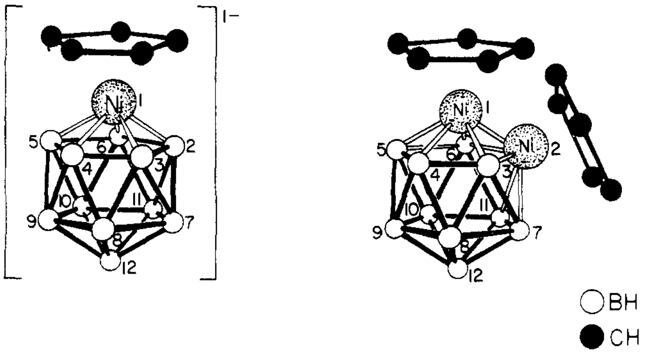

Figure 1. Proposed structures of $[(B_{11}H_{11})Ni(C_5H_5)]^-$ and $B_{10}H_{10}(NiC_5H_5)_2$.

Good yields of I were also obtained by treating $[(C_4H_9)_4N]B_{11}H_{13}$ with $(C_5H_5)_2Ni$ in refluxing 1,2-dimethoxyethane in the absence of a reductant; however, the reaction proceeded only very slowly at room temperature. With the addition of catalytic amounts of Na-Hg, the reaction went to completion in several hours. The noncondensable gas evolved in the reaction was collected and identified as H_2. Slightly more than 1 mol of H_2 was produced for each mole of I isolated on work-up.

The 80.5-MHz ^{11}B nmr spectrum of I in acetonitrile consisted of three sharp doublets of relative area 1:5:5 at −19.9(134), −16.0(135), and +5.1(128) (chemical shift, ppm, relative to $BF_3{\cdot}O(C_2H_5)_2$ (coupling constant, Hz)). The 60-MHz proton nmr spectrum was obtained in acetonitrile solution and consisted of two sharp singlets with relative area 5:12 at τ 4.62 and 6.95, respectively. The former resonance was assigned to the cyclopentadienyl moiety and the latter to the methyl protons of the tetramethylammonium cation. Distinctive infrared absorptions appeared at 2490 (s), 1020 (s), 950 (s), 910 (m), 829 (m), 728 (m) (cm^{-1} (intensity); taken in a Nujol mull). Cyclic voltammetry in acetonitrile demonstrated a reversible reduction wave at $E_{p/2} = -1.50$ V. These data are consistent with the icosahedral structure represented in Figure 1.

The reaction of $[(CH_3CH_2)_3NH]_2B_{10}H_{10}$ in 1:3 acetonitrile:1,2-dimethoxyethane with an equimolar amount of $[CpNiCO]_2$ afforded a deep brown solution. Column chromatography on Florisil with dichloromethane-hexane as eluant afforded golden brown crystals of II in 45% yield. An alternative method of preparation of II which gave high yields (70%) involved the direct interaction of quaternary ammonium salts of $B_{10}H_{10}^{2-}$ with $(C_5H_5)_3Ni_2^+$[2] in tetrahydrofuran. *Anal.* Calcd for $B_5C_5H_{10}Ni$: B, 29.55; C, 32.83; H, 5.52; Ni, 32.10. Found: B, 29.88: C, 32.62; H, 5.44; Ni, 31.48. Mass spectral data proved the peak of maximum intensity in the parent envelope to be at *m/e* 363. A peak of medium intensity occurred at *m/e* 188 and a smaller peak occurred at *m/e* 190 which were assigned to the $(C_5H_5)_2\,^{58}Ni^+$ and $(C_5H_5)_2\,^{60}Ni^+$ ions, respectively. The electronic spectrum in dichloromethane was 475 (755), 376 (3880), 300 (23,900), 239 (64,400) $(\lambda_{max} m\mu(\Sigma_{max}))$.

The ^{11}B nmr spectrum of II at 80.5-MHz consisted of four doublets with relative area 1:1:2:1 at −54.3 (138), −26.1 (134), −21.3 (150), and −6.7 (144 (chemical shift, ppm, relative to $BF_3{\cdot}O(CH_2CH_3)_2$ (coupling constant, Hz)). The 60-MHz proton nmr spectrum taken in 1,2-dimethoxyethane consisted of one sharp singlet at τ 4.54. This was assigned to the protons on two equivalent cyclopentadienyl rings. The infrared spectrum obtained in a Nujol mull showed characteristic absorptions at 2500 (s), 1015 (s), 905 (m), 890 (m), 850 (s), 840 (s), 745 (m) (cm^{-1} (intensity)). Cyclic voltammetry in dichloromethane demonstrated two reversible reduction waves at −0.27 and −1.35 V. These data are consistent with either the ortho or meta isomer of $(C_5H_5Ni)_2B_{10}H_{10}$. X-Ray crystallography studies are in progress to differentiate between these two possibilities.

The cage opening reaction of $B_{10}H_{10}^{2-}$ with a proton in the presence of ligands to form $B_{10}H_{12}(ligand)_2$ species is thought to involve a nido intermediate.[3] A similiar mechanistic step may initially occur during the reaction of $B_{10}H_{10}^{2-}$ with $(C_5H_5)_3Ni_2^+$. These observations suggest the possibility of synthesizing a large variety of metalloborane species by reaction of closo-borane anions with metal electrophiles, *e.g.*, II-$C_6(CH_3)_6)_2Co^+$. This and related mechanistic points related to the formation of I and II are under investigation.

Both I and II are water and air stable species, unlike many nido metalloboranes[4,5] previously reported. The compound II can be heated to 350° and subsequently sublimed at 265° over a period of hours with only partial decomposition. Compound I is stable in H_2O_2-H_2O and can be recovered unreacted after boiling several days in ethylene glycol-KOH. These compounds provide pleasing examples of the ability of polyhedral electron counting rules[6-8] to predict, on an *a priori* basis, the existence and relative stability of closo-metalloboranes.[8].

Acknowledgment. This work was supported in part by the Office of Naval Research. We would also like to thank C. G. Salentine for obtaining 80.5-MHz ^{11}B nmr spectra.

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(8) C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95,** 7633 (1973), predicted $(C_5H_5Ni)_2B_{10}H_{10}$ to be a stable isolable species.

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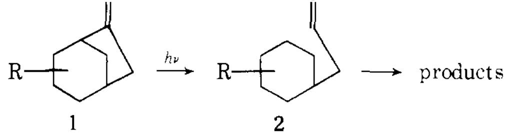
Conformational Control in the Photochemistry of Substituted Bicyclo[3.2.1]octan-6-ones

Sir:

Study of the photochemical α-cleavage of bicyclo[3.2.1]octan-6-ones (**1**) affords an opportunity to examine the conformational behavior of the derived biradical intermediates, **2**.[1,2] There are now many reports of the control of photochemical reactions by ground state conformation,[3-5] along with evidence that changes in conformation may occur specifically in the excited state.[5] There are also good examples of conformational effects on behavior of



1
2

Scheme I

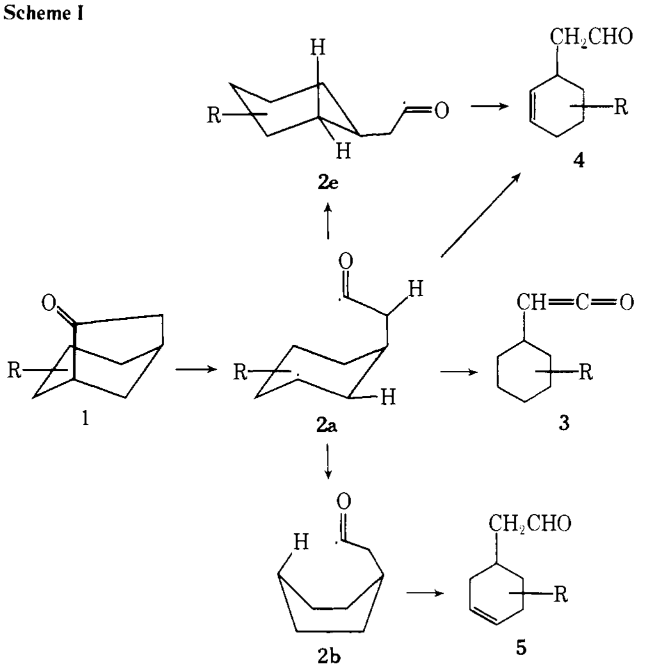
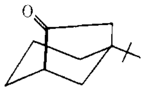
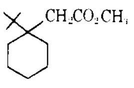
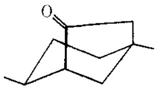
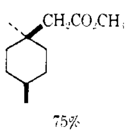
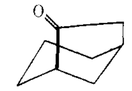
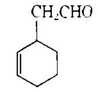
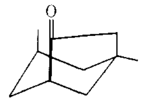
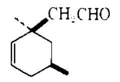
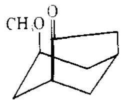
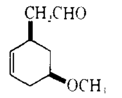
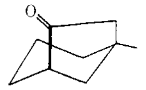
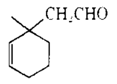
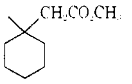
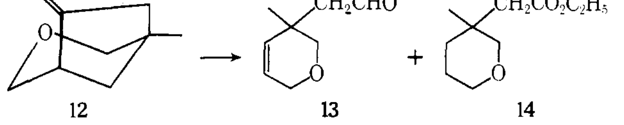


Table I. Products of Photolysis of Bicyclo[3.2.1]octan-6-ones

	Product and yield	
Bicyclooctanone	Aldehyde	Methyl ester (from ketene)
 6	<0.5%	 96%
 7	<4%	 75%
 8	 93%	<0.5%
 9	 ~85%	<2%
 10	 85%	<0.5%
 11	 44%	 51%

biradical intermediates when the lifetime of the biradical is not an issue.[2,4,6] In contrast to these earlier investigations the bicyclooctanones **1** provide a system in which such effects will be observable only if conformational relaxation of biradical **2** competes successfully with the hydrogen transfer which leads to products. That is, conformational equilibration of **2** can influence the course of reaction only if **2** is sufficiently long lived. If the lifetime and energy content of **2** permit the application of ground state conformational principles, then the transformations shown in Scheme I below require consideration. We note the generally accepted conclusions[7] that cyclohexyl radical behaves conformationally like cyclohexane or cyclohexanone and that the radical center itself is effectively planar or nearly so. Initially formed **2a**.(axial acyl side chain) could undergo hydrogen transfer from side chain to ring to give ketene **3**, or from ring to side chain to give aldehyde **4**; alternatively **2a** could invert to **2e** (equatorial acyl side chain) and possibly also to **2b**, from which **4** and **5**, respectively, could arise on hydrogen transfer from ring to side chain. It should be noted that the only disproportionation possible from **2e** leads to aldehyde **4**. On the other hand, if hydrogen transfer is rapid relative to conformational change, then all products will be derived directly from **2a**. At present, insufficient quantitative information is available to permit reliable prediction of the behavior of the intermediate **2**, and we have, therefore, investigated this matter through photolysis of several substituted bicyclooctanones of known stereochemistry. Solutions of these ketones (~0.014 *M*) in benzene containing ~3.5% (v/v, ~0.88 *M*) methanol were irradiated through Pyrex (λ >2800 Å) at 30 ± 0.5°. Products were isolated and purified by preparative vapor phase chromatography (vpc). The results are presented in Table I.[8]

These data reveal an excellent correlation between the fate of biradical **2** and expected conformational effects in the six-membered ring. Ketones **6** and **7**, for which **2a** is the stable conformation of the intermediate, yield ketene and essentially no aldehyde. Although formation of aldehyde from **2a** is geometrically feasible, this path does not compete successfully with that leading to ketene.[9] For ketones **8–10** the inverted conformer **2e** is clearly the more stable, and here the product is aldehyde with essentially no ketene. Ketone **11** should yield a conformationally balanced intermediate with similar equilibrium concentrations of **2a** and **2e**, and in this case the observed product is a mixture of aldehyde and ketene. In qualitative agreement with the behavior of **11** is the earlier observation[10] that irradiation of the related oxabicyclooctanone **12** in ethanol furnishes aldehyde **13** and ester **14** in the ratio 1.2:1. None of these reactions furnished aldehyde **5** from the boat conformation **2b**; in the case of ketone **8** the appropriate compound, 3-cyclohexeneacetaldehyde (**5**, R = H),[11] was on hand and as little as 2.5% of this product would have been detected.



These observations then indicate that the conformational equilibria of Scheme I must be taken into consideration and that disproportionation of the biradical intermediate **2** occurs from the stable cyclohexane chair conformer(s) in each instance. This suggests that it should be possible to obviate these conformational effects by sufficiently increasing the rate of hydrogen transfer in **2a** or alternatively by sufficiently decreasing the rate of inversion of **2a** to **2e**; in either case the product should then arise solely from **2a** regardless of the position of the conformational equilibrium. This possibility is presently under investigation.

References and Notes

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(8) Yields were determined by calibrated vpc measurements and are based on converted starting material. Parent ketone **8** was prepared as described by K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31,** 2250 (1966); the ester from **7** was compared with independently prepared authentic material, and the aldehyde from **8** was characterized as its known (D. L. Garin, *J. Org. Chem.*, **34,** 2355 (1969)) 2,4-dinitrophenylhydrazone. All other compounds for which structures are given are new, and they gave satisfactory ir and 220-MHz spectra, as well as high resolution mass spectra or elemental analyses. The syntheses of the new bicyclooctanones will be discussed later.

(9) It is not obvious from examination of molecular models that this specificity reflects a preferential rotational orientation[6] of the acyl side chain. An interesting alternative possibility presently being examined is that it results from a stereoelectronic effect.

(10) S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Amer. Chem. Soc.*, **94,** 7797 (1972).

(11) M. Schwartz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30,** 2425 (1965).

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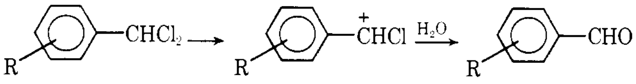
Deuterium Isotope Effects in the Solvolysis of Benzal Chlorides. I. α-Deuterium Isotope Effects and Salt Effects in the Solvolysis of *p*-Methoxybenzal Chloride in Dioxane–Water Mixtures

Sir:

Shiner has proposed that α-deuterium (α-D) isotope effects can be used as a very sensitive guide to transition state structure in solvolysis reactions.[1] He has shown that α-D effects are a function of leaving group (OR $\approx$ F > Cl > Br > I) and mechanism (*i.e.*, variable and predictable according to which step in the overall solvolysis scheme is rate determining).

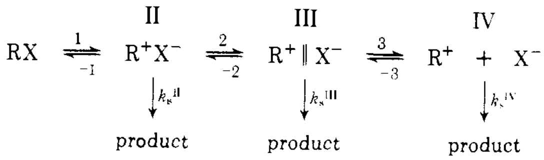
In this communication we show how the variation of the α-D effect with the nature and concentration of added salt can be a powerful tool in the elucidation of the nature of the rate-determining step in solvolysis reactions. To our knowledge this is the first application of α-D isotope effects in conjunction with salt effects to problems in solvolysis.

The kinetics and mechanism of the hydrolysis of benzal chlorides has been the subject of numerous reports.[2-6] All of the available evidence points to a carbonium ion intermediate in these solvolyses. For example, ρ^+ calculated from published data[3] is -5.2 and the rate of hydrolysis is unaffected[4-6] by external nucleophiles thus suggesting that bimolecular SN2 processes are unimportant.



Winstein has shown[7] that several intermediates are necessary to explain certain kinetic observations. For example,[8] the rate at which optically active *threo*-3-*p*-anisyl-2-butylbromobenzene sulfonate racemizes, k_{rac}, exceeds the rate at which solvolysis product is produced, k_t. While addition of certain "special" salts such as $LiClO_4$ can narrow the gap between k_{rac} and k_t, it cannot be eliminated. Presumably, one of these intermediates, the solvent separated ion pair (III, Scheme I), is trapped by anion exchange with perchlorate while II is not. Thus some, but not all, ion pair return can be eliminated. Addition of perchlorate salts has been shown to give rise to this "special" salt effect in several instances.[7-11] Azide ion has also been shown to be an effective scavenger of solvent-separated ion pairs in the solvolysis of α-*p*-anisylethyl-*p*-nitrobenzoate.[12] This system is closely related to that of the present study. Because the perchlorate solvent-separated ion pair cannot return to starting material, the substantial rate increases observed by the addition of small amounts of perchlorate salts have their origin in part in eliminating return from III.

Scheme I



Recently Shiner[1] has used the Winstein scheme in an evaluation of α-D isotope effects in solvolysis. In summary, from a number of different examples he has concluded that maximum α-D effects are expected for reaction whose rate-limiting step is either k_2 or k_3. For reactions whose rate-limiting step is k_1 or any of the capture steps (k_s^{II}, k_s^{III}, or k_s^{IV}) the observed α-D effect is reduced to about 60–80% of its maximum value. This, of course, is due to the higher zero point energy of the transition state for these processes because of the "stiffer" force constants for the α-CH bond if a leaving group or nucleophile is partly bound to the carbonium ion center.

Our results for the α-D effect in *p*-methoxybenzal chloride in various dioxane–water mixtures are given in Table I.

For Cl as the leaving group, Shiner[13,14] has shown that the maximum α-D effect expected is 1.15–1.16. The results reported in Table I show that α-D effects in benzal chlorides can be considerably larger. This is not too surprising since the ground and transition state structures for these hydrolyses are very different than Shiner's system (α-phenylethyl halides). However, there is a marked reduction in the α-D isotope effect in the less aqueous solvents. We interpret this change as signaling the incursion of some rate-limiting attack on III (k_s^{III}) in the less aqueous dioxane–water mixtures. Additional support for this interpretation comes from a study of salt effects and isotope effects in 85% aqueous dioxane.

In both 75 and 85% dioxane, the rate of hydrolysis is increased by addition of $LiClO_4$. Rate *vs.* $[LiClO_4]$ plots are

Table I. α-D Isotope Effects for the Hydrolysis of *p*-Methoxybenzal Chloride in Dioxane–Water Mixtures at 25

% dioxane[a]	k_H/k_D[b]
65	1.20 ± 0.02
75	1.178 ± 0.004
80	1.142 ± 0.005
85	1.127 ± 0.002
90	1.132 ± 0.008

[a] Volume per cent (*e.g.*, 65% dioxane = 65 ml dioxane + 35 ml water). [b] Determined spectrophotometrically by monitoring the appearance of *p*-methoxybenzaldehyde at 275 nm. Except for 65% dioxane each result is an average of about four isotope effects determined by running two H's and two D's at the same time in a Cary 16K at 25.0 ± 0.1°. The errors are standard deviations. From the results reported here and other unpublished work, we estimate the standard error of most isotope effects determined in this way is ±0.005. Because of the rapid rate of hydrolysis, the 65% dioxane isotope effect is the average of 11 H runs compared to 11 D runs.