symmetrically substituted olefins, such as 2-methyl-2-butene (Markovnikov rule). In these electrophilic reactions the methyl group is believed to exert its effect by stabilizing the intermediate cation.[6] Consequently, if the σ-bridged cation were an intermediate in the hydrochlorination of norbornene and related olefins, the presence of the 1-methyl substituent would be expected to exert a similar (albeit smaller) stabilizing effect on one of the two isomeric cations produced by addition of the proton to the double bond. This stabilizing influence would be expected to make itself felt in the transition states leading to those isomeric cations, resulting in a major directive effect in the hydrochlorination of bornylene and 1-methylnorbornene. The absence of any significant directive influence observed in this study is therefore incompatible with the formation of a σ-bridged carbonium ion in the hydrochlorination reaction.[16]

(16) See also H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 3900 (1967).

(17) Research assistant on Grants G 19878 and GP 6492 X supported by the National Science Foundation.

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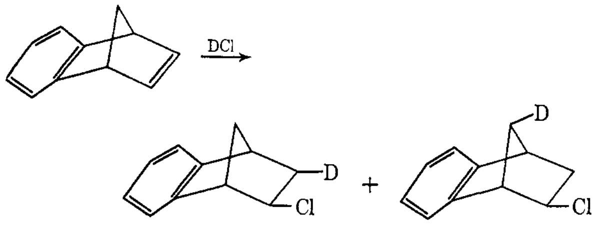
Deuteriochlorination of Norbornene and Apobornylene. Evidence for the Trapping of the Norbornyl Cation in an Unsymmetrical State

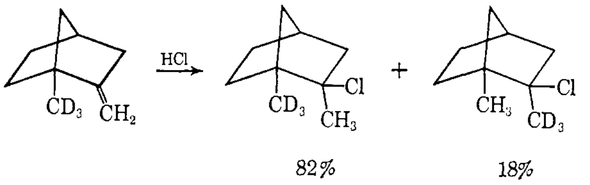
Sir:

The deuteriochlorination of benzonorbornadiene in methylene chloride at −78° has been reported to give a 50:50 mixture of the two deuteriochlorides anticipated either for a bridged cation or a fully equilibrated pair of classical cations[1] (1). We have now observed that under identical conditions norbornene adds deuterium chloride to give *exo*-norbornyl chloride-d_1 with an unequal distribution of deuterium at the *exo*-C-3 and *syn*-C-7 positions. Clearly the reaction cannot involve the symmetrical σ-bridged norbornyl cation as the sole reaction intermediate.



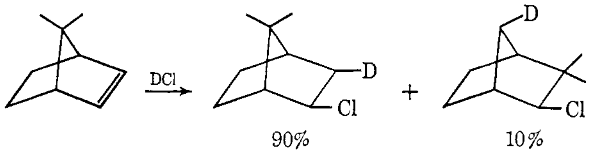
(1)

We previously demonstrated that the addition of hydrogen chloride to 1-methyl-d_3-2-methylenenorbornane proceeded without the scrambling required by a nonclassical intermediate[2] (2). However, there appears to be growing acceptance for the position that tertiary norbornyl cations are classical.[3] Accordingly, we turned our attention to the addition of deuterium chloride to norbornene to see if we could trap the secondary norbornyl cation in its classical unsymmetrical form.[4]



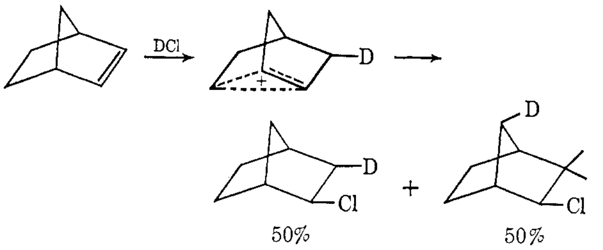
(2)

The addition of deuterium chloride to apobornylene in ethyl ether or in methylene chloride at −78° proceeds to give 90% of apoisobornyl chloride-d_1, with the deuterium in the *exo*-3 position, together with 10% of the Wagner–Meerwein rearranged product, with the position of the deuterium presumably in the *syn*-7 position, but not established experimentally (3).



(3)

The structure of *exo*-3-*d*-apoisobornyl chloride is confirmed by the pattern of the pmr signal[5] of the methine proton α to chlorine. The distinct doublet at δ 3.85 with $J \sim 8$ cps indicates that it arises from *endo*-2-H and *endo*-3-H coupling.[6,7] In apoisobornyl chloride this absorption appears as a quartet, similar to that observed in isobornyl chloride, rather than the multiplet observed in bornyl chloride.[8] The significant point about this experiment is that the pmr spectrum fails to show any measurable formation of *endo* chloride. It has been argued that such additions to norbornene systems should be forced to proceed *endo* by the 7,7-dimethyl substituents in the absence of σ bridging to control the reaction path.[9,10] On this basis, it might have been anticipated that the addition of deuterium chloride to norbornene would proceed to give equal amounts of the two isomers (4) in the same way that benzonorbornadiene yields a 50:50 mixture.[1,11]



(4)

This expectation is not realized. Deuterium chloride adds rapidly (3 min) to norbornene in methylene chloride at −78° to yield 60% of *exo*-3-*d*-*exo*-norbornyl chloride, 34% of *syn*-7-*d*-*exo*-norbornyl chloride, and about 6% of the hydride-shifted product (5). The

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(1) S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

(2) H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 466 (1967).

(3) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

(4) Compare (a) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964); (b) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(5) Taken with a Varian A-60A spectrometer using carbon tetrachloride solution and tetramethylsilane as standard.

(6) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

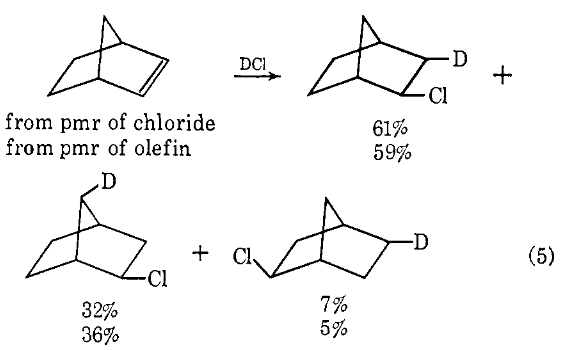
(7) P. M. Subraminian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(8) T. J. Flautt and W. F. Erman, *J. Am. Chem. Soc.*, **85**, 3212 (1963).

(9) J. A. Berson, "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 130–133.

(10) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 371 (1965); R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, **87**, 379 (1965).

(11) In this discussion we are ignoring any small secondary isotope effect of the deuterium substituent in directing the chloride ion to the two alternative neighboring positions.



(5)

position of the deuterium was established both by the pmr spectrum of the chloride and the pmr spectrum of the olefin produced by dehydrohalogenation of the chloride. Excellent agreement was realized between the two independent analyses, lending confidence in the reliability of the procedure and the correctness of the signal assignments.[12,13]

We realized similar results and similar excellent agreement between these independent analyses for deuteriochlorinations carried out at -78° in ethyl ether and in pentane.[14]

These results are clearly incompatible with the interpretation which assumes the formation of a σ-bridged norbornyl cation as the sole reaction path. They can be accommodated by a mechanism involving a rapidly equilibrating pair of classical carbonium ions which are trapped before they have been fully equilibrated. Alternatively, they might be accommodated by assuming the intervention of two different mechanisms, one involving a carbonium ion intermediate and the other involving a concerted four-center addition.[4b] The latter possibility appears to be incompatible with a number of facts.

(1) Under identical conditions benzonorbornadiene gives a 50:50 mixture of the two isomers.[1] However, there does not appear to be any sound reason to propose that the addition to norbornene involves a concerted four-center addition which is not equally probable for benzonorbornadiene.

(2) A concerted four-center addition should be expected to give a major amount of *endo* product in the hydrochlorination of apobornylene.[9,10,15] Yet no significant *endo* product is observed.

(3) A four-center addition of hydrogen chloride to 1-methylnorbornene should give the two isomeric secondary chlorides, both of them stable to the reaction conditions. However, the secondary chloride at C-3 and the tertiary chloride at C-2 are obtained as the kinetically controlled products.[16] Similarly, bornylene yields the same distribution of isomeric *exo* chlorides, with no evidence of any *endo* derivatives.[16]

Consequently, there appears to be no reasonable basis to consider a four-center addition of hydrogen chloride as a significant factor in these reactions. The reaction cannot involve a σ-bridged norbornyl cation as the sole intermediate. We could, of course, interpret the results in terms of a mixture of equilibrating classical and static nonclassical carbonium ions. However, this would require the postulate that equilibrating classical carbonium ions can give practically exclusive *exo* substitution in norbornyl cations containing 7,7-dimethyl substituents. Once we accept this point, it constitutes a direct violation of Occam's razor to include nonclassical ions in our interpretation.

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[12] The spectrum of the chloride was taken as a 30% benzene solution using tetramethylsilane as standard.

[13] K. Tori, *et al.*, *Can. J. Chem.*, **42**, 926 (1964); *Tetrahedron Letters*, 9 (1966). The olefin, obtained in 95% yield by dehydrohalogenation of the chloride at 110° with the sodium salt of 2-cyclohexylcyclohexanol, was examined as a 10% solution in deuteriochloroform.

[14] Stille and his co-workers also observed that hydrochlorination of 2,3-dideuterionorbornene in pentane at -78° did not yield products anticipated for a bridged intermediate.[4b] In contrast to their results, our procedure produced a minor amount ($\sim$6%) of hydride-shifted derivative, facilitating the interpretation.

[15] Both hydroboration and epoxidation of apobornylene yield the *endo* products predominantly (research in progress with J. H. Kawakami). We are indebted to Mr. Kawakami for the sample of apobornylene used in the present study.

[16] H. C. Brown and K.-T. Liu, *J. Am. Chem. Soc.*, **89**, 3898 (1967).

[17] Research assistant on Grants G 19878 and GP 6492 X supported by the National Science Foundation.

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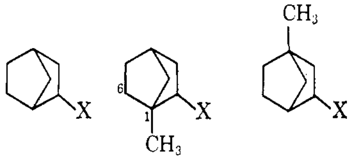
Protonic Acid Additions to 1-Methylnorbornene. The Absence of Orientational Control Attributable to Participation

Sir:

A methyl substituent at the 1 position of norbornane produces a considerable enhancement of the solvolysis rate of a 2-*exo* leaving group (V *vs.* IV) (Table I[1–7]). Such a bridgehead methyl has no appreciable effect on the reactivity of a 2-*endo*-tosylate (II) or on that of either a 3-*exo* (VI) or a 3-*endo* group (III).



endo series	I	II	III
rel rates			
X = OTs, 25°	1.00	1.14	0.73
exo series	IV	V	VI
rel rates			
X = Cl, 70°	280 (1.00)	15,000 (52)	292 (1.04)
X = OTs, 25°	1.0	68	1.1

Steric interactions between the 1-methyl and the 2-*exo* substituents do not appear to be sufficiently large to account for more than a portion of the rate enhancement observed for V.[8] This enhancement is then pre-

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[1] Abstracts, 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1956, p 29-O; Ph.D. Thesis of P. von R. S., Harvard University, 1956, pp 248–259; *cf.* ref 2 and 3.

[2] (a) D. E. McGreer, *Can. J. Chem.*, **40**, 1554 (1952); (b) S. Beckmann and B. Geiger, *Ber.*, **95**, 2101 (1962); (c) S. Beckmann and R. Schaber, *ibid.*, **88**, 1703 (1955); S. Beckmann and G. Eder, *ibid.*, **91**, 2878 (1958); (d) M. Hanack and R. Hähnle, *ibid.*, **95**, 191 (1962).

[3] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1525 (1967).

[4] (a) D. C. Kleinfelter and P. von R. Schleyer, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 43P; D. C. Kleinfelter, *Dissertation Abstr.*, **22**, 428 (1961); (b) J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 182.

[5] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, 87, 375 (1965).

[6] N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. II*, No. 64 (1955); N. J. Toivonen, *Nord. Kjemikermøte, 8th Meeting, Oslo, 1953*, 237 (1953); S. Beckmann and R. Schaber, *Ann.*, **585**, 154 (1954); S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956); **90**, 1564 (1957).

[7] J. A. Berson, A. W. McRowe, R. G. Bergman, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2563 (1967), and related accompanying papers.

[8] M.-H. Rei, Ph.D. Thesis, Purdue University, 1966.