evidence, however, that a suggested four-center mechanism is not important (8(b), 8(c)). It is necessary at this juncture to raise the question why the product in hydrochlorination of VIII contains only an extremely small fraction of dichloride VI and no measurable amount of VII. While the bridged ion Ib is expected to be more stable than bridged ion IIb, ion III should be substantially less stable than IV because of the inductively electron-withdrawing capacity of the chlorine atom.* Wilt has observed a similar orientation in hydrochlorination of norbornene substituted at the 1-position with the inductively electron-withdrawing ammonium function (6). We interpret the formation of IX to the almost complete exclusion of VI and VII as clear evidence that bridging is not involved in the transition state for hydrochlorination of VIII.

Although the argument does not preclude intervention of intermediates of different geometry at later stages on the reaction coordinate, the principle (9) that the stability of an intermediate is reflected in the stability of the precursory transition state implies that the first intermediate in hydrochlorination of VIII is not bridged.

We find support for the importance of the inductive effect in the surprising unreactivity of VIII relative to V or norbornene (XI). Under conditions (CCl_4, -78°C) where V or XI react completely with HCl in less than ten minutes, VIII does not react measurably over an eight-hour interval. In order to confirm this striking difference in reactivity, competitive experiments were carried out. Hydrochlorination in CCl_4 at -78° of a 50:50 mixture of either VIII and V or VIII and XI results in rapid quantitative uptake of HCl by V and XI but no detectable reaction of VIII.

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* Both Wagner-Meerwein rearrangement and 6,2-hydride shift convert IV into itself and would be undetected (1, 2).

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