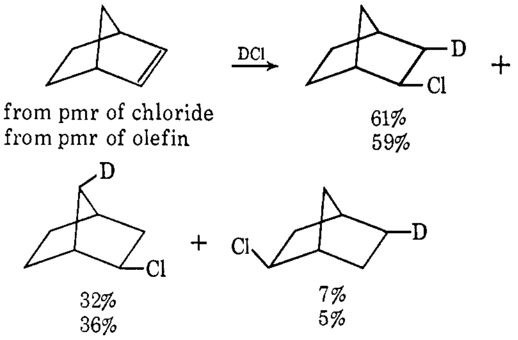

(5)

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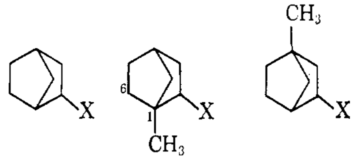
Protonic Acid Additions to 1-Methylnorbornene. The Absence of Orientational Control Attributable to Participation

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.

Table I. Solvolysis Rates of Norbornyl Derivatives

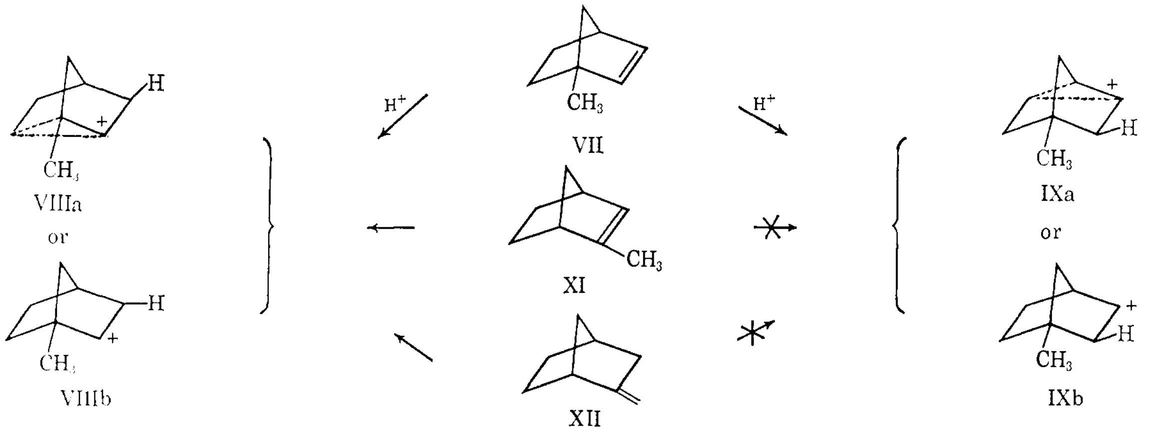
Derivative	Temp, °C	Solvent	k_1, sec^{-1}	Rel rate 25°	Rel rate 70°	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu, 25°
2-*endo*-Norbornyl tosylate (I)[5]	25.0[a]	CH_3COOH	8.28×10^{-8}	1.00	1.00	25.8	−4.4
1-Methyl-2-*endo*-norbornyl tosylate (II)[b]	25.0[a]	CH_3COOH	9.46×10^{-8}	1.14	1.17	25.9	−3.9
	49.84		$(2.95 \pm 0.01) \times 10^{-6}$				
	74.84		$(5.94 \pm 0.04) \times 10^{-5}$				
	99.7		$(7.47 \pm 0.11) \times 10^{-4}$				
1-Methyl-3-*endo*-norbornyl tosylate (III)[c]	25.0[a]	CH_3COOH	6.02×10^{-8}	0.73	0.79	26.1	−4.1
	49.84		$(1.91 \pm 0.02) \times 10^{-8}$				
	74.84		$(4.02 \pm 0.02) \times 10^{-5}$				
	99.7		$(5.02 \pm 0.11) \times 10^{-4}$				
2-*exo*-Norbornyl tosylate (IV, X = OTs)[5]	25.0[a]	CH_3COOH	2.33×10^{-5}	280 (1.00)	100	21.6	−7.2
1-Methyl-2-*exo*-norbornyl tosylate (V, X = OTs)[d]	25.24	CH_3COOH	$(1.25 \pm 0.02) \times 10^{-3}$	15,000 (52)			
1-Methyl-3-*exo*-norbornyl tosylate (VI, X = OTs)[e]	25.0	CH_3COOH	$(2.42 \pm 0.02) \times 10^{-5}$	292	1.34	22.7	−3.4
	49.84		$(5.01 \pm 0.05) \times 10^{-4}$	(1.04)			
2-*exo*-Norbornyl chloride (IV, X = Cl)	25.0	80% ethanol	2.21×10^{-8}			23.3	−15.4
	70.0		$(4.47 \pm 0.04) \times 10^{-6}$		1.00		
	85.0		$(1.95 \pm 0.04) \times 10^{-5}$				
1-Methyl-2-*exo*-norbornyl chloride (V, X = Cl)[1,2c,6]	70.0	80% ethanol	$(3.06 \pm 0.03) \times 10^{-4}$		68		
1-Methyl-3-*exo*-norbornyl chloride (VI, X = Cl)[1,2c,6]	70.0	80% ethanol	$(4.96 \pm 0.08) \times 10^{-6}$		1.11		

[a] Calculated rates. [b] Melting point near room temperature. PNB mp 122.5–122.9°.[1,2c,6] [c] Oil at 25°; PNB mp 91.4–91.9°. [d] Decomposes easily; highest melting point was 53.5–55.5°; PNB mp 96.8–97.4°.[1,2c,6] [e] Mp 44.0–44.5°; alcohol mp 67.7–68.6°; PNB mp 95.0–95.9°.[7]

sumably the result of participation by the C_1–C_6 bonding electrons as the *exo* leaving group ionizes to form either the methyl-stabilized bridged ion or the classical tertiary ion.

The same 2 and 3 cations might, in principle, be generated by a different method under directly competitive circumstances, by addition of a proton to 1-methylnorbornene (VII). If appreciable C–C bridging were present in the transition states for such protonic additions (VIIIa *vs.* IXa, or VIIIa *vs.* IXb), then products derived from the 2 cation (VIII) should predominate over those from the 3 cation (IX), and the methyl group in VII should have a marked orienting influence. In view of the greatly differing relative solvolysis rates of V and VI this possibility might well be considered to be a likely one.

Additions to the related olefins XI[1] and XII[1] were also studied under similar conditions: ethereal HCl gave tertiary chloride X (X = Cl), while aqueous HCl gave mostly V (X = Cl) with a little X (X = Cl).[1,2c,6] No VI (X = Cl) was detected in the product obtained with either of these olefins. Similarly XI and XII reacted with formic acid at 70° to give mainly V (X = O-OCH),[1,2c,6] but other isomers were formed at higher temperatures. However, VI (X = OOCH) was quite stable toward refluxing formic acid and did not rearrange to V (X = OOCH) in appreciable amounts. These results showed that ions VIII and IX were not interconverting under the addition conditions and furnish additional examples of the relative slowness of 3,2-norbornane hydride shifts when only secondary sites are involved.[7,9,10]



This expectation is not realized in fact. Addition of formic acid and of aqueous and ethereal HCl to VII[1] (Table II) gives very nearly a 50:50 mixture of products derived from VIII and from IX, VI, and V (and/or X), respectively. The methyl group in VII has virtually no directive influence in these additions.

Electrophilic additions to olefins seem definitely to have carbonium ion character, *e.g.*, Markovnikov's

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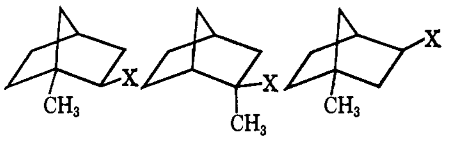
(9) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

(10) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831, 5355 (1966); C. J. Collins and M. H. Leitzke, *ibid.*, in press.

Table II. Products of Additions to 1-Methylnorbornene (VII)



Conditions	V	X	VI
HCOOH, 70°, X = OOCH	≈50%[a]		≈50%[a]
HCl-H_2O, reflux, X = Cl	43%[b]	6%[b]	51%[b]
HCl-Et_2O, 25°, X = Cl		54%[b]	46%[b]

[a] Analysis by analytical distillation of the alcohols V (X = OH), bp 177°, and VI (X = OH), bp 183°. Oxidation of VI (X = OH) gave 1-methyl-3-norbornanone, a low melting solid (2,4-DNP mp 133.2–133.4°), and 1-methyl 1,3-*cis*-cyclopentanedicarboxylic acid, mp 95.0–96.6°, anhydride mp 78.7–79.4°.[1,2c,6] (1-Methyl-2-norbornanone 2,4-DNP had mp 167.2–167.8°.) [b] Analysis by solvolysis.[1,2c,6]

rule is followed and rearrangements are observed, but the exact definition of the transition states has been difficult.[11] The present results show that no significant charge delocalization due to bridging is present in the transition state of the proton-addition step.

Unsymmetrical molecules such as 1-methylnorbornene (VII) and bornene should thus be ideal substrates for the study of the relationship between bridging and the stereochemistry of addition of unsymmetrical reagents, such as D^+Y^- and X^+Y^-. If the electrophilic fragments, D^+ and X^+, become attached indiscriminately to the 2 and 3 positions of the olefins, then bridging cannot be involved in the transition state for their addition. If, despite this lack of preference, these electrophiles become attached *exo*, then factors other than bridging must be responsible for this stereospecificity.

The results of addition reactions already described in the literature[4b,12] with symmetrically substituted norbornenes suggest that electrophiles tend to become attached *exo* in the kinds of reactions studied here, *even in the presence of hindering 7,7-dimethyl groups.*[13] Torsional effects[14] may contribute to the *exo* selectivity observed in such instances.

(11) P. B. D. de la Mare and R. Boulton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966; M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 245 (1964); B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1965," John Wiley and Sons, Ltd., London, 1966, p 104 ff.

(12) S. J. Cristol, *et al.*, *J. Org. Chem.*, **31**, 2719, 2726, 2733, 2738, 2741 (1966), and previous papers; H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964); J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, **88**, 4922 (1966).

(13) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3898, 3900 (1967); T. T. Tidwell and T. G. Taylor, footnote 6, ref 3.

(14) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

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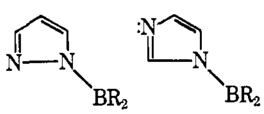
Poly(1-boryl)imidazoles

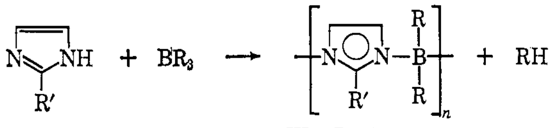
Sir:

The geometric and electronic features of a 1-borylpyrazole fragment (I), which is a 1,3-dipole, are suitable for the formation of a variety of novel boron heterocycles (pyrazaboles), coordinating ligands, and transition metal compounds (poly(1-pyrazolyl)borates).[1,2] On the other hand, it would be expected that the electronically similar but geometrically disparate 1-borylimidazole fragment (II), which is a 1,4-dipole, would be incapable of forming comparable homoassociation products but would form polyassociated structures instead. This has been borne out by the following findings.



I II

When an equimolar mixture of triethylborane and imidazole was refluxed in xylene, ethane was evolved (eq 1), although at a rate much slower than in the analogous reaction with pyrazole.[3] The resulting product was soluble in aromatic hydrocarbons and chloroform



(1)

IIIa, R = Et; R′ = H
b, R = Bu; R′ = H
c, R = Et; R′ = Me

but not in methanol. It was an elastomer, with an inherent viscosity of 0.5–0.7, which showed a 5% weight loss at 373°, underwent a glass transition at −12°, and displayed a sharp endotherm at 435°. Structure IIIa[4] was assigned on the basis of elemental analysis[5] (*Anal.* Calcd for $[C_7H_{13}BN_2]_n$: C, 61.8; H, 9.57; B, 7.94; N, 20.6. Found: C, 62.8; H, 9.82; B, 8.13; N, 20.0) and the nmr spectrum, which had singlets at τ 2.48, 3.24, and 9.67 in a 1:2:10 ratio assigned to 2-H, 4,5-H, and the ethyl hydrogens,[6] and was consistent with C_{2v} symmetry of the imidazolyl nucleus. The molecular weight ranged from about 6000 to 12,000 (osmometry in chloroform) giving *n* values in the 40–80 range. Poly(1-dibutylborylimidazole) (IIIb) was prepared and identified similarly.

These polymers are stable to air and boiling water, but are hydrolyzed slowly by boiling alkali and rapidly by boiling hydrochloric acid.

By contrast, the reaction of triethylborane with 2-methylimidazole gave the cyclic tetramer IIIc (*n* = 4) as the sole reaction product in 99% yield. The structure assignment was consistent with elemental analysis and molecular weight determination (*Anal.* Calcd for $[C_8H_{15}BN_2]_4$: C, 64.0; H, 10.0; B, 7.21; N, 18.7; mol wt, 600. Found: C, 64.5; H, 10.3; B, 7.31; N, 18.9; mol wt (ebullioscopic in benzene), 630) as

(1) S. Trofimenko, *J. Am. Chem. Soc.*, **88**, 1842 (1966).

(2) S. Trofimenko, *ibid.*, **89**, 3165, 3170 (1967).

(3) This is understandable, since the imidazole–triethylborane complex cannot eliminate ethane through a low-energy, concerted intramolecular transition state, as is the case with the corresponding pyrazole complex, and this reaction has to proceed intermolecularly.

(4) It is understood that a positive charge is delocalized in the imidazole ring and a negative charge resides on boron.

(5) The high C, H, B, and low N values indicate contamination by triethylborane, probably as endcapping groups.

(6) The appearance of B-bonded ethyl group hydrogens as a singlet has been noted before: L. H. Toporcer, R. E. Dessy, and S. I. E. Green, *Inorg. Chem.*, **4**, 1649 (1965).