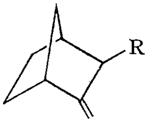
The 2-Methylene-3-norbornyl Cation

By C. W. JEFFORD* and W. WOJNAROWSKI

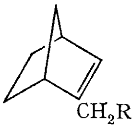
(**Institut de Chimie,*† *Strasbourg, France and Department of Chemistry, Temple University, Philadelphia, Pa.* 19122)

ONE of the contended criteria for the non-classical 2-norbornyl cation is its *exo*-stereospecificity of attack by external nucleophiles. It has been argued that the absence of *endo*-attack need not be a characteristic property of such a non-classical ion but could result from simple steric obstruction on the *endo*-side or from the microscopic windshield wiper effect of the dynamically migrating 1,6-bond of the classical ion.[1] We now present our findings concerning the behaviour of the 2-methylene-3-norbornyl cation which is surely a *non*-equilibrating classical ion.

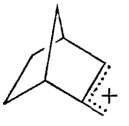
The treatment of *exo*-3-bromo-2-methylenenorbornane (I)‡ with silver acetate in 50% aqueous acetone gave a mixture of *exo*-3-hydroxy-2-methylenenorbornane (II), 2-hydroxymethylnorborn-2-ene (III), and their corresponding acetates (IV and V). The alcohols and acetates were obtained pure by reduction of the mixture with lithium aluminium hydride and acetylation with acetic anhydride respectively followed by chromatographic separation. The ratio of (II) to (III) and (IV) to (V) was 1·5—2·2 : 1. No other products were detected by v.p.c. or n.m.r. analysis. The structures of (II)–(V) were assigned without difficulty from their spectral data§ (see Table). The *exo*-structure of (II), for example, was established unequivocally by the manifestation of long-range coupling between the *endo*-C(3) and *anti*-C(7) protons (^4J $\sim$1·5 Hz.) and the negligible coupling between the protons on *endo*-C(3) and -C(4) which emerged from the spin–spin decoupled spectra.¶,[2,3] The products clearly arise *via* the intermediacy of the allylic cation (VI). The product composition indicates that attack by solvent at C(8) and *exo* at C(3) are favoured to about the same extent, but that no *endo*-C(3) product is formed. From this result it can be concluded that the exclusive *exo*-attack at C(3) is a property of a non-equilibrating classical as well as a non-classical 2-norbornyl ion.[4] It is interesting to note that a consideration of torsional interactions correctly predicts *exo*-attack rather than *endo*- at C(3), but nevertheless fails to account for



(I) R=Br
(II) R=OH
(IV) R=OAc



(III) R=OH
(V) R=OAc



(VI)

---

† A laboratory associated with the C.N.R.S.

‡ Compound (I) was prepared by the action of *N*-bromosuccinimide on 2-methylnorborn-2-ene. Details of this reaction will be described elsewhere.

§ Compounds (I)—(V) gave acceptable elemental analyses.

¶ Unpublished findings of K. C. Ramey.

TABLE

Chemical shifts[a] (A) *and* C=C *stretching frequencies*[b] (B) *of norbornene derivatives*

	A				B
Compound	H(4)	H(2)	H(1)	H(8)	$\nu_{C=C}$
(I)	2·56	4·44	2·78	5·12	1661
(II)	2·24	3·83	2·66	4·96	1664
(IV)	2·33	5·02	2·69	4·95	1669
(III)	2·81	5·72	2·81	4·15	1629
(V)	2·80	5·80	2·80	4·58	1635

[a] in $CDCl_3$ with added Me_4Si as standard (in p.p.m.); [b] neat (in cm.$^{-1}$).

the formation of the hydroxy- and acetoxy-methylnorbornenes (III and V).[5]

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society, for the support of this work.

(*Received November* 14*th*, 1967; *Com.* 1237.)

---

[1] *Cf.*, G. Dann Sargent, *Quart. Rev.*, 1966, **20**, 301.

[2] A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 1964, 2223.

[3] The present data agreed completely with those recently described for compound (II) (H. Krieger, K. Manninen, and J. Paasivirta, *Suomen Kem.*, 1966, **39**, *B*, 8.

[4] For related kinetic data, see C. F. Wilcox, jun., and R. G. Jesaitis, *Chem. Comm.*, 1967, 1046.

[5] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 701.