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π-ELECTRON PARTICIPATION IN THE *ENDO,ENDO*-DIMETHANONAPHTHADIENYL SYSTEM

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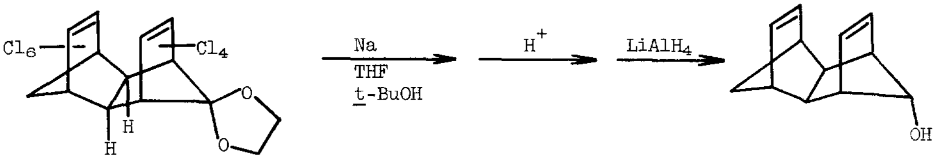
The norbornyl ring system has proven to be uniquely informative as regards (1) factors which affect anchimerically assisted ionization, and (2) the nature of carbonium ion intermediates (1-3). One of the most interesting observations is the rate difference of 10^{11} found for solvolysis of 7-norbornyl (I) and *anti*-7-norbornenyl (II) derivatives (4). The great reactivity of II was attributed to powerful anchimeric assistance by the double bond which leads to an electron delocalized nonclassical intermediate. More recent results still are accommodated best with the original postulation (5,6). We wish to report the solvolysis results for system IV which has the structure modified so that another double bond is proximate to the *anti*-7-norbornenyl double bond but remote from the leaving group.

Dechlorination of the decachloro-*endo*,*endo*-dimethanonaphthalene ketal III (7) with sodium-THF-*t*-butyl alcohol (8) followed by mild acid hydrolysis and then lithium aluminum hydride reduction (8) led to *anti*-alcohol IV-OH, m.p. 94-97°; homogeneous vpc analysis.*



III IV

Assignment of an *anti* configuration for the hydroxyl group of IV-OH is based on several lines of evidence. First of all, the intermediate ketone should show the same stereoselectivity for

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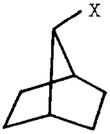
* Satisfactory elemental analyses were obtained for IV-OH, IV-OPNB, and all intermediate compounds.

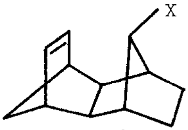
lithium aluminum hydride reduction as 7-nonbornenone (8) and afford the anti epimer. Secondly, the IV-OH nmr spectrum exhibits the triplet vinyl proton pattern used for configurational assignment of anti-7-substituted norbornenes (9). Finally the solvolysis results are in accord with expectations for this assignment. Alcohol IV-OH was converted by the usual pyridine procedure to anti-p-nitrobenzoate IV-OPNB, m.p. 148-149°.

anti-p-Nitrobenzoate IV-OPNB hydrolyzed in 70% aqueous dioxane with good first order kinetics, the rate constants being 13.8×10^{-5} sec^{-1} at 121.0° and 2.53×10^{-5} sec^{-1} at 100.0°. The remote double bond makes IV-OPNB ca. 10^3 times more reactive than anti-7-norbornenyl p-nitrobenzoate II-OPNB (3b) and increases the rate enhancement over the 7-norbornyl system to 10^{14}. The structural arrangement of IV provides one of the highest known driving forces toward ionization. This is shown by the following comparison of relative solvolysis rates at 25°:



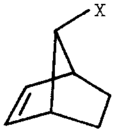
1.0

I(4)



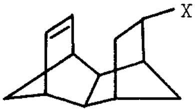
1.2×10^{10}

V(4,10)



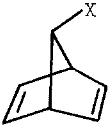
1.4×10^{11}

II(4)



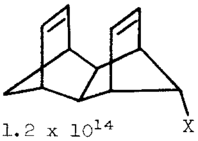
1.8×10^{13}

VI(11)



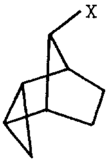
1.0×10^{14}

VII(4,12)



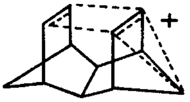
1.2×10^{14}

IV



$1.8 - 10 \times 10^{14}$

VIII(3)*



IX

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* Comparison at 100° and 90° (3).

A sample of IV-OPNB was hydrolyzed in 70% aqueous dioxane for 12 hours at 121° in the presence of 2 equivalents of sodium bicarbonate. Only unrearranged anti-alcohol IV-OH was. detected upon examination of the product with a variety of vpc columns. The nmr spectrum of the crude solvolysis product was identical with the one for pure IV-OH.

Such extreme reactivity of IV-OPNB in solvolysis must mean that ionization proceeds with π-electron participation from both the remote and homoallylic double bonds. This coupled with stereochemical control which is analogous to the anti-7-norbornenyl system strongly suggests the intermediacy of a highly stabilized extensively electron delocalized nonclassical ion IX.

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