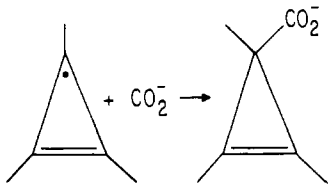
irradiated with an electron beam from a 3-MeV Van de Graaff accelerator in a magnetic field of 0.5 T with the sample flowing into an NMR spectrometer probe within 1 s, the CIDNP spectra shown in Figure 2 was obtained.[9] The chemistry observed on pulse radiolysis of a formate solution is well established and known to yield CO_2^- by hydrogen abstraction by the OH radical from the formate ion.[10] At the same time, the hydrated electron converts the cyclopropenyl cation to the cyclopropenyl radical. The spectrum shown in Figure 2 is that of trimethylcyclopropenyl carboxylic acid generated by the combination of the CO_2^- with the cyclopropenyl radical.



The important point is that the three methyl groups in the acid are equally polarized,[11] showing that during the lifetime of the correlated pair (10^{-8} s) all three methyl groups are experiencing the same time-averaged hyperfine interaction. This allows us to put a lower limit on the rate constant of the valence bond tautomerization of 10^8 s^{-1} at 292 K.

The limits for the barrier in the potential surface is set between 3.5 and 7 kcal/mol by combining the ESR and NMR data obtained at different temperatures and by estimating the preexponential factor to be 10^{13}. Of course, it is possible that the lower limit is affected by the constraints of the matrix.

Acknowledgment. We are indebted to A. D. Trifunac and L. Dalton for help and advise on the pulse radiolysis-NMR and ELDOR experiments, respectively. G.L.C. acknowledges support by NSF Grant CHE 7821789.

(9) The apparatus used for this experiment has been described by Trifunac and Evanocho [A. D. Trifunac and W. T. Evanochko, *J. Am. Chem. Soc.*, **102**, 4598 (1980)].

(10) J. Rubani and G. Stein, *Trans. Faraday Soc.*, **58**, 2150 (1962).

(11) The signal intensities of the two types of CH_3 groups are identical after normalizing for the numbers of protons involved.

C-H Activation in Completely Saturated Hydrocarbons: Direct Observation of M + R-H → M(R)(H)

Andrew H. Janowicz and Robert G. Bergman*

Department of Chemistry, University of California and Materials and Molecular Research Division Lawrence Berkeley Laboratory Berkeley, California 94720

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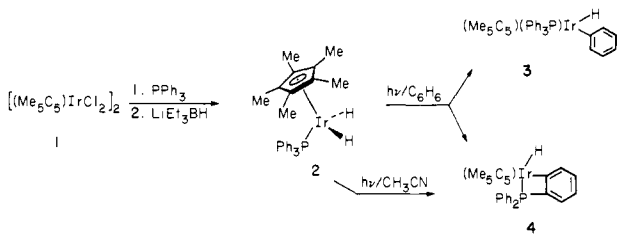
One of the most intriguing goals of homogeneous organotransition-metal chemistry is the possibility of carrying out selective chemical transformations on, or functionalizing, very unreactive materials such as saturated hydrocarbons.[1] The longest known examples of intermolecular C-H activation in saturated hydrocarbons are those involving the use of soluble platinum salts at relatively high temperatures[2] and more recently porphyrin complexes.[3] However, in none of these cases has it been possible to detect intermediate hydridoalkylmetal complexes formed by direct oxidative addition to a C-H bond, and in some there is evidence for free radical mechanisms.[3f,4]

Scheme I



There are a number of cases now known involving *intramolecular* oxidative addition to unactivated C-H bonds.[5] However, most of these systems steadfastly resist reaction with C-H bonds not present in the same molecule as the metal center. In important recent work, it was observed that reactive species generated from certain Ir and Re precursors react with completely saturated hydrocarbons.[6] However, both of these systems involve multiple hydrogen-atom loss in the hydrocarbon and require an added alkene as hydrogen acceptor. Direct, one-stage oxidative addition (reaction 1) has been observed so far only at C-H bonds which

$$M + R\text{-}H \rightarrow M(R)(H) \qquad (1)$$

can be considered at least weakly activated,[7] either because they are aryl or vinyl C-H or because they are adjacent to activating groups or atoms (e.g., aryl, carbonyl, cyano, R_3Si, or the metals themselves, as in α or β elimination). We now wish to report the discovery of an organotransition-metal system capable of *intermolecular oxidative addition to single C-H bonds in saturated hydrocarbons*, leading to hydridoalkylmetal complexes in high yield at room temperature in homogeneous solution.

Our investigations began with the preparation of the dihydridoiridium(III) complex **2** shown in Scheme I, which can be obtained in 42% yield by treatment of dimer[8] **1** with triphenylphosphine followed by lithium triethylborohydride. Irradiation

(1) (a) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (d) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; p 179ff. (e) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 222ff.

(2) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725.

(3) (a) Groves, J. T. *Adv. Inorg. Biochem.* **1979**, *1*, 119. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (c) Groves, J. T.; Van Der Puy, M. *Ibid.* **1976**, *98*, 5290; (d) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413. (e) Groves, J. T.; Kruper, W. J.; Jr. *Ibid.* **1979**, *101*, 7613. (f) Hill, C. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6374.

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(5) For examples, see: (a) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732. (b) Clark, H. C.; Goel, A. B.; Goel, S. *Inorg. Chem.* **1979**, *18*, 2803. (c) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728. (d) Empsall, H. D.; Hyde, E. M.; Markham, R.; McDonald, W. S.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1977**, 589. (e) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59 and references cited there; (f) Bennett, C. R.; Bradley, D. C. . *Chem. Soc., Chem. Commun.* **1979**, 29. (g) Andersen, R. A.; Jones, R. A.; Wilkinson, *J. Chem. Soc., Dalton Trans.* **1978**, 446. (h) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (i) Chappell, S. D.; Cole-Hamilton, D. *J. Chem. Soc., Chem. Commun.* **1980**, 238. (j) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (k) Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795. (l) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60.

(6) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (b) Crabtree, R. H.; Mellea, M. F., Mihelcic, J. M.; Quirk, J. M. *Ibid.*, in press. (c) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, *1243*.

(7) Examples: (a) Berry, M.; Elmitt, K.; Green, M. L. H. *J. Chem. Soc., Dalton, Trans* **1979**, 1950. (b) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. *Nouv. J. Chim.* **1977**, *1*, 187. (c) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432. (d) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073; **1978**, *100*, 7577. (e) Bradley, M. G.; Roberts, D. A.; Geoffroy, G. L. *Ibid.* **1981**, *103*, 379. (f) Rausch, M. D.; Gastinger, R. G.; Gardner, S. A.; Brown, R. K.; Wood, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 7870.

(8) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

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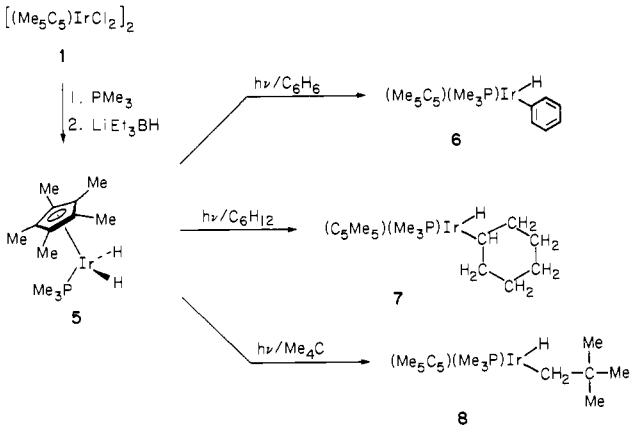
Scheme II

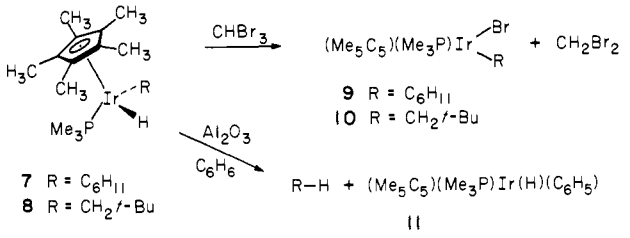


($\lambda_{max} \geq 275$ nm; high pressure Hg lamp, Pyrex filter) of this material in benzene resulted in extrusion of dihydrogen,[7a,b,9] leading to the hydridophenyl complex **3** and the ortho-metalated complex **4** (47:53 ratio), presumably via the coordinatively unsaturated complex $(Me_5C_5)(Ph_3P)Ir$. Irradiation in other solvents (e.g., acetonitrile, cyclohexane) gave either all or mostly (see below) ortho metalation. As indicated above, irradiative loss of H_2 and formation of **3** and **4** in these reactions has considerable precedent in related systems.

In an effort to make ortho metalation less favorable, we decided to prepare the complex analogous to **2**, containing a trimethylphosphine ligand in place of the PPh_3 group (**5**). As in the synthesis of **2**, treatment of **1** with the appropriate phosphine, followed by $LiEt_3BH$, gave **5** in 43% yield.[10] Irradiation in benzene resulted in clean loss of H_2 and attack on solvent, leading to hydridophenyliridium complex **6**. However, when the irradiation was carried out in cyclohexane, a new material was formed (90% yield at 74% conversion of starting material after 5.5 h of irradiation) in which both the Me_3P and pentamethylcyclopentadienyl ligands were clearly intact.[11] Although thermally stable at room temperature, it was very sensitive both to air and chromatography supports (eliminating cyclohexane in certain cases; see below). Purification was finally effected, although with significant loss of material, by rapid chromatography using 4% THF/cyclohexane eluent on alumina III under air-free conditions, followed by evaporation of solvent. The structure of this material was confirmed as that of (η^5-pentamethylcyclopentadienyl)(trimethylphosphine)hydridocyclohexyliridium(III) (**7**, Scheme II) on the basis of spectral data and chemical conversion to the more sparingly soluble bromocyclohexyl complex **9** (see below). For **7**: ^{1}H NMR (C_6D_6) δ 1.87 (dd, J = 1.9, 0.7 Hz, Me_5C_5), 1.25 (d, J = 9.5 Hz, PMe_3), 0.80, 1.50–2.30 (br, C_6H_{11}), −18.67 (d, J = 36.7 Hz, Ir-H); ^{13}C NMR (C_6D_6) δ 92.36 (d, J = 3.4 Hz, $C_5(CH_3)_5$), 19.69 (d, J = 35.7 Hz, $P(CH_3)_3$), 10.75 (s, $C_5(CH_3)$, 44.58 (d, J = 4 Hz, C_6H_{11} (β-C)), 43.96 (d, J = 2 Hz, C_6H_{11} (β-C)), 32.92 (s, C_6H_{11} (γ-C)), 32.85 (s, C_6H_{11} (γ-C)), 28.33 (s, C_6H_{11} (δ-C)), 3.27 (d, J = 7.1 Hz, C_6H_{11} (α-C)); FDMS, m/e 488, 486.

The intermediate formed on irradiation of **5**, presumably $(MeC_5)(Me_3P)Ir$, also reacts with neopentane. Irradiation of **5** in neopentane solvent gives, after 5.3 h of irradiation time (80% NMR yield after 83% conversion), a new complex once again seen

Scheme III



by NMR spectroscopy to contain alkyl and hydride ligands and intact Me_5C_5 and Me_3P groups. Its structure is assigned as **8**, the hydridoalkyl complex analogous to **7**, on the basis of spectral data and conversion to the corresponding bromoneopentyl complex **10**. Data for **8**: ^{1}H NMR (C_6D_6) δ 1.82 (dd, J = 1.7, 0.7 Hz, Me_5C_5), 1.21 (d, J = 9.6 Hz, PMe_3), 1.28 (s, $CH_3)_3$); 1.5 (complex m, CH_2), −17.67 (d, J = 36.5 Hz, IrH); ^{13}C NMR (C_6D_6) δ 92.00 (d, J = 3.4 Hz, $C_5(CH_3)_5$), 19.68 (d, J = 36.7 Hz, $P(CH_3)_3$), 10.62 (s, $C_5(CH_3)_5$), 33.83 (s, $(CH_3)_3$), 35.71 (s, $C(CH_3)_3$), 6.20 (d, J = 7.1 Hz, CH_2). Treatment of **7** and **8** with almost any oxidizing or electrophilic reagent (e.g., $ZnBr_2$, H_2O_2, Br_2) results in reductive elimination of the hydrocarbon. In a particularly mild reaction, which accounts for part of the difficulty encountered in purification by chromatography, stirring **7** with Al_2O_3 in benzene solution for 1 h generates cyclohexane (95% yield) and the hydridophenyl complex **6**; neopentane is similarly formed in 98% yield from **8**.

As indicated above, we believe these reactions proceed by loss of H_2 from **5** to form the coordinatively unsaturated species $(Me_5C_5)(Me_3P)Ir$. We have carried out some preliminary studies which support this view and which make other mechanisms (especially those involving free organic radicals) seem quite unlikely. First, irradiation of **5** in C_6D_{12} gave only H_2 and $(Me_5C_5)(Me_3P)Ir(D)(C_6D_{11})$. Second, **5** was irradiated in a 50:50 mixture of cyclohexane and neopentane. The products **7** and **8** were formed in a 0.88 ratio, indicating insertion favors a *primary* over a secondary C–H bond; radicals exhibit just the opposite selectivity.

The isotope effect experiment might also have been useful for a crossover study. However, decomposition occurs on mass spectroscopy of the hydridoalkyl complexes, and we have not been successful in obtaining accurately reproducible peak intensities in FDMS. As an alternative, therefore, we decided to take advantage of the very different hydride NMR chemical shifts of **7** and **8** and irradiated **5** in a mixture of neopentane and cyclohexane-d_{12}. Inspection of the Me_5C_5 region of the spectrum showed both hydrocarbons had reacted to a similar extent. While some cyclohexyl-d_{11} hydride crossover product (ca. 10%) was formed in this experiment, the majority of the reaction was clearly intramolecular.

Following the observations summarized immediately above, we reexamined the irradiation of the triphenylphosphine complex **2** in cyclohexane. As state earlier, the predominant product of this reaction is the ortho-metalated complex **4**. However, a significant amount (ca. 30%) of a second hydride is also formed in this reaction. Preliminary NMR data suggest this material is the intermolecular C–H activation product analogous to **7**, having PPh_3 in place of the PMe_3 ligand. Thus even in the presence of a proximate aromatic group, intermolecular reaction appears to be possible for the iridium center.

We are now in the process of seeking reagents which will allow conversion of the alkyl groups in **7** and **8** into functionalized organic compounds. In addition, we are carrying out experiments aimed at probing the mechanism of the oxidative addition more deeply. Perhaps most important, however, is the issue of selectivity.[1] Clearly the intermediate generated on irradiation of **5** has already achieved the first and perhaps most crucial type of selectivity—it reacts more readily with C–H bonds in other molecules, even hydrocarbons, than it does with those present in its own ligands. It is now important to determine how effectively the unsaturated intermediate discriminates in reactivity between different types of C–H bonds in reactant molecules and, if this type of "external" selectivity is low, whether analogues of **5** can

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be prepared in which it is increased. Experiments directed at these goals are under way.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U. S. Department of Energy under Contract W-7405-ENG-48. We are grateful to the Johnson-Matthey Corporation for a generous gift of iridium chloride.

Registry No. 1, 12354-84-6; **2**, 80145-87-5; **3**, 80146-08-3; **4**, 80145-86-4; **5**, 80146-01-6; **6**, 80146-02-7; **7**, 80145-83-1; **8**, 80145-84-2; **9**, 80145-85-3; **10**, 80160-32-3; cyclohexane, 110-82-7; neopentane, 463-82-1.

Deuterium Isotope Effects on the Solvolysis of 1-(1-Adamantyl)ethyl Sulfonate Esters

V. J. Shiner, Jr.,* Thomas E. Neumann, and Robert D. Fisher

Department of Chemistry, Indiana University Bloomington, Indiana 47405

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In a series of papers[1-5] we have proposed that secondary alkyl sulfonates which solvolyze by a k_c limiting mechanism without internal return show α-deuterium kinetic isotope effects (α-*d* KIEs) in the range 1.15–1.16. This mechanism is exemplified by 3,3-dimethyl (pinacolyl) sulfonates which show α-d KIEs in this range in all solvents studied;[2] internal return is apparently reduced to insignificance by rapid rearrangement of the secondary to the tertiary ion in the intimate ion pair. Similar α-d KIEs are expected if the rate-determining step is attack by an oxygen nucleophile on a reversibly formed ion or ion-pair intermediate. On the other hand, if further unimolecular separation, dissociation, or β-hydrogen elimination from a reversibly formed ion pair is rate determining, the α-d KIE is expected to be in the range 1.22–1.23, values characteristic of the solvolysis of 2-adamantyl esters.[5] Of course, a mixture of these rate-determining steps would give values in between these limits. The α-d KIE may be lower than 1.15 if rate-determining loss of the leaving group is assisted by an external or internal nucleophile.

In support of an alternate mechanism of solvolysis which minimizes the importance of internal return, it has been suggested[6] that α-d KIEs lower than the limiting value of 1.22–1.23 may be due to steric effects in the initial state. In support of this contention it was reported that 1-(1-adamantyl)ethyl *p*-bromobenzenesulfonate (I-OBs) solvolyzes in 97% trifluoroethanol–3% water with an α-d KIE of only 1.11. It has been recognized for some time[7] that steric crowding tends to increase vibrational frequencies and H/D fractionation factors. However, in limiting solvolyses the transition state is expected to be less crowded than the initial state, leading to the conclusion that sterically hindered reactants should show larger not smaller α-d KIEs.

We wish to report the results of a more extensive study of the solvolysis of the title esters which shows that steric hindrance is not the cause of the reported lower isotope effect. Table I gives solvolysis rates α-d and β-d_3 rate effects and products for the title esters in nine different solvents. Two general features are of importance to the present argument.

Table I. Rates, Isotope Effects, and Product Yields for Solvolysis of 1-(1-Adamantyl)ethyl Sulfonates

solvent[a]	leaving gp[b]	k_H[c]	$k_H/k_{\alpha\text{-d}}$	$k_H/k_{\beta\text{-d}_3}$	product yields[d] sub	elimn	rearr
98H	OPms	178.5	1.116	1.120	31.5	4.4	64.1
90H	OPms	43.58	1.113	1.135	26.0	4.4	68.6
80H	OPms	39.17	1.120	1.146	26.8	7.4	65.7
97T	OBs	29.70	1.111	1.151	30.5	7.4	62.1
80T	OBs	33.49	1.119	1.153	30.6	7.5	62.0
70T	OBs	35.90	1.122	1.151	33.3	6.1	60.5
80E	OBs	0.512	1.147				
70E	OBs	1.374	1.144	1.256	66.7	13.0	20.3
60E	OBs	3.459	1.123	1.214	56.0	15.0	29.0

[a] 98H is 98% hexafluoroisopropyl alcohol–2% water; 97T is 97% trifluoroethanol–3% water; 80E is 80 vol.% ethanol–20% vol.% water, etc. [b] OPms is pentamethylbenzenesulfonate[8] and OBs is *p*-bromobenzenesulfonate. [c] *k*'s are in units of 10^{-5} s^{-1}, measured spectrophotometrically at 25 °C. Standard errors in the rate constants are generally about 0.1% and the reproducibility was about ±0.3%.[9] [d] Product yields were determined by analysis of the ^{2}H NMR spectra of reaction mixtures, initially about 0.1 M in α-d ester in the various solvents after about 10 half-lives of solvolysis. The products and the ranges, in the several solvents, of their δ values relative to external Me_4Si-d_{12} measured with a Varian HR 220 spectrometer operating at 33.8 MHz were 1-(1-adamantyl)-ethanol and ethers, 3.32–3.50; 1-(1-adamantyl)ethane, 5.80–5.91; rearranged homoadamantyl substitution products, 1.93–2.25.

(1) Although the α-deuterium effect is low in fluorinated alcohol solvents, it is solvent dependent and not nearly so low in some ethanolic solvents. Therefore, some factor other than initial state crowding must be the most important cause of the lower effects.[10]

(2) The β-d_3 effects show variations with solvent parallel to the variations in α-d effects, strongly suggesting a common origin; since there is no reason to expect a low initial state fractionation factor for the methyl group, such a cause for the low α-d effect is unlikely.

We know of no cause for such large changes in isotope effects for a given reactant, as are illustrated in Table I, other than a change in the rate-determining step.[11] The only way for the mechanism of solvolysis of these esters to change, since S_N2 attack is out of the question,[12] is for internal return to take place in at least some of the solvents or for neighboring group participation to change drastically with solvent.[14]

We note that in the 70E and 80E solvents the α-d effects are very close to the values of 1.15–1.16 characteristic of pinacolyl (3,3-dimethyl-2-butyl) esters in a variety of solvents and that the β-d_3 effects also are close to the values of 1.19–1.21 for the pinacolyl analogues.[2] If the small fraction of elimination product were formed from an ion or ion-pair intermediate, this could contribute an increase of a few percent in the β-d_3 effects but only if there is a significant proportion of internal return.

The fact that the solvents in which the isotope effects are low also give the greatest proportions of rearranged substitution suggests that the lowering of the effects is due to the rearranged or partially rearranged structure of the transition state. If the bond to the oxygen of the leaving group is replaced by a tran-

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(9) Seib, R. C.; Shiner, V. J., Jr.; Sendijarevic, V.; Humski, K. *J. Am. Chem. Soc.* **1978**, *100*, 8133–8137.
(10) That fractionation factors are not strongly influenced by solvent is most relevantly demonstrated by the fact that certain sulfonate esters such as pinacolyl[2] and 2-adamantyl[5] which react by a constant mechanism show isotope effects on solvolysis that are not affected by solvent changes.
(11) Hartshorn, S. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9002–9012.
(12) It has been suggested that pinacolyl sulfonate esters are subject to "nucleophilic solvation",[13] despite their neopentyl type structure and low S_N2 reactivity with strong nucleophiles. It is apparent that any such effect cannot be the cause of the variation in α and β isotope rate effects here reported because the larger effects, which would correspond to lesser nucleophilic involvement, are in the more nucleophilic solvents.
(13) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.
(14) Shiner, V. J., Jr.; Tai, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 436–442.

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