

N, 13.99. Found: C, 71.72; H, 6.02; N, 13.74.

Photostimulated reaction of enolate **9** with **1** was conducted according to procedure A to give, by GC analysis, a 45% recovery of starting material **1** and a 17% yield of ketone **10**.

Inhibited dark reaction of enolate **9** with **1** by procedure B, modified by adding 15 mol % (0.065 g) of DTBN to the 2-chloroquinoxaline, gave by GC analysis a 51% recovery of **1** and <3% of **10**.

**Treatment of 3 and 6 with Potassium Amide.** By use of 17.6 mg of potassium and a small amount of ferric nitrate, 0.45 mmol of KNH<sub>2</sub> in 50 mL of NH<sub>3</sub> was prepared. Quinoxaliny ketone **3** (102 mg, 0.45 mmol) in ether (10 mL) was added to the amide to give a bright orange solution. Stirring for 15 min, quenching, and extraction as described in procedure A gave an 85% recovery of **3** and no detectable trace of **4**. Similar treatment of ketone **6** gave only recovered **6**.

**Dark Reaction of Enolate 2 with 4-Chloroquinazoline (11a).** 4-Chloroquinazoline (**11a**) was synthesized by the method of Armarego.<sup>15</sup> Procedure B gave 95% of 1-(quinazolin-4-yl)-3,3-dimethyl-2-butanone (**12a**) as yellow crystals after recrystallization from hexane-toluene: mp 118-119 °C; IR (CDCl<sub>3</sub>) 3060 (w, CH), 1625 cm<sup>-1</sup> (s, C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.27 (s, 9 H,

*t*-Bu), 6.20 (s, 1 H, enol CH), 7.57 (m, 5 H, aromatic), 14.7 (br s, 1 H, enol OH). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.78; H, 7.13; N, 12.33.

Procedure B was modified by adding 0.45 g (100 mol %) of DTBN to **11a** before addition to the enolate. This resulted in yellow crystals of **12a** (95%) isolated by recrystallization as in the previous experiment.

**Dark Reaction of Enolate 2 with 4-Chloro-2-phenylquinazoline (11b).** Procedure B gave a yellow solid, which upon recrystallization from toluene-hexane afforded a 93% yield of 1-(2-phenylquinazolin-4-yl)-3,3-dimethyl-2-propanone (**12b**): mp 153-157 °C; IR (CHCl<sub>3</sub>) 3400 (br, enol), 3080, 3020 (CH), 1680 cm<sup>-1</sup> (s, C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.30 (s, 9 H, *t*-Bu), 6.22 (s, 1 H, enol CH), 7.43 (m, 7 H, aromatic), 8.17 (m, 2 H, aromatic), 15.57 (br s, 1 H, enol OH). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.84; H, 6.68; N, 9.17.

Procedure B was repeated, but 100 mol % (0.45 g) of DTBN was added to the ethereal solution of **11b** before addition to the enolate. This afforded light yellow crystals, which were recrystallized from toluene-hexane to give 97% of **12b**.

**Registry No.** 1, 1448-87-9; 2, 51742-96-2; 3, 37053-07-9; 4, 37053-02-4; 5, 51689-86-2; 6, 80360-33-4; 7, 80360-34-5; 8, 80360-35-6; 9, 72610-66-3; 10, 80360-36-7; 11a, 5190-68-1; 11b, 6484-25-9; 12a, 80360-37-8; 12b, 80360-38-9; potassium amide, 17242-52-3.

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## Solvolytic and Stable Ion Studies of 1,1'-Diadamantylmethyl Cations<sup>1a</sup>

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A series of 1,1'-diadamantylmethyl carbocation systems were studied under solvolytic and stable ion conditions. At low temperatures in superacid solutions, tertiary 1,1'-diadamantylmethyl derivatives (except *tert*-butyl-1,1'-diadamantylmethyl) gave the corresponding static carbenium ions. From the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data, the ion from secondary 1,1'-diadamantylmethyl precursors is assigned the rearranged 4-(1-adamantyl)-3-homoadamantyl cation structure. However, this species is not static but undergoes fast Wagner-Meerwein shifts even at very low temperatures (≈-140 °C) to give a set of six equivalent carbenium ions. There is no evidence for bridging. In solvolysis, the relatively low α-CH<sub>3</sub>/H rate ratios of the 1,1'-diadamantylmethyl and di-*tert*-butylmethyl systems strongly suggest that both secondary substrates undergo anchimerically assisted ionization of modest magnitude.

### Introduction

While primary systems typically solvolyze by nucleophilic displacement (S<sub>N</sub>2) and tertiary systems by ionization to carbocations (S<sub>N</sub>1),<sup>2</sup> the solvolysis mechanism of secondary systems was not fully understood mechanistically until the importance of nucleophilic solvent assistance was recognized.<sup>3</sup> The overall solvolysis rate constant (*k*<sub>o</sub>) can be treated as the sum of the solvent assisted rate

constant (*k*<sub>s</sub>) and neighboring group or anchimeric assisted rate constant (*k*<sub>Δ</sub>).<sup>3</sup> The limit as *k*<sub>Δ</sub> and *k*<sub>s</sub> tend toward zero is *k*<sub>c</sub> (the rate constant for an anchimerically and nucleophilically unassisted process).

Earlier work established the 2-adamantyl system (1, R = H) as a standard for limiting secondary solvolysis, i.e., with *k*<sub>s</sub>/*k*<sub>c</sub> and *k*<sub>Δ</sub>/*k*<sub>c</sub> ratios near unity.<sup>3</sup> Since solvent assistance (*k*<sub>s</sub>) is ruled out by severe hindrance to backside attack, di-*tert*-butylmethyl systems (**2**) were also examined as possible acyclic models for limiting (*k*<sub>c</sub>) solvolysis.<sup>4</sup> However, the exclusive formation of rearranged products from the secondary substrate (**2a**) and the low α-methyl/hydrogen rate ratio, **2b**/**2a** = 10<sup>5.3</sup> (vs. 10<sup>7.5</sup> for 2-adamantyl),<sup>3b,5</sup> indicated that there might be a *k*<sub>Δ</sub> contribution preferentially accelerating the rate of **2a** over **2b**.<sup>4</sup>

Would the 1,1'-diadamantylmethyl system (**3**) overcome this problem and serve as an alternative limiting (*k*<sub>c</sub>) secondary system under solvolytic conditions? Solvent

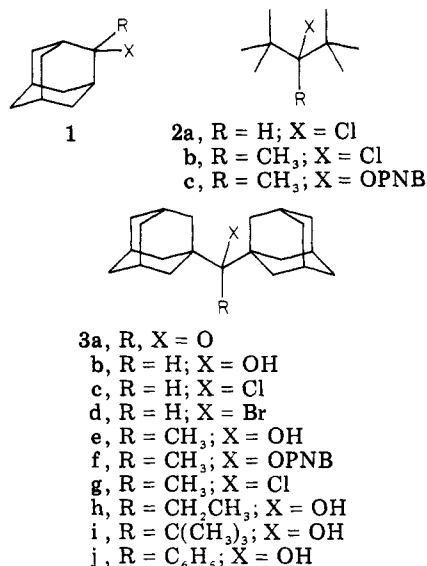
(1) (a) Stable Carbocations, part 235. For part 234, see G. A. Olah, A. P. Fung, T. N. Rawdah, and G. K. S. Prakash, *J. Am. Chem. Soc.*, 103, 4646 (1981); (b) University of Southern California; (c) Universität Erlangen Nürnberg; (d) Princeton University.

(2) For evidence that not all tertiary systems are S<sub>N</sub>1, see, T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Am. Chem. Soc.*, 101, 2486-2488 (1979); M. P. Jansen, K. M. Koshy, N. N. Mangru, and T. T. Tidwell, *ibid.*, 103, 3863-3867 (1981).

(3) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 92, 2538-2540 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, 92, 2540-2542 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, 92, 2542-2544 (1970); (d) T. W. Bentley and P. v. R. Schleyer, *ibid.*, 98, 7658-7666 (1976); (e) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *ibid.*, 98, 7667-7674 (1976); (f) T. W. Bentley, C. T. Bowen, D. H. Merten, and P. v. R. Schleyer, *ibid.*, 103, 5466-5475 (1981); (g) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, 14, 1 (1977).

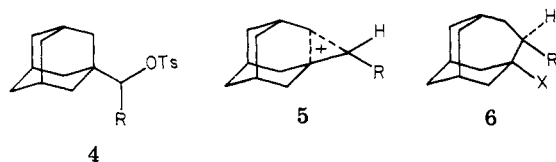
(4) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *J. Am. Chem. Soc.*, 92, 3789-3791 (1970).

(5) (a) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 94, 4628-4634 (1972); (b) J. S. Lomas, P. K. Luong, and J.-E. Dubois, *J. Org. Chem.*, 44, 1647-1654 (1979).



assistance ( $k_a$ ) is ruled out in the 1,1'-diadamantylmethyl system (as in 2) because of severe backside hindrance. Anchimeric assistance ( $k_A$ ) might be less favorable in 3c,d than in 2a since ring expansion (although giving a more stable tertiary carbocation) would generate a less stable homodamantyl ring system.<sup>9</sup> Homodamantane is calculated to be more strained than adamantane by 8–11 kcal/mol.<sup>10</sup>

However, there is precedence for the occurrence of a  $k_A$  process in the parent adamantylmethyl system. Optically active primary 1-adamantylmethyl tosylate (4, R = D) solvolyzes with complete retention of configuration via a  $k_A$  pathway.<sup>7</sup> Identical products are found after solvolysis of 1-adamantylmethyl (4, R = H) and 3-homoadamantyl (6, R = H) derivatives under the same conditions.<sup>6,7</sup> Either the bridged species 5 (R = D) or the chiral 3-homoadamantyl cation (6, X = +, R = D) can be the intermediate on the basis of these data. However, since both 4 and 6 (with halide leaving groups) give only the same static classical 3-homoadamantyl cation (6, X = +) under stable ion conditions<sup>11</sup> (with no indication of bridging),<sup>12</sup> 5 is probably involved only as a transition state in the solvolysis mechanism.



The situation with the corresponding secondary  $\alpha$ -(1-adamantyl)ethyl system (4, R = CH<sub>3</sub>) is less clear. The observation of partial retention of configuration upon solvolysis of optically active 4 (R = CH<sub>3</sub>),<sup>13</sup> a small amount

(6) J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475–4484 (1966).

(7) S. H. Ligero, R. Sustmann, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 4571–4573 (1969).

(8) The dehydration of  $\alpha,\alpha$ -di(1-adamantyl)ethanol (3e) proceeds through the corresponding unrearranged carbenium ion: J. S. Lomas, *J. Org. Chem.*, **46**, 412–415 (1981).

(9) The reluctance of adamantane ring expansion has also been employed recently by T. Ando, H. Yamataka, A. Morisaki, J. Yamawaki, J. Kuramochi, and Y. Yukawa, *J. Am. Chem. Soc.*, **103**, 430–436 (1981).

(10) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005–8025 (1973).

(11) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 194–197 (1973).

(12) P. v. R. Schleyer, D. Lenoir, P. Mison, G. Liang, G. K. S. Prakash, and G. A. Olah, *J. Am. Chem. Soc.*, **102**, 683–691 (1980).

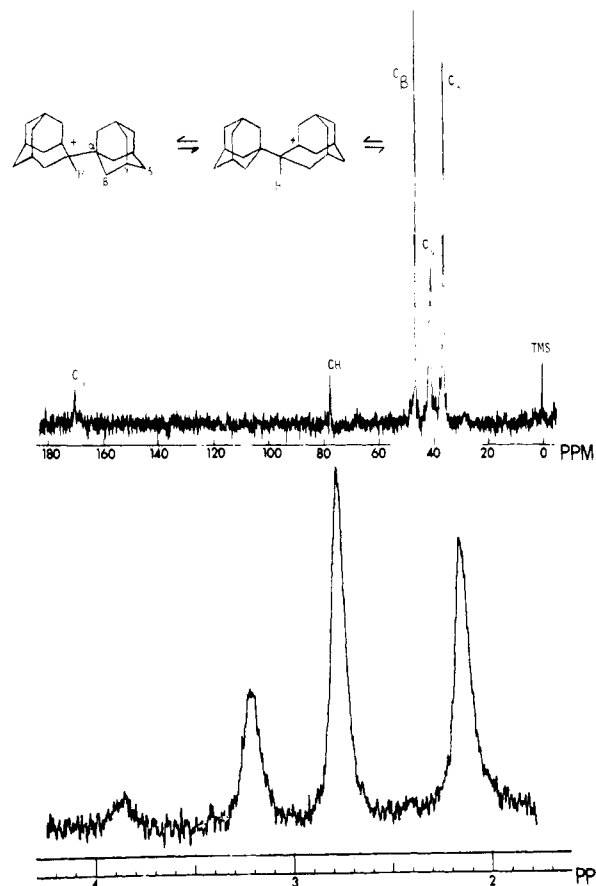


Figure 1. <sup>1</sup>H NMR (bottom) and proton-decoupled <sup>13</sup>C NMR spectra of equilibrating 4-(1-adamantyl)-3-homoadamantyl cation in FSO<sub>3</sub>H·SbF<sub>5</sub>/SO<sub>2</sub>ClF solution at -85 °C.

of rearranged product (6, R = CH<sub>3</sub>), and a primary kinetic isotope effect ( $k_H/k_D$ ) of only 1.11<sup>14</sup> are consistent with weakly assisted  $k_A$  processes. However, net retention was also observed for 2-adamantyl (1) solvolysis and this may be explained by frontside attack of the solvent separated ion pair.<sup>3e</sup> The similar solvent sensitivity of 4 (R = CH<sub>3</sub>) and 2-adamantyl tosylate (1, R = H, X = OTs)<sup>3f</sup> argue for an essentially nonassisted ( $k_a$ ) mechanism.

We now report the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic behavior of secondary and tertiary 1,1'-diadamantylmethyl derivatives (3) under stable ion conditions. The structural information obtained is employed to help interpret the solvolysis mechanism and the nature of the intermediates involved. The results are also pertinent to the question of  $\sigma$  bond participation.<sup>15</sup>

## Results and Discussion

All the 1,1'-diadamantylmethyl derivatives employed in this study were obtained from the previously known<sup>16</sup> 1,1'-diadamantyl ketone 3a. The tertiary alcohols were prepared in the usual manner by Grignard and organolithium reactions on 3a. Table I lists the <sup>1</sup>H and <sup>13</sup>C NMR data of the precursors.

(13) T. W. Bentley, S. H. Ligero, M. A. Imhoff, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 1970–1973 (1974).

(14) A value of about 1.22 is the expected limiting  $\alpha$ -d effect for solvolysis of secondary alkyl arenesulfonates: cf. J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 2551–2553 (1971); V. J. Shiner and R. D. Fisher, *ibid.*, **93**, 2553–2554 (1971).

(15) (a) G. A. Olah, *Acc. Chem. Res.*, **9**, 41–52 (1976); (b) H. C. Brown (with comments by P. v. R. Schleyer), "The Nonclassical Ion Problem", Plenum Press, New York, 1977.

(16) J. H. Wieringa, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 2071–2074 (1972).

Table I.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Parameters of Diadamantylmethanols in  $\text{CDCl}_3$  at 30 °C

compd	$\delta$	CR OH	$\alpha$	$\beta$	$\gamma$	$\delta$	other groups
3b	$^1\text{H}$	3.00		2.2	2.4	2.2	OH
	$^{13}\text{C}$	87.8 (d, 145)	39.8 (s)	41.4 (t, 125)	29.9 (d, 134)	38.4 (t, 124)	
3e	$^1\text{H}$			2.32	2.40	2.18	$\text{CH}_3$ , 1.45; OH, 1.86
	$^{13}\text{C}$	80.6 (s)	45.0 (s)	39.6 (t, 127)	30.4 (d, 134)	38.4 (t, 126)	$\text{CH}_3$ , 20.7 (q)
3h	$^1\text{H}$			2.34	2.34	2.08	$\text{CH}_2$ , 2.10 (q, 7.6); $\text{CH}_3$ , 1.32 (t, 7.6); OH, 2.60
	$^{13}\text{C}$	80.2 (s)	47.0 (s)	39.5 (t)	30.3 (d)	38.5 (t)	$\text{CH}_2$ , 24.1 (t); $\text{CH}_3$ , 12.5 (q)
3i	$^1\text{H}$			2.65	2.42	2.10	$\text{CH}_3$ , 1.78 (s)
	$^{13}\text{C}$	91.3		41.2	31.1	38.4	$\text{CH}_3$ , 14.1
3j	$^1\text{H}$			2.30	2.30	2.02	$\text{C}_6\text{H}_5$ , 7.75, 8.00; OH, 2.38
	$^{13}\text{C}$		45.9	40.6	30.4	38.2	$\text{C}_6\text{H}_5$ , 129.6, 129.1, 128.5, 126.9, 126.5
3a	$^1\text{H}$			2.42	2.42	2.12	
	$^{13}\text{C}$		50.4 (s)	40.5 (dd, 126, 129)	29.6 (d, 134)	37.9 (t, 126)	

<sup>a</sup> Both proton and carbon-13 chemical shifts are in parts per million from the external  $\text{Me}_4\text{Si}$  (capillary) signal. Multiplicities and coupling constants are given in parentheses: d = doublet, t = triplet, s = siglet, dd = doublet of doublets, q = quartet.

Table II. First-Order Solvolysis Rate Constants for 1,1'-Diadamantylmethyl and Di-*tert*-butylmethyl Halides and Esters

compd	solvent	temp, °C	$k_1, \text{s}^{-1}$	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu			
1,1'-diadamantylmethyl chloride (3c)	80% aq ethanol	101.4	$3.93 \times 10^{-4} \text{ }^a$	23.6	-11.4			
		75.0	$3.28 \times 10^{-5} \text{ }^a$					
		25.0	$9.10 \times 10^{-8} \text{ }^b$					
	90% aq ethanol	104.4	$1.63 \times 10^{-4} \text{ }^a$					
		90.0	$4.26 \times 10^{-5} \text{ }^a$					
		75.6	$9.24 \times 10^{-6} \text{ }^a$					
di- <i>tert</i> -butylmethyl chloride (2a) <sup>c</sup> $\alpha, \alpha$ -di- <i>tert</i> -butylethyl chloride 1,1'-diadamantylmethyl bromide	80% aq ethanol	25.0	$1.60 \times 10^{-8} \text{ }^b$	25.4	-9.1			
		25.0	$8.91 \times 10^{-10} \text{ }^b$					
		25.0	$1.73 \times 10^{-4} \text{ }^d$					
	90% aq ethanol	75.5	$6.66 \times 10^{-4} \text{ }^a$					
		49.8	$3.92 \times 10^{-5} \text{ }^a$					
		25.0	$1.63 \times 10^{-6} \text{ }^b$					
90% aq acetone	101.1	$3.15 \times 10^{-4} \text{ }^a$	18.2	-26.5				
	89.7	$1.51 \times 10^{-4} \text{ }^a$						
	75.0	$4.72 \times 10^{-5} \text{ }^a$						
	25.0	$5.06 \times 10^{-7} \text{ }^b$						
	$\alpha, \alpha$ -di(1-adamantyl)ethyl <i>p</i> -nitrobenzoate (3f)	90% aq acetone			100.9	$1.48 \times 10^{-3} \text{ }^a$	26.2	-2.0
					89.6	$4.82 \times 10^{-4} \text{ }^a$		
75.0			$1.01 \times 10^{-4} \text{ }^a$					
60.0		$1.75 \times 10^{-5} \text{ }^b$						
40.0		$1.32 \times 10^{-6} \text{ }^b$						
25.0		$1.51 \times 10^{-7} \text{ }^b$						
$\alpha, \alpha$ -di- <i>tert</i> -butylethyl <i>p</i> -nitrobenzoate (2c)	60% (w/w) aq dioxane	40.0	$1.64 \times 10^{-6} \text{ }^e$					
	90% aq acetone	40.0	$1.19 \times 10^{-7} \text{ }^f$					

<sup>a</sup> Rate constants determined conductometrically. <sup>b</sup> Calculated from data at other temperatures. <sup>c</sup> Reference 13. <sup>d</sup> V. J. Shiner, Jr., and G. F. Meirer, *J. Org. Chem.*, 31, 137-142 (1966). <sup>e</sup> J. E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1971-1974 (1973). <sup>f</sup> Estimated from the dioxane/water value, using Winstein-Grunwald correlation with  $m = 1$ ; see E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846-854 (1948).

Table III. Comparison of the Solvolysis Rates of Adamantylmethyl and *tert*-Butylmethyl Systems

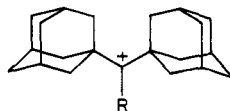
conditions	relative rates					
	1,1'-diadamantylmethyl	di- <i>tert</i> -butylmethyl	$\alpha$ -(1-adamantyl)ethyl	2-adamantyl	$\alpha, \alpha$ -diadamantylethyl	$\alpha, \alpha$ -di- <i>tert</i> -butylethyl
chlorides, 25 °C, 80% ethanol	$10^{4.7}$	$10^{2.7} \text{ }^a$	$10^{1.5} \text{ }^b$	1 <sup>b</sup>	$10^{9.3} \text{ }^c$	$10^{7.9}$
<i>p</i> -nitrobenzoates, 40 °C, 90% acetone					$10^{1.1}$	1
$\alpha\text{-CH}_3/\text{H}$ ratios, 25 °C	$10^{5.7} \text{ }^c$	$10^{5.3} \text{ }^a$	$10^{5.9} \text{ }^d$	$10^{7.5} \text{ }^e$		

<sup>a</sup> See ref 4. <sup>b</sup> From bromide, using  $k(\text{Br}/\text{Cl}) = 10^{1.7}$  for 1-adamantyl (see ref 22). <sup>c</sup> From OPNB, using  $k(\text{Cl}/\text{OPNB}) = 10^{4.4}$  derived from *tert*-butyl. <sup>d</sup> For bromides (see ref 21). <sup>e</sup> See ref 3b.

Since the solubility of the 1,1'-diadamantylmethyl derivatives **3c-d,f** is below the level ( $\sim 10^{-2}$  M) necessary for titrimetric solvolysis measurements (even at 100 °C in 90% acetone), all solvolysis rates were measured conductometrically. Even in the concentration range used ( $\sim 10^{-3}$  M), temperatures of at least 50 °C and solvents with low water content were necessary to affect total dissolution. These

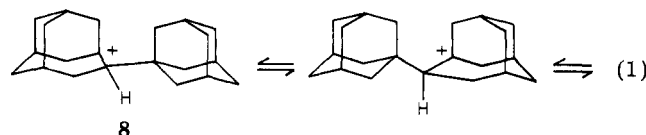
factors limited the choice of substrates to the secondary chloride (**3c**) and bromide (**3d**), and to the tertiary *p*-nitrobenzoate (**3f**). Attempts to prepare tertiary chloride **3g** failed (see Experimental Section). Tables II and III list the first-order solvolytic rate constants and compare the relative rate ratios of diadamantylmethyl and di-*tert*-butylmethyl systems.

The 1,1'-diadamantylmethyl cations **7a-7c** and **7e-7f** (**7d** was found to be unstable) were generated in either  $\text{SbF}_5/\text{SO}_2\text{ClF}$ ,  $\text{FSO}_3\text{H}-\text{SbF}_5/\text{SO}_2\text{ClF}$ , or  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  solutions at  $-78$  or  $-130$  °C. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts and coupling constants of these ions are summarized in Table IV.

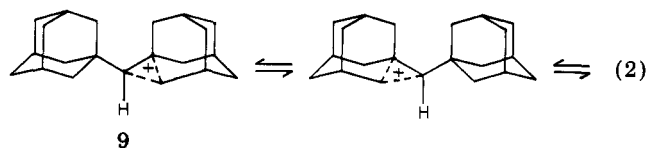


- 7a, R = H  
 b, R =  $\text{CH}_3$   
 c, R =  $\text{CH}_2\text{CH}_3$   
 d, R =  $\text{C}(\text{CH}_3)_3$   
 e, R =  $\text{C}_6\text{H}_5$   
 f, R = OH

**Structure of Carbocations Generated from Diadamantylmethyl Derivatives under Superacidic Conditions.** The  $^1\text{H}$  NMR spectrum (Figure 1) at  $-85$  °C of the carbocation generated from secondary alcohol **3b** displays only four proton absorptions at  $\delta_{\text{H}}$  3.85 (one proton), 3.22 (six protons), 2.78 (12 protons), and 2.15 (12 protons). The observed chemical shifts definitely rule out the static secondary carbocation structure, **7a**, with the positive charge localized at the carbonyl carbon,  $^+\text{CH}$ . Such methine hydrogens directly attached to a secondary carbocationic site generally resonate 10–13 ppm downfield from  $\text{Me}_4\text{Si}$  (at  $\delta_{\text{H}}$  12.8 for the isopropyl cation).<sup>17</sup> The absence of a protonated hydroxyl group ( $-\text{OH}_2^+$ ) and the appearance of a strong oxonium ion ( $\text{H}_3\text{O}^+$ ) signal indicate the total ionization of the precursor alcohol **3b**. The relatively simple and symmetrical  $^1\text{H}$  NMR spectrum also excludes a static 4-adamantyl-3-homoadamantyl cation structure **8** formed via ring expansion. The observed  $^1\text{H}$  NMR spectrum can only be interpreted in terms of either a set of equilibrating classical cations **8** (eq 1) or a set of equilibrating delocalized nonclassical cations **9** (eq 2). If the structure is represented as a set of rapidly equilibrating classical cations **8**, then the secondary cation **7a** should be involved in the equilibrium as a high lying intermediate or a transition state. The experimentally observed methine proton chemical shift at  $\delta_{\text{H}}$  3.85 would be ideal for a methine proton adjacent to a carbocationic center (in **8**).



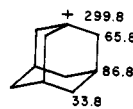
four equivalent structures



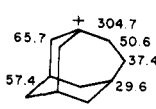
four equivalent structures

In order to clarify the structure of the secondary cation we obtained the  $^{13}\text{C}$  NMR spectrum in  $\text{FSO}_3\text{H}:\text{SbF}_5/\text{SO}_2\text{ClF}$  solution (Figure 1). The five carbon resonances observed, at  $\delta_{13\text{C}}$  171.9 (s), 75.2 (d,  $J_{\text{C-H}} = 136.9$  Hz), 45.9 (t,  $J_{\text{C-H}} = 132.6$  Hz), 40.1 (d,  $J_{\text{C-H}} = 127.0$  Hz), and 35.4 (t,  $J_{\text{C-H}} = 132.6$  Hz), indicate the presence of five kinds of

carbon atoms in the ion. The observed highly deshielded  $\text{C}_\alpha$  at  $\delta_{13\text{C}}$  171.9 and relatively shielded cationic CH resonance at  $\delta_{13\text{C}}$  75.2 for the ion eliminate static **7a** or **8** as possible structural alternatives. A static secondary carbocationic center would be expected to show a  $^{13}\text{C}$  NMR shift at about  $\delta_{13\text{C}}$  320 (e.g., the 2-propyl cation  $\delta_{13\text{C}}$  319.0).<sup>17</sup> Any type of static bridgehead cation is also clearly ruled out based on comparisons with the observed shifts at the cationic centers in both the 3-homoadamantyl and 1-adamantyl cations,<sup>11</sup> **6** and **10** ( $\delta_{13\text{C}}$  304.7 and 299.8, respectively). A simple way to assign the classical vs.



10



6, R = H; X = +

nonclassical structure of a carbocation involves the difference in the sum of the  $^{13}\text{C}$  chemical shifts for all carbons for a carbocation in comparison with the sum for the corresponding hydrocarbon or the ion precursor.<sup>12</sup> This total deshielding value of all the carbon atoms going from the precursor alcohol **3b** to the ion is  $[(75.2 - 87.8) + (171.9 - 39.8) \times 2 + (45.9 - 41.4) \times 6 + (40.1 - 29.8) \times 6 + (35.4 - 38.4) \times 6] = 322.4$  ppm. This value not only is too large for a protonated alcohol or some complex with  $\text{SbF}_5$  but also clearly indicates a classical cationic species.<sup>12</sup> The structure of choice thus is the equilibrating set of 4-(1-adamantyl)-3-homoadamantyl cations, **8** (six equivalent isomers). The degenerate equilibrating nonclassical ion structure **9** (six equivalent isomers) is clearly ruled out on the basis of the chemical shift difference which would be expected to be much lower than the observed value.<sup>12</sup> There is no detectable contribution of secondary cation **7a** as there is no equilibrium shift change between  $-60$  and  $-140$  °C. The structure **7a** thus must only be involved as a high lying intermediate or a transition state. The energy barrier for the equilibration process in **8** through Wagner-Meerwein shift seems to be extremely low ( $<5.0$  kcal/mol) as it cannot be frozen even at  $-140$  °C.

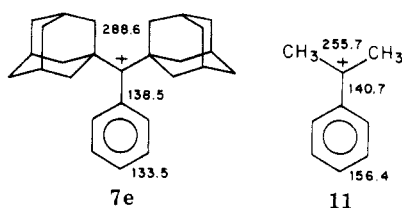
We have also prepared the tertiary  $\alpha,\alpha$ -di(1-adamantyl)ethyl and  $\alpha,\alpha$ -di(1-adamantyl)propyl cations **7b** and **7c** from their precursor alcohols. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data on these ions (Table IV) show the regular carbenium nature of these systems. The cationic centers are substantially deshielded in both cases ( $\delta_{13\text{C}}$  327.1 and 323.3, respectively). Both the tertiary cations **7b** and **7c** were found to be stable even at  $0$  °C, showing no temperature-dependent behavior. However, the equilibrating cation **8** is unstable above  $-40$  °C and irreversibly decomposes to a complex mixture of products. Attempts to prepare the *tert*-butyldiadamantylmethyl cation **7d** were, however, not successful in either  $\text{SbF}_5/\text{SO}_2\text{ClF}$  or  $\text{FSO}_3\text{H}:\text{SbF}_5/\text{SO}_2\text{ClF}$  even at  $-130$  °C.

The tertiary  $\alpha,\alpha$ -di(1-adamantyl)phenylmethyl cation **7e** (prepared from the alcohol **3j**) showed interesting spectroscopic behavior. Little charge is delocalized to the phenyl ring. For example, the para carbon is rather shielded ( $\delta_{13\text{C}}$  133.5) relative to those in other tertiary benzylic cations, e.g., by about 23 ppm vs. the cumyl cation **11**.<sup>18</sup> The chemical shift comparisons shown in **7e** and **11** emphasize the differences in charge distribution, which results from very unfavorable steric repulsion between the aryl ring and adamantyl  $\beta$ -hydrogens. This forces the ring to twist and largely eliminates conjugation with the empty

(17) (a) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173–212 (1973); (b) G. A. Olah and D. J. Donovan, *J. Am. Chem. Soc.*, **99**, 5026–5039 (1977).

(18) G. A. Olah, A. D. Porter, C. L. Jueell, and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044–2052 (1972); G. A. Olah, A. L. Berrier, and G. K. S. Prakash, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 1998–2002 (1981).

p lobe of the cationic center.

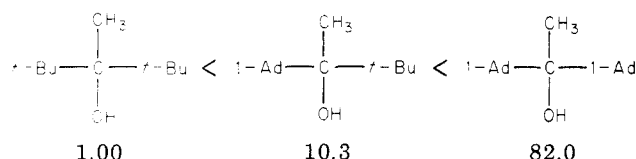


A close analogy for this finding is available. No evidence was found for aryl resonance in the solvolysis of di-*tert*-butylphenylmethyl *p*-nitrobenzoate.<sup>19</sup> This was also attributed to similar steric effects.

The protonated ketone **7f** obtained from **3a** behaves unexceptionally.<sup>20</sup> The <sup>13</sup>C NMR data of **7f** are listed in Table IV.

**Solvolysis of the 1,1'-Diadamantylmethyl Derivatives.** The rate constants for solvolysis of the secondary 1,1'-diadamantylmethyl chloride (**3c**) and bromide (**3d**) and the tertiary  $\alpha,\alpha$ -di(1-adamantyl)ethyl *p*-nitrobenzoate (**3b**) are listed along with those for model compounds in Table II. The comparisons of Table III raise two major questions. Why do the 1,1'-diadamantylmethyl systems solvolyze  $10^{1.1}$ – $10^{2.0}$  faster than their di-*tert*-butylmethyl counterparts? The  $\alpha$ -CH<sub>3</sub>/H ratios for the 1,1'-diadamantylmethyl and the di-*tert*-butylmethyl systems,  $10^{5.7}$  and  $10^{5.3}$ , respectively, are significantly lower than the value ( $10^{7.5}$ ) for 2-adamantyl. Does this indicate  $\sigma$  participation in the secondary systems, **2a**, **3c**, and **3d**? These questions will be answered in order.

1-Adamantyl substituents stabilize carbocations more than *tert*-butyl groups. This was first noted in the faster solvolysis of 1-adamantylmethyl tosylate than neopentyl tosylate (4.2 times, HCOOH, 50 °C).<sup>6</sup> While interpretation of this result is complicated by anchimeric assistance,<sup>6,7</sup> even larger ratios are found in the secondary  $\alpha$ -(1-adamantyl)ethyl tosylate/pinacolyl tosylate = 8.4 in 97% hexafluoro-2-propanol at 25 °C<sup>3f</sup> and tertiary  $\alpha$ -(1-adamantyl)- $\alpha$ -methyl ethyl bromide/*tert*-butyl-1-methyl ethyl bromide = 10 in 80% ethanol at 25 °C systems.<sup>21,22</sup> Results directly comparable to our findings (Table III) have been obtained by Lomas and Dubois.<sup>5b,8</sup> The relative rates of dehydration increase as 1-adamantyl groups replace *tert*-butyl substituents in the following series (0.006 M, H<sub>2</sub>SO<sub>4</sub>, 25 °C):



We have examined the possibility that steric effects might be responsible for the greater reactivity of 1-adamantyl vs. *tert*-butyl substituted systems. While molecular models indicate that *tert*-butyl and 1-adamantyl groups in **2** and **3** should have the same effective size,

quantitative evaluations are possible through empirical force field (molecular mechanics) calculations.<sup>10,23</sup> Table V summarizes the results<sup>24</sup> with the hydrocarbons as models for the initial states and the carbocations as models for the solvolysis transition states. The  $\Delta$  strain values (hydrocarbon vs. carbocation) are comparable for the secondary 1,1'-diadamantylmethyl and di-*tert*-butylmethyl systems. No significant solvolysis rate difference is expected on this basis. In the corresponding tertiary cases, the calculations predict that on steric grounds 1,1-di-*tert*-butylethyl derivatives should solvolyze up to 10 times faster than  $\alpha,\alpha$ -di(1-adamantyl)ethyl substrates. Similar conclusions have been reached by Lomas.<sup>8</sup> As the experimental results (e.g., Table III) are opposite, factors other than steric must be controlling this behavior.<sup>25</sup>

Convincing evidence that a 1-adamantyl group, presumably due to  $\beta$ -branching hyperconjugative and inductive effects, is inherently a better electron donor than *tert*-butyl is derived from the dipole moments of corresponding halides,<sup>26</sup>  $\sigma^*$  constants,<sup>27</sup> and  $pK_a$  measurements of carboxylic acids.<sup>6</sup>

The reduced 1,1'-diadamantylmethyl  $\alpha$ -CH<sub>3</sub>/H ratio is most simply explained by  $\sigma$  participation in the secondary system. The molecular mechanics calculations of Table V indicate only a very modest strain difference; ionization to give the tertiary  $\alpha,\alpha$ -di(1-adamantyl)ethyl cation should be disfavored by only 0.4 kcal/mol relative to the secondary system. This would result only in a  $\alpha$ -CH<sub>3</sub>/H ratio decrease of  $10^{0.2}$ , instead of the larger value,  $10^{1.8}$ , observed experimentally (Table III).

The stable ion results indicate that the secondary 1,1'-diadamantylmethyl cation **7a** is higher in energy (by 5 kcal/mol or less) than the rearranged tertiary 4-(1-adamantyl)-3-homoadamantyl cation **11**. This reflects the inherent tertiary–secondary cation energy difference (ca. 15 kcal/mol) reduced by the greater strain in the homoadamantane skeleton (ca. 8–11 kcal/mol for the parent systems). Since solvation differences in such highly crowded species should be minimal, much of the driving force for rearrangement might be available to lower the energy of the solvolysis transition state. The magnitude required to explain the decrease in  $\alpha$ -CH<sub>3</sub>/H ratio, about 2 kcal/mol, is consistent with the driving force available.

However, only unrearranged alcohol (**3b**) was recovered from solvolysis of **3c** in aqueous acetone buffered with potassium carbonate or 2,5-lutidine. While the expected product of participation, 4-(1-adamantyl)-3-homoadamantanol **6** (R = ad, X = OH), was not synthesized independently, no evidence for its formation was found. The steric congestion at the tertiary 3-homoadamantyl cation center inhibits nucleophilic attack, and the considerably more stable secondary alcohol **3b** is formed preferentially under the reaction conditions employed. Such rearrangements during product formation are simply the converse of rearrangements occurring during ionization. Putting it another way, the transition state for formation of secondary product from a tertiary carbocation may lie

(19) See: H. Tanida and H. Matsumura, *J. Am. Chem. Soc.*, **95**, 1586–1593 (1973); W. Duisman and C. Rüchardt, *Chem. Ber.*, **106**, 1083–1098 (1973); J. S. Lomas and J. E. Dubois, *J. Org. Chem.*, **40**, 3303–3304 (1975); *Tetrahedron*, **34**, 1597–1604 (1978).

(20) (a) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586–3590 (1967); (b) G. A. Olah, J. L. Grant, and P. W. Westerman, *J. Org. Chem.*, **40**, 2102–2108 (1975).

(21) D. J. Raber, R. C. Fort, Jr., E. Wiskatt, C. W. Woodworth, P. v. R. Schleyer, J. Weber, and H. Stetter, *Tetrahedron*, **27**, 3–18 (1971).

(22) Calculated from the rate of the chloride (H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845–1854 (1949); assuming a Br/Cl ratio of 40; P. v. R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 2700–2707 (1960).

(23) (a) G. J. Gleicher and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582–593 (1967); (b) R. C. Bingham and P. v. R. Schleyer, *ibid.*, **93**, 3189–3199 (1971).

(24) We express our thanks to D. L. Khoury for carrying out these calculations.

(25) The similarity of steric effects in 1,1'-diadamantylmethyl and di-*tert*-butylmethyl systems is also indicated by X-ray and force field calculations. See O. Erner and Cl-D. Böedecker, *Chem. Ber.*, **114**, 652–659 (1981).

(26) I. B. Mazeika, I. S. Yanokovskaya, and J. Polis, *Zh. Obshch. Khim.*, **41**, 1633–1635 (1971).









(27) J. Weber, Ph.D. Thesis, Institute für Organische Chemie der Technischen Hochschule Aachen, 1966.

Table IV. <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopic Data<sup>a</sup> on Diadamantylmethyl and Rearranged Cations

cation	$\delta$	CR	$\alpha$	$\beta$	$\gamma$	$\delta$	other groups
8	<sup>1</sup> H	3.85		2.78	3.22	2.15	
	<sup>13</sup> C	75.2 (d, 136.9 Hz)	171.9 (s)	45.9 (t, 136.1 Hz)	40.1 (d, 127 Hz)	35.4 (t, 132.6 Hz)	
7b	<sup>1</sup> H			2.60	2.60	2.15	CH <sub>3</sub> , 3.81
	<sup>13</sup> C	327.1 (s)	68.1 (s)	39.9 (t)	27.9 (d)	34.6 (t)	CH <sub>3</sub> , 39.9 (q)
7c	<sup>1</sup> H			2.55	2.55	2.05	CH <sub>3</sub> , 3.95 (q); CH <sub>3</sub> , 1.62 (t)
	<sup>13</sup> C	323.3 (s)	67.2 (s)	39.9 (t)	29.3 (d)	34.7 (t)	CH <sub>2</sub> , 41.9 (t); CH <sub>3</sub> , 11.0 (q)
7e	<sup>1</sup> H			2.50	2.50	2.00	C <sub>6</sub> H <sub>5</sub> , 7.40 (meta), 7.90 (ortho, para)
	<sup>13</sup> C	288.9 (s)	68.4 (s)	40.6 (t)	28.7 (d)	34.6 (t)	C <sub>6</sub> H <sub>5</sub> , 138.5 (C <sub>i</sub> , 133.5 (C <sub>p</sub> ), 128.1 (C <sub>o</sub> ), 124.6 (C <sub>m</sub> )
7j	<sup>1</sup> H			2.34	2.34	1.98	OH, 13.04 (s)
	<sup>13</sup> C	253.4 (s)	52.6 (s)	38.1 (t)	27.1 (d)	34.5 (t)	

<sup>a</sup> The <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are in parts per million from external capillary tetramethylsilane. Multiplicities and coupling constants are given in parentheses: d = doublet, s = singlet, t = triplet, q = quartet.

Table V. Molecular Mechanics Calculation Results on Di-*tert*-butylmethyl and Diadamantylmethyl Systems

				
steric energy <sup>a</sup>	12.45	11.78	22.11	20.63
$\Delta H_f^\circ$ (gas, 25 °C)	-60.01	(-54.80) <sup>c</sup>	-58.11	(-56.77) <sup>c</sup>
strain energy	6.02	6.10	15.00	14.18
				
steric energy	34.33	33.75	44.82	44.71
$\Delta H_f^\circ$ (gas, 25 °C)	-60.69	(-55.39) <sup>c</sup>	-57.96	(-55.25) <sup>c</sup>
strain energy	19.56	19.73	29.37	29.92

<sup>a</sup> All energies are in kcal/mol. <sup>b</sup> Ad = 1-adamantyl. <sup>c</sup> This assumes a group increment of 0.0 kcal/mol for a carbonium ion.

below the transition state for formation of the tertiary product.

### Conclusions

Structures of various 1,1'-diadamantylmethyl cations are best elucidated by direct <sup>1</sup>H and <sup>13</sup>C NMR measurements in stable ion media. The ion derived from the secondary precursor **3a** is of particular interest: A rapidly equilibrating set of six equivalent rearranged 4-(1-adamantyl)-3-homoadamantyl bridgehead cations **8** is assigned to this species. The failure to obtain rearranged alcohol product on solvolysis is misleading; the secondary 1,1'-diadamantylmethyl cation is probably only a transition state (or possibly an intermediate) for the degenerate rearrangement. This process is indicated to have a barrier less than 5 kcal/mol.

Due to enhanced hyperconjugation or inductive effects, 1-adamantyl substituents stabilize carbocations to a greater extent than *tert*-butyl groups. The effect on solvolysis rates is a factor of about 10 per 1-adamantyl group.

It is likely that  $\sigma$  participation in the solvolysis of the secondary 1,1'-diadamantylmethyl and the di-*tert*-butylmethyl<sup>4</sup> systems enhances the rates of the extent of about 10<sup>1.5</sup>. Empirical force field calculations indicate that steric effects have only a modest effect, so that most of the decrease in  $\alpha$ -CH<sub>3</sub>/H ratios from the 2-adamantyl value (Table III) can be attributed to anchimeric assistance during solvolysis of the secondary substrates.

### Experimental Section

Microanalysis were kindly performed, in part, by Hoffmann-LaRoche, Inc., Nutley, NJ. Infrared spectra were determined on a Perkin-Elmer 237B spectrophotometer. Melting points were

determined on either a Mettler FP1 or a Laboratory Devices Mel-Temp and are uncorrected.

1,1'-Diadamantyl ketone (**3a**) was prepared similarly to the method used in the synthesis of di-*tert*-butyl ketone.<sup>28</sup> A dispersion of 2.0 g of sodium was prepared by adding small portions of sodium metal to a flask containing vigorously stirred boiling xylene. The xylene was replaced by 250 mL of hexane by repeated washing and decantation. During a 1-h period 10 g of 1-adamantyl cyanide (Aldrich) was added to the refluxing sodium dispersion under nitrogen. The mixture was then refluxed with vigorous stirring for 7 h. After the mixture was cooled, 50 mL of water was added cautiously to the orange solution to decompose excess sodium. The layers were separated, the aqueous phase was extracted with hexane (2 × 100 mL), and the combined extracts were washed with water. The imine was extracted from the hexane with 2 N hydrochloric acid (3 × 100 mL), and the acid extracts were washed once with hexane. The acid phase was made 5 N by addition of concentrated hydrochloric acid and refluxed for 5 h to hydrolyze the imine. The ketone was extracted from the aqueous phase with diethyl ether (3 × 100 mL) and the extracts were washed with water and dried over anhydrous sodium sulfate. Removal of solvent gave 6.5 g (70%) of the ketone: mp after one recrystallization from ethanol, 183.0 – 186.8 °C (lit.<sup>16</sup> mp 185.6 – 186.0 °C); IR (CCl<sub>4</sub>)  $\nu$  2925, 2500, 2845, 1671, 1450, 991 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  1.95 (s, 18 H), 1.72 (s, 12 H).

1,1'-Diadamantylmethanol (**3b**). 1,1-Diadamantyl ketone (**3a**; 1.1 g) in 30 mL of anhydrous diethyl ether was added over a 20-min period to a suspension of 0.1 g of lithium aluminum hydride (Ventron) in 20 mL of diethyl ether. After the mixture was stirred for 24 h at room temperature, addition of 0.1 mL of water, 0.1 mL of 15% sodium hydroxide, and 0.3 mL of water gave a dense white precipitate and a clear supernatant which was decanted. Evaporation of solvent gave **3b** as a white solid: yield, 1.0 g (95%); mp 196.0 – 197.1 °C (pentane); IR (CCl<sub>4</sub>) 3631, 2900,

2840, 1450, 1361, 1344, 1021  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ ), unresolved multiplet  $\delta$  2.1–1.5.

Anal. Calcd for  $\text{C}_{21}\text{H}_{32}\text{O}$ : C, 83.94; H, 10.74. Found: C, 83.92; H, 10.79.

**1,1'-Diadamantylmethyl Bromide (3d).** A solution of 0.13 g of phosphorous tribromide in 3 mL of dry benzene was added during 15 min to a solution of 0.25 g of **3b** in 5 mL of dry benzene at 0 °C. Stirring was continued for 30 min at 0 °C, 1 h at 25 °C, and then 2 h at 40 °C. After being cooled, the solution was poured onto 10 g of ice, the layers were separated, and the aqueous layer was extracted with benzene ( $3 \times 5$  mL). The benzene extracts were washed with 5 mL of saturated sodium carbonate solution and water and dried over anhydrous sodium sulfate. Removal of solvent gave a pale yellow solid, which was chromatographed on silica gel with benzene. The crude bromide eluted very quickly and had mp 178.3–179.8 °C. Recrystallization from 30–60 °C petroleum ether at –10 °C gave 0.14 g (47%) of white needles: mp 182.0–182.6 °C; IR ( $\text{CCl}_4$ )  $\nu$  2930, 2875, 1451, 1354, 1346, 1103; NMR ( $\text{CCl}_4$ )  $\delta$  3.59 (s, 1 H), 1.95 (br, 18 H), 1.67 (br 9 H).

Anal. Calcd for  $\text{C}_{21}\text{H}_{31}\text{Br}$ : C, 69.41; H, 8.60; Br, 22.00. Found: C, 69.21; H, 8.87; Br, 22.03.

**1,1-Diadamantylmethyl Chloride (3c).** Thionyl chloride (4 mL) was added rapidly to **3b** (0.20 g). There was an immediate evolution of gas. The reaction mixture was stirred at room temperature for 6 h and then refluxed for 2 h. Excess thionyl chloride was removed by repeated addition and removal of benzene ( $3 \times 10$  mL) at reduced pressure. The crude chloride was chromatographed on silica gel with hexane and eluted essentially with the solvent front. The chloride was recrystallized from 30–60 °C petroleum ether to give 0.13 g (61%) of white needles: mp 158.7–159.8 °C; IR ( $\text{CCl}_4$ )  $\nu$  2900, 2845, 1452, 1359, 1346, 1309, 1100, 984, 977, 718, 695  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  3.20 (s, 1 H), 1.90 (br, 18 H), 1.67 (br 12 H).

Anal. Calcd for  $\text{C}_{21}\text{H}_{31}\text{Cl}$ : C, 79.08; H, 9.80. Found: C, 79.01; H, 9.81.

**1,1'-Diadamantylethanol (3e).** A solution of 1.0 g (3.4 mmol) of 1,1'-diadamantyl ketone (**3a**) in 50 mL of anhydrous diethyl ether was added over a 30-min period to a solution of 3 mL (6.6 mmol) of methyllithium (2.2 N; Ventron) in 20 mL of ether at 0 °C under nitrogen. The reaction mixture was stirred overnight at 25 °C and then poured onto 20 mL of water, and the layers were separated. The aqueous phase was extracted with ether ( $2 \times 20$  mL), and the combined organics were washed with water and dried over anhydrous sodium sulfate. Removal of solvent and three recrystallizations from 30–60 °C petroleum ether gave 0.47 g (45%) of the tertiary alcohol: mp 200.0–202.5 °C; IR ( $\text{CCl}_4$ )  $\nu$  3600, 2900, 2828, 1460, 1380, 1119, 890  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  1.89 (br, 18 H), 1.68 (br 12 H), 1.01 (s,  $\text{CH}_3$ ), 0.91 (br, OH).

Anal. Calcd for  $\text{C}_{22}\text{H}_{34}\text{O}$ : C, 84.02; H, 10.90. Found: C, 83.98; H, 10.92.

**1,1'-Diadamantylethyl *p*-Nitrobenzoate (3f).** Alcohol **3e** (0.27 g, 1.0 mmol) in 10 mL of anhydrous diethyl ether under nitrogen was treated with 0.4 mL (1.0 mmol) of methyllithium (2.2 N) at 0 °C. After 5 min 0.17 g of freshly recrystallized *p*-nitrobenzoyl chloride in 10 mL of ether was added to the bright yellow solution of the alcoholate. Stirring was continued at room temperature for 2.5 h. The mixture was washed with water and saturated sodium bicarbonate at 0 °C and then dried over anhydrous magnesium sulfate. Recrystallization of the crude product from warm acetone gave 0.08 g (20%) of pale yellow needles. The material steadily decomposed above 190 °C and then melted sharply at ca. 241–243 °C to give a dark orange melt.<sup>29</sup> IR ( $\text{CCl}_4$ )  $\nu$  2900, 1722, 1535, 1350, 1280  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  8.28 (d, 4 H), 2.00 (br, 18 H), 1.79 (s, 3 H), 1.69 (br, 12 H).

Anal. Calcd for  $\text{C}_{29}\text{H}_{37}\text{NO}_4$ : C, 75.13; H, 8.05; N, 3.02. Found: C, 75.15, 74.99; H, 8.13, 8.36; N, 2.65, 2.63.

**Attempted Preparation of 1,1'-Diadamantylethyl Chloride (3g).** **Method A.** To 0.20 g of **3e** was added 4 mL of thionyl chloride at 25 °C; immediate evolution of gas occurred. After the mixture was stirred at 25 °C for 4 h and then 2 h at reflux, excess thionyl chloride was removed at reduced pressure. The yellow oil was chromatographed on a silica gel column with hexane to

give 0.15 g (79%) of a white solid: mp 111–113 °C (acetone). It was obvious from the IR and NMR spectra that elimination to *gem*-1,1'-diadamantylethylene (**3b**) had occurred: IR ( $\text{CCl}_4$ )  $\nu$  3106, 3050, 2900, 2838, 1606, 1450, 1351, 1342, 1308, 1211, 1101, 1063, 898  $\text{cm}^{-1}$ ; NMR ( $\text{CCl}_4$ )  $\delta$  4.98 (s, 2 H), 1.95 (br, 18 H), 1.70 (br, 12 H).

Anal. Calcd for  $\text{C}_{22}\text{H}_{32}$ : C, 89.12; H, 10.88. Found: C, 88.97; H, 10.77.

**Method B.** A solution of 0.11 g (0.35 mmol) of **3e** and 0.1 mL of pyridine (1.4 mmol) in 10 mL of chloroform was added gradually to a solution of 0.05 g (0.50 mmol) of thionyl chloride in 10 mL of chloroform at 0 °C. The reaction mixture was stirred for 2 days at 0 °C and then the entire mixture eluted down a silica gel column with pentane. Removal of solvent gave material identical with **3h**.

**Method C.** The method of Brown and Rei<sup>30</sup> was also tried. A 0.11-g solution of **3e** in 10 mL of pentane was introduced by syringe into the reaction vessel (via the introductory port) containing 10 mL of pentane at –78 °C saturated with dry hydrogen chloride and a catalytic amount of ferric chloride. After 40 min the reaction mixture was aspirated to remove hydrogen chloride and allowed to warm at –10 °C. The solution was filtered cold and solvent removed at –15 °C to give a white solid again identical with the olefin **3h**.

**Solvolytic rate determinations** were carried out by measuring the change in conductance vs. time of an approximately  $10^{-3}$  M solution of substrate in the desired solvent. Ethanol was purified by refluxing with magnesium followed by distillation through a 60-cm silver jacketed column. Acetone was refluxed with potassium permanganate, dried over Drierite, and distilled prior to use. Solvents made without distillation, from spectro quality (MCB) acetone, gave the same rates and were used as well. Either a Wayne-Kerr Universal Balance Bridge B641 or a self-balancing Wheatstone recording Bridge (designed by Dr. C. J. Lancelot)<sup>31</sup> was used to follow the change in conductance. Typically the substrate, solvent, and a small magnetic stirring bar were sealed into a specially designed conductance cell (capacity ca. 20 mL) and stirred for about a quarter-life at 15 °C below the temperature at which the rate was to be measured. The cell was transferred to a constant temperature bath and shaken for 2–5 min. The reaction was then followed through at least 3 half-lives, data points being recorded at about every 5% reaction. The raw data was processed by computer with a general least squares program, LSKIN.<sup>32</sup> All rates were run at each temperature at least in duplicate and then averaged. Activation parameters were obtained by computer fit of the rates at two or more temperatures to the Eyring equation, using the program C2+.<sup>33</sup>

**Preparative solvolyses of 3c,d** were carried out by heating the substrate in aqueous acetone buffered with excess potassium carbonate or 2,6-lutidine for at least 10 half-lives. The product was then poured into water and extracted with diethyl ether. After drying over anhydrous sodium sulfate the solvent was removed at reduced pressure. The infrared and NMR of the recovered material were identical with the spectra of the starting alcohol **3b**. Coinjection of the recovered alcohol and 1,1'-diadamantylmethanol (**3b**) on GLC showed no separation or peak broadening with retention times as long as 50 min.

**Preparation of Diadamantylmethyl Cations.** The secondary and tertiary diadamantylmethyl cations were prepared by addition of solution of the substrates in  $\text{SO}_2\text{ClF}$  to a well-stirred solution of either  $\text{SbF}_5$ ,  $\text{FSO}_3\text{H}/\text{SbF}_5$ , or  $\text{FSO}_3\text{H}$  in  $\text{SO}_2\text{ClF}$  at dry ice/acetone bath temperature (ca. –78 °C) or ethanol/liquid  $\text{N}_2$  bath temperature (ca. –130 °C). The solutions of diadamantylmethyl cations were generally light yellow or brown in color and they provided the corresponding alcohols (except **3d**) or ketone **3a** upon quench with  $\text{SO}_2\text{ClF}/\text{NaHCO}_3$  slurry at –78 °C.

<sup>1</sup>H NMR spectra were recorded on a Varian Associates Model A56/60 spectrometer equipped with a variable-temperature probe.

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$^{13}\text{C}$  NMR spectra were recorded on either a Varian Associates Model XL-100 spectrometer equipped with a variable-temperature probe or on a Varian Associates Model FT-80 spectrometer equipped with a broad-band variable-temperature probe. The chemical shifts in parts per million are referenced from capillary tetramethylsilane.

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**Registry No.** 2a, 29728-48-1; 2b, 5857-67-0; 2c, 40544-10-3; 3a, 38256-01-8; 3b, 54821-21-5; 3c, 54781-14-5; 3d, 80514-81-4; 3e, 75782-41-1; 3f, 80514-82-5; 3g, 80514-83-6; 3h, 80514-84-7; 3i, 80514-85-8; 3j, 80514-86-9; 7a, 80514-87-0; 7b, 80514-88-1; 7c, 80514-89-2; 7e, 80514-90-5; 7f, 80514-91-6; 8, 80514-92-7; 2,2,4,4-tetramethylpentane, 1070-87-7; di-*tert*-butylmethylum, 80514-93-8; 2,2,3,4,4-pentamethylpentane, 16747-45-8; 1,1-di-*tert*-butylethylum, 80514-94-9; 1,1'-methylenebistricyclo[3.3.1.1<sup>3,7</sup>]decane, 54781-15-6; bis(tricyclo[3.3.1.1<sup>3,7</sup>]decan-1-yl)-1,1-ethylidene, 75782-42-2; 1-adamantyl cyanide, 23074-42-2.

## Regiochemistry of the Association Step in $\text{S}_{\text{RN}}1$ Reactions: Kinetically Controlled Coupling of *aci*-Nitronate Ions and *p*-Nitrobenzyl Radicals<sup>1</sup>

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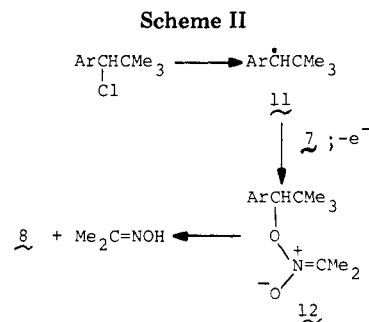
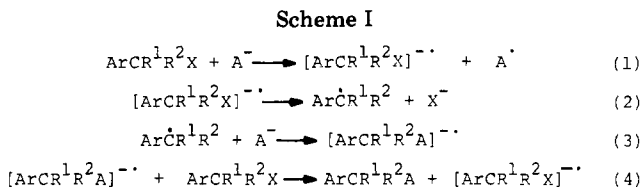
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The regiochemistry of the coupling between *p*-nitrobenzyl radicals and *aci*-nitronate ions in the association step of  $\text{S}_{\text{RN}}1$  reactions is shown to be dependent on steric factors. Branching at the carbon which is  $\alpha$  to the reaction site causes a shift in product distribution toward O-alkylation (C-O bond formation) and away from C-alkylation (C-C bond formation). The association step is believed to be a kinetically controlled irreversible process. Evidence for lack of rearrangement of *aci*-nitronate esters to C-alkylates is presented.

Nucleophilic substitution at a saturated carbon by a reaction which involves a chain process having radical anions and free radicals as intermediates has been ably exploited by Kornblum and co-workers.<sup>2</sup> These reactions belong to a general class of substitutions which have been conveniently termed  $\text{S}_{\text{RN}}1$ .<sup>3</sup> The steps in this reaction for a *p*-nitrobenzyl substrate are presented in Scheme I.<sup>4</sup>

Our interest in these reactions was aroused by their apparent insensitivity to steric hindrance as amply demonstrated in the tertiary *p*-nitrobenzyl system (Scheme I,  $\text{R}^1 = \text{R}^2 = \text{Me}$ ).<sup>2</sup> In particular, we wished to prepare compounds such as 1 and 2 whose analogue 3<sup>5</sup> and other related compounds<sup>6</sup> had been prepared by other workers in our department. The compound 3 and its analogues display dynamic NMR (DNMR) phenomena.<sup>5-7</sup> We wished to determine the effect on rotational barriers and conformational preferences of replacing the *tert*-butyl groups by the  $\text{CMe}_2\text{NO}_2$  moiety. Our approach involved reaction of the substrates 4, 5, and 6 with lithium 2-nitro-2-propanide (7). These attempts were frustrated by the occurrence of an ionic chain substitution process with



4,<sup>8</sup> the incursion of a radical anion, radical chain elimination process (the  $\text{E}_{\text{RC}}1$  reaction) with 5,<sup>9</sup> and the exclusive formation of the ketone, 8, with 6.<sup>10</sup> The last reaction was clearly demonstrated to be occurring solely by an  $\text{S}_{\text{RN}}1$  mechanism, unlike the lower homologues 9 and 10, where  $\text{S}_{\text{N}}2$  processes intruded.<sup>10</sup> The sole formation of 8 (none of the C-alkylate, 2, was formed) was interpreted

(1) (a) Supported by Grant C73-15098 from the Australian Research Grants Committee. (b) Abstracted from the Ph.D. thesis of David Randles, The University of Sydney, Oct 1979.

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