to give a colorless solution. GC analysis showed complete consumption of 14 and the appearance of a new compound with a shorter retention time. This was shown to be $(CF_3CH_2O)_3(CN)_3$ by spiking the solution with an authentic sample. A sample of the product was treated with CH_2Cl_2/H_2O; the material in the CH_2Cl_2 was identical with the known triazine by IR.

Acknowledgment. This work was supported by the Office of Naval Research, Code 473.

Registry No. **1**, 15562-09-1; **3**, 52801-29-3; **4**, 75780-65-3; **5**, 75767-45-2; **6**, 75767-46-3; **7**, 75767-47-4; **8**, 75767-48-5; **9**, 75767-49-6; **10**, 75767-50-9; **11**, 75767-51-0; **12**, 4134-43-4; **13**, 75767-52-1; **14**, 75767-53-2; **15**, 75767-54-3; **16**, 75767-55-4; **17**, 75767-56-5; **18**, 75767-57-6; **19**, 75767-58-7; **20**, 1919-48-8; **21**, 75767-59-8; **22**, 75767-60-1; **23**, 75767-61-2; **24**, 54416-56-7; methanol, 67-56-1; 2,2,2-trifluoroethanol, 75-89-8; 1,1,1,3,3,3-hexafluoro-2-propanol, 920-66-1; phenol, 108-95-2; 3-nitrophenol, 554-84-7; 3-(trifluoromethyl)phenol, 98-17-9; pentafluorophenol, 771-61-9; 4-nitrophenol, 100-02-7; 2,2-dinitro-2-fluoroethanol, 17003-75-7; 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, 368-66-1; 2,2-dinitro-2-fluoroacetamide, 15562-10-4; *p*-nitrophenyl fluorodinitroacetimidate, 75767-62-3; 2,4,6-trichloro-1,3,5-triazine, 108-77-0; 2,4,6-tris(2,2,2-trifluoroethoxy)-1,3,5-triazine, 1547-96-2; fluorodinitromethane, 7182-87-8.

Primary and Secondary Kinetic Isotope Effects in the Acid-Catalyzed Dehydration of 1,1′-Diadamantylmethylcarbinol in Aqueous Acetic Acid

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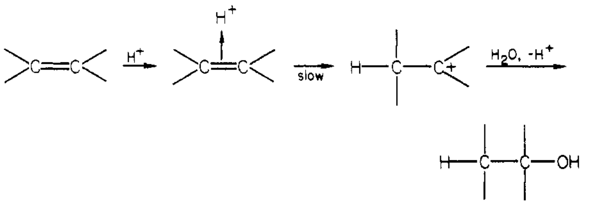
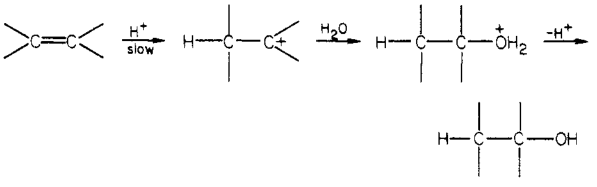
The sulfuric acid catalyzed dehydration of 1,1′-diadamantylmethylcarbinol in anhydrous acetic acid proceeds exclusively to 1,1-bis(1-adamantyl)ethylene. The secondary deuterium isotope effect of 1.32 found for this reaction shows that carbonium ion formation from the protonated alcohol is rate determining. In the presence of water, however, capture of the carbonium ion competes with deprotonation, introducing a primary isotope effect. Consequently, the overall KIE rises, reaching 3.18 for 80% aqueous acetic acid. Analysis of the KIE for 80–100% aqueous acetic acid is consistent with a simple classical mechanism involving reversible formation of the intermediate carbonium ion. The primary isotope effect upon deprotonation is at the most 2.98, indicative of an asymmetric transition state close to the carbonium ion.

It is generally agreed that the acid-catalyzed hydration of olefins proceeds via protonation, reaction of the resulting carbonium ion with water, and final deprotonation of the oxonium ion to alcohol. Nevertheless, the finer details of this mechanism remained controversial for many years.[1] Various kinetic criteria, formerly believed to support rate-determining collapse of a π-complex intermediate to a carbonium ion (eq 1), did not rule out an A-S_E2 mechanism where protonation of the olefin is rate determining (eq 2). The finding of general acid catalysis in the case of simple olefins,[1c] following unsuccessful attempts,[2] finally established this latter mechanism, already adopted for functionally substituted olefins. As a consequence of microscopic reversibility, the rate-determing step of alcohol dehydration must then be carbonium ion deprotonation, as has been shown directly in the case of 1,2-diphenylethanols.[3]



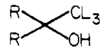
(1)



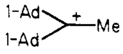
(2)

As to the mechanism of alcohol dehydration in *nonaqueous media*, little is known. Rocek's assertion that in 85% to 100% aqueous acetic acid heterolysis of the protonated alcohol is rate determining, based as it is on the interpretation of an acidity function correlation,[4] cannot be taken as conclusive. However, we have shown that the isotope effects on the kinetics and products of the dehydration of di-*tert*-butylmethylcarbinol, **1**, in anhydrous acetic acid are consistent with rate-determining heterolysis.[5] This reaction is unfortunately complicated by the fact that the intermediate di-*tert*-butylmethylcarbonium ion can rearrange to the triptylidimethylcarbonium ion and that, consequently, only small kinetic isotope effects would be observed even if deprotonation were rate determining. It was of interest therefore to seek a system where no such rearrangement was likely to occur.

1,1′-Diadamantylmethylcarbinol, **2**, was chosen on the grounds that rearrangement of the corresponding carbonium ion, **3**, would lead to formation of the homoadamantyl system, **4**. Homoadamantane is, according to



1, R = *t*-Bu
2, R = 1-Ad
h, L = H;
d, L = D



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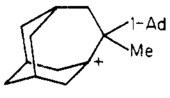

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0022-3263/81/1946-0412$01.00/0

Table I. Rate Constants, k_H and k_D, for Sulfuric Acid Catalyzed Dehydration of 1,1′-Diadamantylmethylcarbinols, 2h and 2d, in Acetic Acid/Water Mixtures at 25 °C

$[H_2O]$	$[H_2SO_4]$	k_H, s^{-1}	k_D, s^{-1}	k_H/k_D
0.033	0.0003	3.19×10^{-4}	2.37×10^{-4}	1.35
0.033	0.0015	1.49×10^{-3}	1.11×10^{-3}	1.34
0.033	0.006	5.50×10^{-3}	4.16×10^{-3}	1.32
0.033	0.015	1.45×10^{-2}	1.09×10^{-2}	1.33
1.14	0.0059	7.94×10^{-4}	4.29×10^{-3}	1.85
1.14	0.0294	4.57×10^{-3}	2.51×10^{-3}	1.82
2.81	0.0285	1.15×10^{-3}	4.79×10^{-4}	2.39
2.81	0.173	1.10×10^{-2}	4.71×10^{-3}	2.34
5.58	0.164	2.81×10^{-3}	1.02×10^{-3}	2.75
5.58	0.500	1.53×10^{-2}	5.77×10^{-3}	2.66
11.13	0.146	5.00×10^{-4}	1.57×10^{-4}	3.18
11.13	0.444	2.27×10^{-3}	7.14×10^{-4}	3.18

molecular mechanics calculations, 8–12 kcal/mol (depending on the force field chosen) more strained than adamantane.[6] Taken with the fact that proton elimination from the substituted 3-homoadamantyl cation would lead to a strained bridgehead olefin, this energy difference should be enough to inhibit olefin formation by any route not involving the methyl group protons. A further point in favor of this system is that, since it is highly congested, problems arising out of nucleophilic solvent attack on the carbonium ion intermediate should be minimized.

Results and Discussion

Addition of 1,1′-diadamantyl ketone[7] to the appropriate methyllithium compounds, CH_3Li or CD_3Li, gave the required alcohols. Dehydration of the normal alcohol in anhydrous acetic acid containing sulfuric acid gave an almost quantitative yield of 1,1-bis(1-adamantyl)ethylene. The amount of alcohol remaining after 10–15 reaction half-lives was less than 0.1% and no trace of acetate could be detected. The reaction products therefore support the line of reasoning presented above. The product-forming step is deprotonation of the methyl group; consequently, if this step is also rate determining the primary isotope effect on C–H(D) bond breaking should be quite obvious since no escape route involving proton loss elsewhere in the carbonium ion is accessible. This contrasts with the situation presented by dehydration of the di-*tert*-butyl analogue 1, where rearrangement occurs, increasing with the acid concentration, and the nonrearranged olefin is isomerized with a rate constant only 10 times less than that of dehydration.[5]

The kinetic isotope effect, k_H/k_D, measured in solutions of sulfuric acid in commercial 100% acetic acid at 25 °C, was 1.335 ± 0.011. When, however, water was added to the solvent the kinetic isotope effect rose, reaching 3.18 for a mixture containing 11 M water (Table I and Figure 1). The alcohol was insufficiently soluble in more aqueous media for measurements to be taken any further. Within experimental error, for a given water concentration, the kinetic isotope effect was independent of the acidity.

The amount of normal alcohol remaining after reaction in acetic acid containing 11 M water or obtained from olefin in the same solvent mixture was estimated to be 1.2%, which means that the equilibrium constant for the olefin hydration reaction is about 1.1×10^{-3} M^{-1}. Allowance was made for the residual alcohol in calculating the rate constants but we can ignore this reverse reaction in considering the isotope effects upon alcohol dehydration.

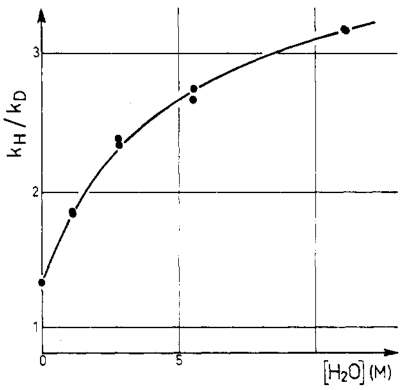

Figure 1. Dependence of the kinetic isotope effect for dehydration of 1,1′-diadamantylmethylcarbinol in aqueous acetic acid upon the water concentration: experimental points; line calculated with $s = 1.316$, $h = 0.221$, and $d = 0.659$.

Assuming that dehydration proceeds by rapid preequilibrium protonation of the alcohol followed by carbonium ion formation and deprotonation, we can write eq 3, where A stands for 1,1′-diadamantylmethylcarbinyl, and

$$AOH \overset{K}{\rightleftharpoons} AOH_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + A^+ \xrightarrow{k_2} \text{product} \quad (3)$$

K and k_2 include acid and base concentrations, respectively,[8] as shown in eq 4 and 5.

$$k_{obsd} = \frac{Kk_1k_2}{k_{-1}[H_2O] + k_2} \quad (4)$$

$$k_H/k_D = \left[\frac{Kk_1k_2}{k_{-1}[H_2O] + k_2}\right]_H \cdot \left[\frac{Kk_1k_2}{k_{-1}[H_2O] + k_2}\right]_D^{-1} \quad (5)$$

Two extreme situations can immediately be discounted. In the first, $k_{-1}[H_2O]$ is much greater than k_2; deprotonation of the carbonium ion will be rate determining and the kinetic isotope effect will be a constant equal to $[Kk_1k_2/k_{-1}]_H[Kk_1k_2/k_{-1}]_D^{-1}$. The second possibility is that k_2 is much greater than $k_{-1}[H_2O]$; this is the situation which arises when the water concentraton is very small, but if k_{-1} were so small that $k_{-1}[H_2O]$ is negligible for all $[H_2O]$ then the kinetic isotope effect would again reduce to a constant, the secondary effect upon carbonium ion formation, $(Kk_1)_H(Kk_1)_D^{-1}$. Since manifestly neither of these results is applicable we shall fit the data to the more general expression.

Putting $(Kk_1)_H(Kk_1)_D^{-1} = s$, $(k_{-1}/k_2)_D = d$, $(k_{-1}/k_2)_H = h$, and $[H_2o] = a$, we obtain

$$(k_H/k_D)/s = (1 + ad)/(1 + ah)$$

whence

$$(k_H/k_D - s)/a = sd - (hk_H/k_D)$$

Taking the observed value of the isotope effect in acetic acid without added water as s, we calculate from the slope and the intercept of the straight line expressed by the last equation that $h = 0.21$ and $d = 0.62$. These values indicate, however, that the amount of water in commerical 100% acetic acid (0.06% by Karl-Fischer titration) has a significant effect on the isotope effect: the terms $(1 + ah)$

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(7) Lomas, J. S.; Dubois, J. E. *Tetrahedron*, in press.

(8) It will be noted that this scheme does not take into account the several protonation–deprotonation equilibria occuring in these media and that we use the analytical water concentration rather than its real concentration. The elementary rate constants are in reality complex functions involving unknown equilibrium constants and concentration terms relating to the various acidic and basic species in solution. These quantities will not, however, be affected by the isotopic substitution, and their investigation is outside the scope of this paper.

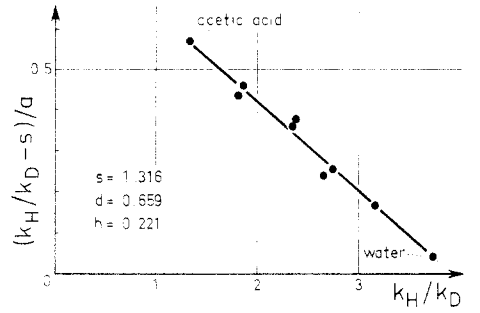

Figure 2. Linear relationship between $(k_H/k_D - s)/a$ and k_H/k_D for the dehydration of 1,1′-diadamantylmethylcarbinol in aqueous acetic acid.

and $(1 + ad)$ would be 1.007 and 1.022, respectively. Consequently, s is slightly less than the experimental value of 1.335: iteration gave self-consistent values for s, h, and d of 1.316, 0.221, and 0.659, respectively. The final correlation is shown in Figure 2. As can be seen from Figure 1, the overall kinetic isotope effect increases asymptotically at high values of the water concentration. The calculated limiting value for pure water is 3.72.

Fry[9a] has analyzed Smith and Goon's data[9b] for solvolysis of certain phenyldimethylcarbinyl derivatives in much the same way as the above, the abnormally high β-deuterium kinetic isotope effects being associated with recombination of the carbonium ion–anion ion pair to reactants in competition with β-hydrogen abstraction by solvent to form olefin. The effect upon k_H/k_D of added anion, which plays much the same role as water in our system, was not investigated.

Two numerical aspects of our results on 1,1′-diadamantylmethylcarbinol merit further comment: the magnitude of the β-D secondary isotope effect[9a,10] upon cabonium ion formation, $(Kk_1)_H(Kk_1)_D^{-1}$, and the primary isotope effect upon deprotonation, k_2^H/k_2^D.

Reckoned on a per atom basis, the value of the secondary β-D KIE (1.096 per deuterium) lies between our value for di-*tert*-butylmethylcarbinol (1.07)[5] and those of Noyce et al. for 2-hydroxy-2-phenylpropionic acid (1.11)[11] and 1,2-diphenylethanol (1.17).[3] It is almost identical with the isotope effects observed in the solvolysis of *tert*-butyl chloride[12] (1.092 to 1.103, depending on the number of deuterium atoms).

The β-deuterium isotope effects in solvolysis are generally attributed to hyperconjugation, and their dependence on structure or substituents can be interpreted in terms of changes in the internal carbonium ion structure, though mechanistic changes, Hammond postulate type effects, and conformational influences may also contribute.[9,10,13] In 1-phenylethyl chloride solvolysis,[14] for example, the β-D isotope effect diminishes with the introduction of electron-donating substituents, which at the same time increase the reactivity. It has been argued that these substituents reduce the conjugative demands on the β-CH(D) bonds,[10b] while Scheppele considers that they decrease the ionic character of the transition state.[10e] Though certain other classes of compound follow the same pattern, for larger structural changes there is no evident relationship between secondary deuterium isotope effects and reactivity.

The relative magnitude of the secondary isotope effects on compounds 1 and 2 is not easily understood. Whereas 2 is about 10^2 times as reactive as 1,[15] it has, contrary to naive expectation, the higher secondary isotope effect. Discussion of this result consists in finding the answers to two separate questions. (1) What causes the difference in reactivity? (2) Why are the isotope effects different? The short answer to the first question must be "strain relief" (though we have been unable to confirm this by strain-energy calculations[16]). If this were so we should expect the transition state for 2 to be more reactant-like than that for 1 and, consequently, the β-deuterium isotope effect to be smaller. However, since the overall strain energy change on going from the alcohol to the carbonium ion must be greater for 2 than 1, the magnitude of the steric constraints upon the CH and CD bonds will decrease more in the reaction of 2 than in that of 1. Any steric contribution to the kinetic isotope effects[10f] could therefore be greater for 2 than for 1, but there is nothing to indicate whether such a change in the magnitude (1.07 to 1.096) is compatible with the reactivity difference. In a recent study of *p*-nitrobenzoate solvolysis, for example, γ-D isotope effects were found to be very small and *variable* (1.03 to 1.11 per C_4H_9) for compounds of *closely similar* reactivities.[19]

The only hypothesis which seems capable of explaining the secondary isotope effects is that hyperconjugation and/or bridging by the neighboring CH_3 groups in 1 reduce the requirement for hyperconjugative stabilization of the carbonium ion by the CH(D) bonds. Confirmation of this suggestion would require more data than are at present available.

The second datum arising from our treatment of the kinetic isotope effects is related to the deprotonation of the intermediate carbonium ion. Since $d/h = (k_{-1}/k_2)_D(k^{-1}/k_2)_H^{-1} = (k_2^H/k_2^D)(k_{-1}^H/k_{-1}^D)$, the primary effect upon deprotonation, k_2^H/k_2^D, is confused with the isotope effect upon capture of the carbonium ion by water. The latter will be small and probably inverse (i.e., k_{-1}^H/k_{-1}^D is less than unity[5]) so the deprotonation isotope effect can be reckoned to have at the most a value equal to d/h, that is, 2.98.

Comparable effects have been observed for the deprotonation of the di-*tert*-butylmethylcarbonium ion (maxi-

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[13] For recent work on the conformation dependence of β-deuterium isotope effects, see: (a) Sunko, D. E.; Szele, I.; Hehre, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 5000; (b) De Frees, D. J.; Hehre, W. J.; Sunko, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 2323.

[14] Shiner, V. J.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968** *90*, 418.

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[16] Molecular mechanics calculation of the strain energy changes on going from the initial state to the transition state (modeled by the corresponding hydrocarbon[6] and the carbonium ion,[17] respectively) imply that the carbonium ion energies increase *faster* than those of the hydrocarbon when *t*-Bu is replaced by 1-Ad, so that the rate should *decrease*, contrary to observation. Such calculations are unreliable for the interpretation of small rate differences[15] and possibly both force fields require reparametrization. Though more sophisticated and accurate treatments of hydrocarbons have been developed,[18] the only carbonium ion force field available is virtually that proposed by Gleicher and Schleyer in 1967.[17]

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[18] (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) White, D. N. J.; Bovill, M. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1610. (c) Fitzwater, S.; Bartell, L. S. *J. Am. Chem. Soc.* **1976**, *98*, 5107.

[19] Badger, R. C.; Fry, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1680.

mum 2.67)[5] and the isomerization of 2-aryl-3-methyl-2-butene (2.34),[20] both in acetic acid.

Whether the maximum theoretical C–H isotope effect is reckoned to be 6.2 (zero-point energy only), 10 (allowing for bending vibrations), or higher still if the tunnel effect is included,[21] these are small isotope effects and are therefore indicative of an asymmetric transition state,[22] relatively close either to the carbonium ion or to the product. Since the former is of much higher energy, consideration of the Hammond postulate[23] suggests that the transition state for slow proton transfer will be in fact carbonium ion like.

Conclusion

This reaction, the dehydration of 1,1′-diadamantylmethylcarbinol in aqueous acetic acid, is unusual in that variation of the solvent composition causes the deuterium KIE to vary over a wide range. This phenomenon is attributable to the fact that one of the components of the reaction medium, water, causes the intermediate carbonium ion to revert to starting material, while the major component, acetic acid, is apparently inert. A very simple kinetic scheme leads to an equation which expresses the overall KIE in terms of the water concentration. The data provide values of the secondary isotope effect upon carbonium ion formation and of the primary isotope effect on deprotonation of this ion, the latter without it being necessary to compare elimination rates from labeled and nonlabeled groups. Though neither datum is completely resolved, both are relevant to the mechanism of dehydration and of olefin hydration in partially nonaqueous media. Our observations provide no information about the possible occurrence of π complexes but clearly do not require their involvement in the rate-determining step or steps of these reactions.

Experimental Section

Synthesis of 1,1′-Diadamantylmethylcarbinol, 2. The normal and deuterated alcohols were prepared by addition of 1,1′-diadamantyl ketone to the appropriate methyllithium compound in ether under argon at room temperature: mp 204.5 °C after recrystallization from hexane; IR (CCl_4) 3625 cm^{-1}; NMR (CCl_4) δ 1.03 (s, 3 H of methyl (absent in **2d**)), 1.70 and 1.94 (unresolved m, 30 H of adamantyl groups). The highest peak in the mass spectrum of the normal alcohol (*m/e* 296) corresponds to loss of water; in the case of **2d**, HDO is lost (*m/e* 298). Anal. Calcd for $C_{22}H_{34}O$: C, 84.01; H, 10.90. Found: C, 83.87; H, 10.88.

Dehydration Product of 1,1′-Diadamantylmethylcarbinol. Acid-catalyzed dehydration of the normal alcohol, **2h** (0.6 g), in anhydrous acetic acid containing 0.006 M sulfuric acid (100 mL) for 30 min at 25 °C gave the corresponding 1,1-bis(1-adamantyl)ethylene (0.55 g, 97% yield): mp 110–111.5 °C after recrystallization from hexane; IR (CCl_4) 1607, 895 cm^{-1}; NMR (CCl_4) δ 1.71 and 1.96 (unresolved multiplets, 30 H of adamantyl groups), 5.03 (s, 2 vinylic H). Anal. Calcd for $C_{22}H_{32}$: C, 89.12; H, 10.88. Found: C, 88.98; H, 10.94. The amount of alcohol remaiining was estimated by GLC to be less than 0.1% and no IR absorption attributable to acetate could be detected in the crude reaction product.

Alcohol-Olefin Equilibrium. Alcohol 2 or the corresponding olefin (1–2 mg) was dissolved in anhydrous acetic acid (5 mL). An aqueous acetic acid solution of sulfuric acid was added to make 10 mL (final concentration 11.13 M water, 0.444 M sulfuric acid) and the mixture was thermostated at 25 °C for 2 h. GLC analysis of samples showed an identical alcohol/olefin ratio of 1.2/98.8 regardless of the starting material.

Kinetic Procedure. Rate constants for the dehydration of the alcohols were determined by measuring the rate of disappearance of the alcohol against an internal standard by gas chromatography on Carbowax 20M. The internal standard (1,1′-diadamantyl ketone)(3 mg) and the alcohol (10 mg) were dissolved in anhydrous acetic acid (Merck, 100%, analytical grade, 25 mL). Aqueous media were prepared by taking weighed amounts of water in graduated flasks and completing with stock solutions of 100% sulfuric acid in acetic acid. The reaction was started by adding to 5 mL of the acid medium enough reactant/standard solution to make 10 mL. Samples were taken at appropriate intervals, quenched in aqueous sodium carbonate, and extracted into *n*-hexane.

Since the dehydration is slightly reversible in the presence of water, the first-order kinetic plots depart from linearity after 2–4 half-lives, depending on the water concentration, unless correction is made for the equilibrium alcohol concentration. The forward rate constants given in Table I have been corrected appropriately. Rate constants are reproducible to 1–2%, isotope effects to 3–4%.

Acknowledgment. I am indebted to Professor J. E. Dubois for stimulating and helpful discussions.

Registry No. 2d, 75782-40-0; **2h**, 75782-41-1; 1,1′-diadamantyl ketone, 38256-01-8; 1,1-bis(1-adamantyl)ethylene, 75782-42-2.

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Solvolyses of a Carbonate and a Benzhydryl Chloride inside Micelles. Evidence for a Porous Cluster Micelle

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Two water-insoluble compounds, bis(4-nitrophenyl) carbonate and *p*-chlorobenzhydryl chloride, solvolyze in micelles at rapid rates indicative of highly aqueous binding sites. This is used as evidence against the classical Hartley micelle and in support of a "porous cluster" model bearing water-filled regions where guests bind hydrophobically. The conclusions from the kinetic data agree with those from a variety of other approaches used in this laboratory including ^{13}C NMR, gas solubility, ORD, and molecular models.

Reactivity inside a micelle generally differs from that in bulk water. This fact has been widely used to probe the nature of micellar environments.[1,2] Of course, it is seldom easy to interpret small catalytic or inhibitory effects with

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