Enhanced Reactivity of *exo*-Norbornyl Derivatives. Evidence for σ-Participation in the Absence of Steric Effects

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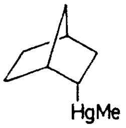
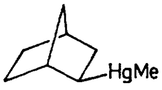
Summary Determinations of the vertical ionization potentials by He I photoelectron spectroscopy and the rates of electrophilic cleavage of *exo*- and *endo*-2-norbornylmethylmercury are consistent with enhanced σ-participation as a mode of charge delocalization in the *exo* epimer.

The significance of the 2-norbornyl system to organic chemistry has been stressed by Olah.[1] Much of the controversy surrounding this area of research has resulted from difficulties in determining whether the greater reactivity of *exo*- compared to *endo*-2-norbornyl derivatives in solvolysis is the result of σ-participation[1,2] or simply increased steric hindrance in the *endo* epimers.[3,4]



(I)



(II)

We recently demonstrated[5] that the effect of the leaving-group RHg^+ on the rate of acetolysis of methylalkylmercury compounds (equation 1) represents a useful measure of the ability of the alkyl group R to delocalize positive charge in the transition state under conditions in which the bond to R itself remains intact. Thus the pseudo-first order rate constants (log k) in equation (1) were found to correlate linearly with the gas phase vertical ionization potential (I.P.) of RHgMe. Moreover, such leaving-group effects were shown to be free of steric contributions from the leaving-group RHg. Substitution of β-methyl groups in R in the series: ethyl, n-propyl, isobutyl, and neopentyl effect little change in either the I.P. or the acetolysis rates of MeHgR. Selected values for such leaving-group effects are shown in the Table.

$$\mathrm{RHgMe} + \mathrm{HOAc} \xrightarrow{k} \mathrm{RHgOAc} + \mathrm{CH_4} \qquad (1)$$

Table. Pseudo-first order rates of methane evolution from RHgMe.[a]

R	$10^7\ k/\mathrm{s}^{-1}$	I.P./eV[b]
Methyl	3·9[c]	9·33
Ethyl	23·5	8·84
n-Propyl	26·3	8·78
Isopropyl	85·8	8·48
t-Butyl	120	8·31
Isobutyl	23·9	8·75
Neopentyl	21·9	8·67
endo-Norbornyl	66·5	8·47
exo-Norbornyl	86·3	8·28

[a] In solvent acetic acid at 37·5 °C. [b] First vertical ionization potential by He I photoelectron spectroscopy. [c] Statistically corrected.

In order to exploit this technique for investigating charge stabilization by the *endo*- and *exo*-2-norbornyl groups, the diastereomeric compounds (I) and (II) were prepared from the corresponding norbornylmercury bromides and each, after distillation under reduced pressure, was shown to be epimerically pure by g.l.c.[6] The significantly larger values of k in the Table for the cleavage of the Me–Hg bond in the *exo* epimer (II) provides direct evidence for σ-participation in the transition state† for a process in which steric effects are unimportant.

Perhaps even more noteworthy are the first vertical ionization potentials of (I) and (II), which represent the energies required for electron detachment according to equation (2). Since the ease of ionization is directly related

$$\mathrm{RHgMe} \rightarrow \mathrm{RHgMe}^{+} + \epsilon \qquad (2)$$

to the stabilization of the positive charge in the cation-radical,[7] the difference between the I.P. of (I) and (II) measures the relative electron release by *endo*- and *exo*-2-norbornyl groups. The measurement is carried out in the gas phase and is free of solvation effects. Moreover, photoionization being a vertical process, it occurs much faster than any nuclear rearrangement and precludes the involvement of steric factors as well.[8] The observed difference in ionization potential (Table) of 0·19 eV is significant. This result requires that formation of the radical-cation of (II) be stabilized by 4·4 kcal mol^{-1} relative to the same process for (I).

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† The measurement of the heats of formation of (I) and (II) is in progress.

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