

**Acknowledgment.** This work was supported by NSF Grant CHE-8816445 and Exxon Chemical Company. R.F.J. gratefully acknowledges a Sloan Foundation Research Fellowship and a Union Carbide Research Innovation Award. We thank L. Messerle for assistance with the low-temperature X-ray data collection.

**Supplementary Material Available:** Tables of spectroscopic and analytical data for **1a–d**, **2a–d**, **3**, and **4** and details of the X-ray structure determination for **2a** (25 pages); listing of observed and calculated structure factors for **2a** (15 pages). Ordering information is given on any current masthead page.

## Solvolysis of 2-(Trifluoromethyl)-2-adamantyl Tosylate. Unexpectedly High Reactivity in Carbocation Formation

Annette D. Allen,<sup>1a</sup> Ramesh Krishnamurti,<sup>1b</sup>  
G. K. Surya Prakash,<sup>1b</sup> and Thomas T. Tidwell\*<sup>1a</sup>

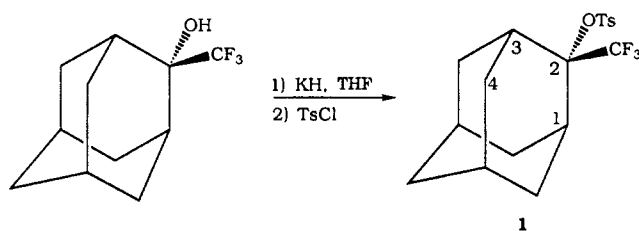
Department of Chemistry, University of Toronto  
Scarborough Campus  
Scarborough, Ontario, Canada M1C 1A4  
Loker Hydrocarbon Research Institute and  
Department of Chemistry  
University of Southern California  
Los Angeles, California 90089-1661

Received September 18, 1989

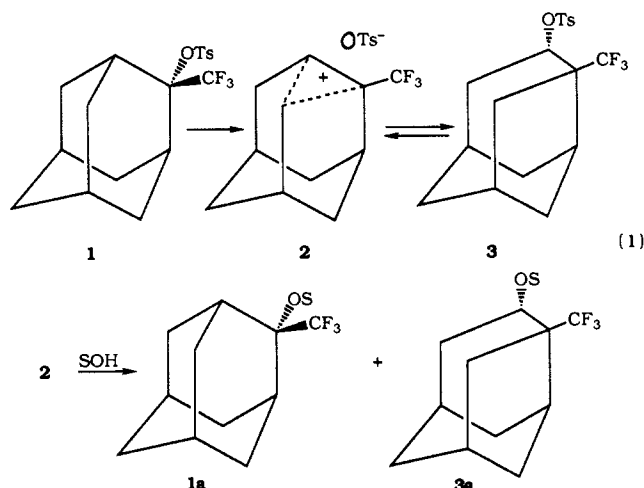
The destabilizing effect of the  $\alpha$ -trifluoromethyl substituent on the formation of carbocations relative to hydrogen typically leads to rate decelerations  $k(\text{H})/k(\text{CF}_3)$  of up to  $10^6$ , although these can be decreased in the presence of strong donor groups.<sup>2</sup> The 2-adamantyl system has been proposed to be a structure in which nucleophilic solvent stabilization of developing positive charge is minimized and carbocation character is maximized in solvolysis,<sup>3</sup> and therefore, this appeared to be a good place to seek a maximal  $k(\text{H})/k(\text{CF}_3)$  rate ratio. On the contrary, this system gives the smallest such ratio known to us.

2-(Trifluoromethyl)-2-adamantyl tosylate (**1**)<sup>4</sup> was obtained by treatment of the corresponding alcohol<sup>5</sup> with KH followed by TsCl. Solvolytic rate constants in four solvents (Table I) are well correlated by  $Y_{\text{OTs}}$ <sup>6a</sup> values at 25 °C by the relation  $\log k = 0.940 (\pm 0.069) Y_{\text{OTs}} - 7.70 (\pm 0.24)$ ,  $r = 0.995$ .

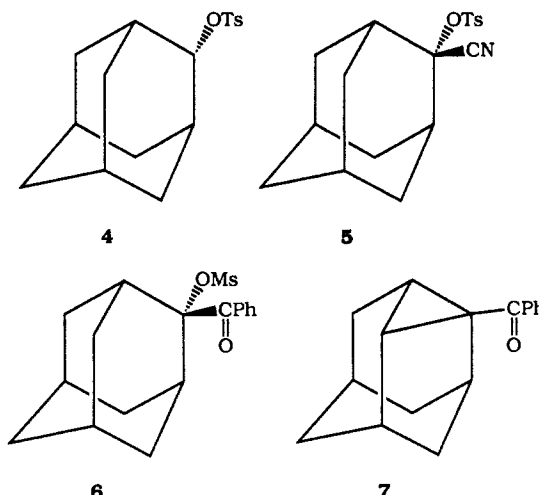
The major products (>90%) from the solvolysis of **1** in  $\text{CF}_3\text{-CO}_2\text{H}$  and  $\text{CF}_3\text{CD}_2\text{OD}$  were the corresponding 3-(trifluoromethyl)-4-*exo*-protoadamantyl derivatives **3a**, together with 2% of unrearranged **1a**. Interruption of the solvolysis of **1** in  $\text{CF}_3\text{-C}$



$\text{O}_2\text{H}$  showed that rearrangement to the isomeric 3-(trifluoromethyl)-4-*exo*-protoadamantyl tosylate **3** occurs, and this reacts further to give the same product mixture of **1a** and **3a** (eq 1). Solvolytic rate constants measured beginning with pure **3** were the same as those observed for **1**, and  $^1\text{H}$  NMR observation of the course of the reaction revealed that **1** converts to **3** at a rate 3 times more rapid than the rate of formation of **3a** from **3**. The results are interpreted in terms of the mechanism of eq 1 involving the ion pair **2**. The existence of equilibrating structures corresponding to the delocalized ion **2** is not excluded.



The reactivity of **1** in the four solvents averages a factor of 2.0 less than that of 2-adamantyl tosylate (**4**), and the rate of **1** calculated for 100% TFE is 700 times greater than that<sup>6b</sup> of 2-cyano-2-adamantyl tosylate (**5**). Both the small size of the  $k(\text{H})/k(\text{CF}_3)$  rate ratio [ $k(\mathbf{4})/k(\mathbf{1})$ ] and the  $k(\text{CF}_3)/k(\text{CN})$  ratio greater than unity are unprecedented; the smallest previous example of the former was 40,<sup>2e</sup> in the presence of the strongly donating pyrrolyl group, and the largest example of the latter was 0.02, in the doubly destabilized system  $\text{ArCR}(\text{OTs})\text{CF}_3$ .<sup>2a</sup>



Solvolysis of **4** in  $\text{AcOH}$ <sup>3d,6c</sup> and **5** in  $\text{TFE}$ <sup>6b</sup> give predominantly unrearranged products, with 0.4% and 9%, respectively, of the rearranged products corresponding to **3**. Reaction of **6** in several solvents also gave predominantly unrearranged products together with small amounts of the 1,3-elimination product **7**.<sup>6c,d</sup>

(1) (a) University of Toronto. (b) University of Southern California.

(2) (a) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1986**, *108*, 3470–3474. (b) Allen, A. D.; Ambidge, I. C.; Che, C.; Micheal, H.; Muir, R. J.; Tidwell, T. T. *Ibid.* **1983**, *105*, 2343–2350. (c) Gassman, P. G.; Tidwell, T. T. *Acc. Chem. Res.* **1983**, *16*, 279–285. (d) Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1–44. (e) Kwong-Chip, J. M.; Tidwell, T. T. *Tetrahedron Lett.* **1989**, *30*, 1319–1322.

(3) (a) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham, R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2538–2540. (b) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *Ibid.* **1970**, *92*, 2540–2542. (c) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *Ibid.* **1972**, *94*, 4628–4634. (d) Lenoir, D.; Hall, R. E.; Schleyer, P. v. R. *Ibid.* **1974**, *96*, 2138–2148. (e) Fărcasiu, D. *Ibid.* **1976**, *98*, 5301–5305. (f) Lomas, J. S.; Luong, P. K.; Dubois, J.-E. *Ibid.* **1977**, *99*, 5478–5480. (g) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1244–1252.

(4) Mp 120–121 °C, characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, high-resolution MS, and an X-ray crystal structure.

(5) Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393–395.

(6) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674. (b) Gassman, P. G.; Saito, K.; Talley, J. J. *Ibid.* **1980**, *102*, 7613–7615. (c) Creary, X.; Geiger, C. C. *Ibid.* **1982**, *104*, 4151–4162. (d) Creary, X. *Ibid.* **1984**, *106*, 5568–5577. (e) Sinnott, M. L.; Storesund, H. J.; Whiting, M. C. *Chem. Commun.* **1969**, 1000–1001.

**Table I.** Solvolytic Rate Constants for 2-(Trifluoromethyl)-2-adamantyl Tosylate (**1**) at 25 °C

solvent <sup>a</sup>	$\gamma_{\text{OTs}}$	$k_{\text{obsd}},^b \text{ s}^{-1}$	$k_{\text{rel}}^c$ (2-AdOTs/ <b>1</b> ) <sup>d</sup>
CF <sub>3</sub> CO <sub>2</sub> H	4.57	$4.97 \times 10^{-4}$	1.81
97% (CF <sub>3</sub> ) <sub>2</sub> CHOH	3.61	$3.43 \times 10^{-5}$	2.84
HCO <sub>2</sub> H	3.04	$1.39 \times 10^{-5}$	1.91
97% CF <sub>3</sub> CH <sub>2</sub> OH	1.83	$1.20 \times 10^{-6c}$	1.37

<sup>a</sup>TFA, HFIP, and TFE are CF<sub>3</sub>CO<sub>2</sub>H, (CF<sub>3</sub>)<sub>2</sub>CHOH, and CF<sub>3</sub>C-H<sub>2</sub>OH, respectively. <sup>b</sup>Measured by UV spectroscopy; at least two determinations of each rate constant. <sup>c</sup>Extrapolated from the following:  $2.71 \times 10^{-4} \text{ s}^{-1}$  (73.4 °C),  $2.83 \times 10^{-5} \text{ s}^{-1}$  (52.1 °C), and  $1.42 \times 10^{-5}$  (45.3 °C);  $\Delta H^\ddagger = 22.5 \text{ kcal/mol}$ ,  $\Delta S^\ddagger = -10.2 \text{ eu}$ . <sup>d</sup>2-AdOTs values from ref 6a.

We attribute the remarkably high reactivity of **1** to a combination of relief of ground-state strain<sup>3c,7</sup> and electron donation from the C<sub>3</sub>-C<sub>4</sub> bond. Even though CF<sub>3</sub> is often thought of as a small group, it is significantly larger than CH<sub>3</sub> by a variety of measures,<sup>8</sup> and steric effects of substituents are proposed<sup>3c</sup> to be enhanced in rigid adamantyl as opposed to more flexible systems. Calculations using the program Macromodel 2 indicate a 4.0 kcal/mol greater energy for the CF<sub>3</sub> in **1** compared to the axial CF<sub>3</sub> in *trans*-4-*tert*-butyl-1-(trifluoromethyl)cyclohexyl tosylate, so the *A* value of 2.5 kcal/mol for CF<sub>3</sub><sup>8a</sup> leads to a crude estimate of 6.5 kcal/mol for the total strain due to CF<sub>3</sub> in **1**. Solvolysis transition states resemble fully formed carbocations,<sup>9a</sup> so essentially all this strain can be lost in the transition state, causing an acceleration in the rate of **1**.

There is strong recent evidence for electron donation from the C<sub>3</sub>-C<sub>4</sub> bond in adamantyl cations,<sup>9b-f</sup> and such participation in **1** leads to the cation **2**, which forms the protoadamantyl ring system **3** (eq 1). The protoadamantyl system is estimated to be 11 kcal/mol more strained than the parent adamantyl system,<sup>3d</sup> but substituents at the 3-position in protoadamantane as in **3** are not crowded.<sup>3d</sup> Thus formation of the transition state leading to **2** results in a decrease in the CF<sub>3</sub> nonbonding interaction of **1** but an increase in ring strain characteristic of **3**. A strong electronic driving force for formation of an ion which diminishes positive charge buildup adjacent to CF<sub>3</sub> is expected.<sup>10</sup> Rearrangement<sup>11a</sup> without appreciable kinetic acceleration<sup>11b,c</sup> occurs in related acyclic systems.

2-Benzoyl-2-adamantyl mesylate (**6**) is more reactive than 2-adamantyl mesylate by factors ranging from 164 to 356,<sup>6c,d</sup> and while steric effects were considered to account for this high reactivity, conjugative effects were favored. Similarly 2-(trimethylsilyl)-2-adamantyl *p*-nitrobenzoate was proposed to "solvolysis without significant steric acceleration".<sup>12</sup> This may be true, but our results suggest that steric effects in formation of 2-adamantyl carbocations should not be underestimated.

The molecular structure of **1** determined by X-ray by Dr. Jeffery Sawyer requires further refinement but shows geometrical distortions due to strain, including bending of the CF<sub>3</sub> group away

from the adjacent axial hydrogens which still have close contacts (2.27 and 2.36 Å) with one of the fluorines. Our own studies of the correlation of chemical reactivity with X-ray structure<sup>13a,b</sup> make us more cautious than others<sup>13c</sup> in cause and effect interpretations of such results, but the structural distortions are at least consistent with major steric interactions, as also seen in 2-cumyl-2-adamantanol.<sup>13d</sup>

In summary, the destabilizing effect of the CF<sub>3</sub> group in the solvolysis of **1** is drastically attenuated, a result attributed to relief of ground-state strain and electron donation from the C<sub>3</sub>-C<sub>4</sub> bond. This result has implications for the consideration of the size of fluorinated groups and for possible effects of steric strain in other adamantyl systems, such as 2-benzoyl-<sup>6c,d</sup> and 2-(trimethylsilyl)adamantyl sulfonates,<sup>12</sup> in which possible steric effects were discounted.

**Acknowledgment.** The financial support of the Natural Sciences and Engineering Research Council of Canada, NATO, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. National Science Foundation and helpful discussions with Professor G. A. Olah are gratefully acknowledged. The Macromodel 2 calculations were carried out by Dr. R. C. Kelly using facilities kindly provided by Professor P. A. Wender at Stanford University.

(13) (a) Allen, A. D.; Kwong-Chip, J. M.; Mistry, J.; Sawyer, J. F.; Tidwell, T. T. *J. Org. Chem.* **1987**, *52*, 4164-4171. (b) Kanagasabapathy, V. M.; Sawyer, J. F.; Tidwell, T. T. *Ibid.* **1985**, *50*, 503-509. (c) Edwards, M. R.; Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 7067-7073. (d) Choi, H.; Pinkerton, A. A.; Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1987**, 225-226.

### Regiocontrolled and Stereocontrolled C-C Bond Formation via Linear Dimerization of Conjugated Dienes Catalyzed by Nickel-Aminophosphinite Complexes

Philippe Denis, André Jean, Jean François Creizy, André Mortreux,\* and Francis Petit

Laboratoire de Chimie Organique Appliquée  
URA CNRS 402, UST Lille Flandres Artois, ENSCL  
BP108, 59652 Villeneuve d'Ascq Cêdex, France

Received May 30, 1989

Linear dimerization of butadiene  $2\text{C}_4\text{H}_6 \rightarrow 1,3,6$ -octatrienes has been shown to occur readily at room temperature on nickel catalysts modified by aminophosphinite ligands  $\text{Ph}_2\text{POCHR}^1\text{CHR}^2\text{NHR}^3$  (AMP).<sup>1</sup> With such complexes, obtained by interaction between  $\text{Ni}(\text{COD})_2$  and these AMP ligands, the reaction rate is ca. 1-2 orders of magnitude higher than observed in other systems using either morpholine,<sup>2</sup> ethanol,<sup>3</sup> or *P*-methyloxaphospholidines<sup>4</sup> as modifiers. The higher reactivity of these new Ni-AMP systems prompted us to study the mechanism of the reaction upon using labeled reagents and the extension of this catalysis to other substituted and functionalized 1,3-dienes.

In order to prove the contribution of the pendant NH moiety in the reaction pathway, we have first conducted the reaction with perdeuterated butadiene  $\text{C}_4\text{D}_6$  to obtain almost pure deuterated 1,3,6-octatrienes.<sup>5</sup> A second experiment involved the use of a

(1) Denis, P.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *J. Org. Chem.* **1984**, *49*, 5274.

(2) (a) Heimbach, P. *Angew. Chem.* **1968**, *80*, 967. (b) Bartik, T.; Behler, A.; Heimbach, P.; Ndalut, P.; Sebastian, J.; Sturn, H. *Z. Naturforsch.* **1984**, *39b*, 1529.

(3) Pittman, C. U., Jr.; Smith, L. R. *J. Am. Chem. Soc.* **1975**, *97*, 341.

(4) Richter, W. *J. Mol. Catal.* **1986**, *34*, 145.

(5) The experimental conditions are typically those used in our preliminary work (see ref 1), with the (D)EPHOSNH [ $\text{Ph}_2\text{POCH}(\text{Ph})\text{CH}(\text{Me})\text{NHMe}$ ] ligand.

(7) (a) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855-1868. (b) Fărcasiu, D. *J. Org. Chem.* **1978**, *43*, 3878-3882.

(8) (a) Della, E. W. *J. Am. Chem. Soc.* **1967**, *89*, 5221-5224. (b) Hansch, C.; Leo, A. J. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley, 1979. (c) Charton, M. *Top. Curr. Chem.* **1983**, *114*, 57-91. (d) Meyer, A. Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1567-1572.

(9) (a) Arnett, E. M.; Preto, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 522-526. (b) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *Ibid.* **1987**, *109*, 7816-7823. (c) Laube, T.; Stilz, H. U. *Ibid.* **1987**, *109*, 5876-5878. (d) Lin, M.-H.; Cheung, C. K.; le Noble, W. J. *Ibid.* **1988**, *110*, 6562-6563. (e) Xie, M.; le Noble, W. J. *J. Org. Chem.* **1989**, *54*, 3839-3841. (f) Dutler, R.; Rauk, A.; Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 9024-9029.

(10) (a) Gassen, K.-R.; Kirmse, W. *Chem. Ber.* **1986**, *119*, 2233-2248. (b) Paddon-Row, M. N.; Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6561-6563.

(11) (a) Roberts, D. D.; Hall, E. W. *J. Org. Chem.* **1988**, *53*, 2573-2579. (b) Ward, S.; Rhodes, Y. E. *Abstracts of Papers*, 194th National Meeting of the American Chemical Society, New Orleans, LA; American Chemical Society: Washington, DC, 1987; ORGN 176. (c) Shiner, V. J., Jr.; Seib, R. C. *Tetrahedron Lett.* **1979**, 123-126.

(12) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806-2807.