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DEUTERIOBROMINATION OF BENZONORBORNADIENE. EVIDENCE FOR A NONCLASSICAL ION[1].

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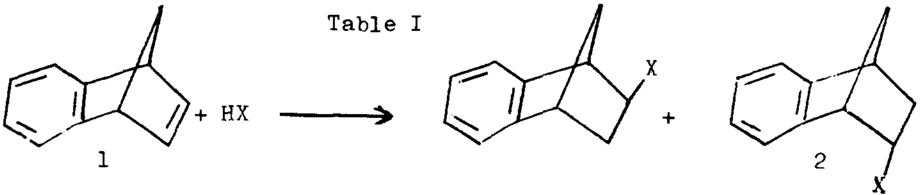
The principle results obtained from a study of polar additions of HX to benzonorbornadiene (1) are summarized in Table I.

Table I



HX	Solvent	Exo %	Endo %
HBr	H_2O	98.6% (± 0.4%)	1.4% (± 0.3%)
HBr	HOAc	94.0% (± 0.4%)	6.0% (± 0.3%)
HBr	CH_2Cl_2	93.6% (± 0.4%)	6.4% (± 0.2%)
HCl[2]	Pentane	100.0%	
HOAc[3]	HOAc	100.0%	

In the case of hydrogen bromide additions,[4] no change in the exo to endo ratio of bromides is observed during the course of the reaction, upon exposure of the products to light, or upon exposure of the products to the reaction conditions. Therefore, the isomer distribution shown in Table I represents the true kinetic products of the reaction. The interference of a free radical component of the reaction was ruled out by adding styrene to the reaction mixtures. In all cases only the Markownikoff addition product to styrene, 1-bromo-1-phenylethane, was formed.

Polar addition of deuterium bromide to I, in methylene chloride, gave a

93.6% to 6.4% mixture of deuterobromides. The mixture was separated by preparative gas liquid chromatography (g.l.c.) for study. The proton magnetic resonance (p.m.r.) spectra of the endo bromide clearly shows that all of the deuterium is in the exo-3-position and that the only endo bromide formed(± 1%) is endo -2-bromo-exo-3-deuterobenzonorbornene (3). It was not possible to make a quantitative determination of the deuterium location in the exo bromide by p.m.r., however the elimination of hydrogen (deuterium) bromide from the exo-deuterobromide, with potassium t-butoxide in t-butyl alcohol, gave a 98^{+}% yield of the olefin benzonorbornadiene. Analysis of the olefin by p.m.r. shows that 37% of the olefin contains deuterium in the 7-position and that there is no deuterium (± 1%) in the 2-position. Finding an olefin with no deuterium in the 2-position presents conclusive evidence for cis elimination in this system. It is known from the p.m.r. spectra that there is some deuterium in the exo position and any trans elimination would lead to an olefin with deuterium in the 2-position. Therefore, only cis elimination takes place in this system, despite the fact that the isotope effect favors trans elimination. Considering the olefin analysis it is obvious that there are two exo-deutero products formed, exo-2-bromo-exo-3-deuterobenzonorbornene (4) and exo-2-bromo-syn-7-deuterobenzonorbornene (5).

The mechanism for the polar addition of deuterium bromide presented in Figure I is based on the products obtained from the above addition reactions. The Figure advances a variety of intermediates for consideration and the products that could come from each. The appearance of endo bromide (3) coupled with the fact that cis-exo (4) and rearranged (5) products are not formed in equal amounts indicates that there is more than one intermediate in the reaction path. The data requires a nonclassical ion, to explain the presence of a rearranged product (5), which is preceded by some other intermediate. If the rearranged product were to come from a rearranged classical ion, some of the endo bromide would have deuterium in the 7-position. There is no reason to include the bridged deuterium ion (6) or the unsymmetrical ion (8) in the reaction path but the data does not rule them out. However the data does require a classical ion (7) to explain the formation of endo bromide and, more importantly, the considerable

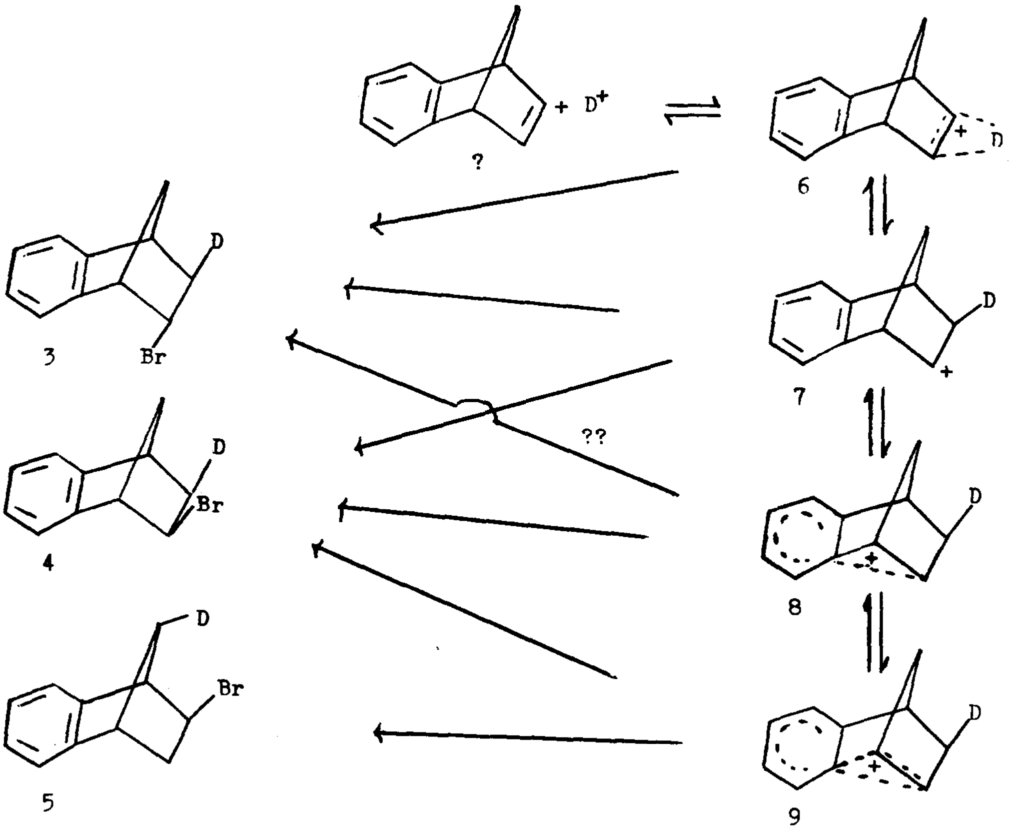
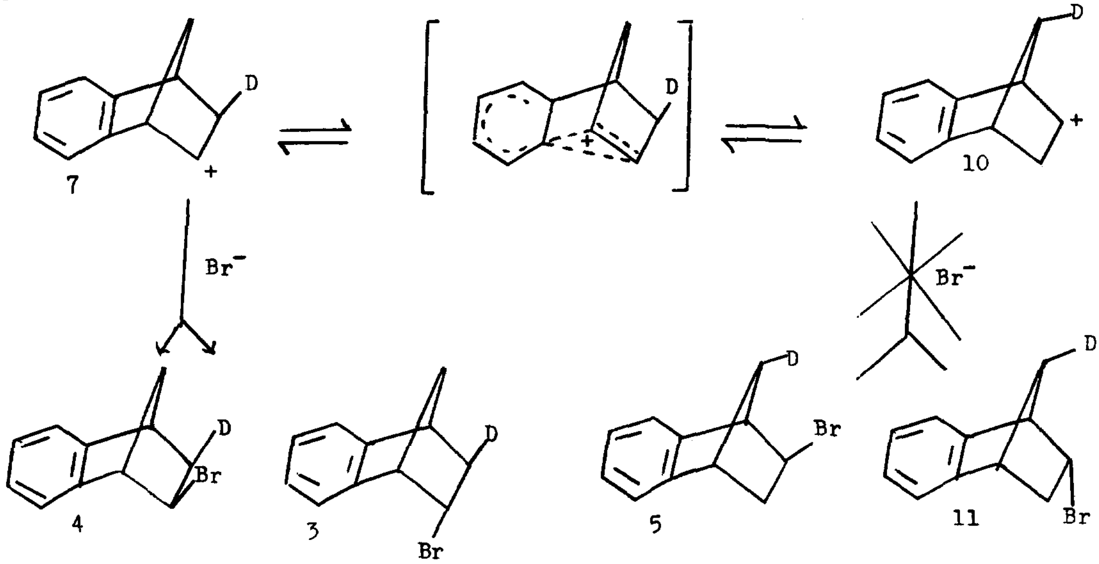


Figure I

excess of *cis*-exo product (4). A symmetrical intermediate would give equal amounts of *cis*-*exo* and rearranged products, assuming a negligible steric isotope effect.[5] The excess of *cis*-*exo* product can not be accounted for by a simple *cis* molecular addition in view of the fact that no *cis*-*endo*, *endo*-2-bromo-*endo*-3-deuterobenzonorbornene, was formed even though *endo* attack is possible as indicated by the formation of *endo* bromide (2).

H.C. Brown[6] has persistently criticized nonclassical ion theory, but if it were actually the case that the symmetrical homobenzylic ion is a transition state between a pair of rapidly equilibrating ions, 7 and 10, as he states, then, since bromide ion attack is equally likely for each member of the equilibrating pair, not only should 4 and 5 be formed in equal amounts, but more importantly, some rearranged *endo* bromide (11) should also be formed. The products obtained in these reactions clearly show the absence of a rearranged classical ion.



We can summarize by saying that the reaction goes to a classical ion which is either attacked by bromide ion, in an *exo* to *endo* ration of 4:1, or procedes to a nonclassical intermediate which gives equal amounts of *cis*-*exo* and rearranged products.

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