

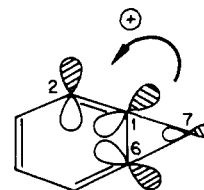
solvolysis.<sup>9</sup> It is therefore reasonable to expect that aryl cations which are comparable in stability to **2** can be produced via solvolysis.<sup>10</sup>

To achieve this goal one should design a substituted aryl cation that is more stable than **1a** by at least 25 kcal/mol. The major difficulty in reaching such large stabilization energies is obvious: The most effective substitution site—the  $\alpha$ -position—is blocked. **1** can be stabilized only by the  $\beta$ - or the  $\gamma$ -substituents. It was suggested that meta electron-donating substituents can stabilize the phenyl cation substantially by “through bond interactions”.<sup>4</sup> Disappointingly, aryl triflates which were prepared according to this theoretical proposal failed to produce the desired **1**.<sup>2b</sup> It was concluded that “substituents are not very effective in providing significant stabilization of singlet aryl cations”.<sup>2b</sup>

We use here ab initio calculations to point out two substitution patterns that stabilize the phenyl cation sufficiently to allow its generation by solvolysis.<sup>10</sup> One of these theoretical predictions has been verified as described in the accompanying paper<sup>11</sup> and the other is under active investigation.

Hyperconjugation between the empty  $2p(C^+)$  orbital and the  $\beta$ -C-R bonds is the key to stabilizing the phenyl cation. According to PMO theory the hyperconjugative stabilization ( $\Delta E$ ) is proportional to  $S^2/\Delta\epsilon$ , where  $\Delta\epsilon$  is the energy difference between the interacting orbitals and  $S$  is their overlap.<sup>12</sup> A  $\beta$ -C-R orbital that lies higher in energy than a C-H orbital is expected (due to a smaller  $\Delta\epsilon$ ) to stabilize the phenyl cation. In agreement with this qualitative argument **1b** is more stable than **1a** by 10 kcal/mol at 3-21G.<sup>5a</sup> C-Si bond orbitals are generally higher in energy than C-C bond orbitals so that  $\beta$ -silyl substituents are likely to be even more stabilizing than  $\beta$ -alkyl groups.<sup>13,14</sup> Indeed, **1c** is more stable than **1b** by 15 kcal/mol and comparable in stability to **2** (3-21G). Furthermore, correlation energy (CE) stabilizes  $\beta$ -silyl cations (e.g.,  $H_3SiCH=CCH_3^+$ ) relative to the corresponding  $\beta$ -alkyl cations (e.g.,  $H_3CCH=CCH_3^+$ ) by 7-10 kcal/mol. Using this correction for the CE, we conclude that **1c** is by a few kilocalories per mole more stable than **2**, and it is therefore amenable to generation by solvolysis.<sup>10</sup> This prediction has recently been verified by Sonoda et al. who showed that the solvolysis of 2,6-bis(trimethylsilyl)phenyl triflate in TFE proceeds via an aryl cation intermediate.<sup>11,15</sup> The same should hold also for the corresponding tin derivatives.<sup>16</sup> 2-(Trimethylsilyl)- and 2,6-dimethylaryl triflates (yielding **1b**) are unreactive<sup>11</sup> in complete agreement with the calculations.

Alternatively, the phenyl cation can be stabilized through hyperconjugation with high-lying strained carbon-carbon bonds<sup>17</sup> as in **3**. The major stabilizing interaction, that between the empty  $2p(C^+)$  orbital and the highest occupied Walsh orbital of the fused cyclopropene ring, is shown schematically in **6**. The resulting stabilization is indeed large; **3** is more stable than **1a** by 23 kcal/mol at 3-21G\*.<sup>8c</sup> Similarly, **3** is by 22 kcal/mol (3-21G\*) more stable than the isomeric **4** where hyperconjugation with the cyclopropene ring is prohibited. Experience with the analogous



**6**

**5** suggests that the addition of correlation energy should stabilize **3** further. As **5** is more stable than **2** by 8 kcal/mol at 6-31G\* but by 14 kcal/mol at MP2/6-31G\* we estimate that **3** is by 5 kcal/mol more stable than **2**. Thus, **3** is well within the stability range which is suitable for solvolytic generation. Interaction **6** induces interesting structural deformations. Relative to the corresponding bonds in cyclopropabenzene<sup>18</sup> the  $C_1$ - $C_6$  bond in **3** is drastically elongated (by 0.34 Å), while the  $C_1$ - $C_2$  bond is shortened by 0.14 Å.<sup>19</sup> The exceptionally long  $C_1$ - $C_6$  distance of 1.67 Å stabilizes **3** because it partially relieves the strain in the cyclopropabenzene skeleton.<sup>18</sup> Severe distortions in the bond angles, such as flattening at  $C_2$ , also occur. Experiments aimed at generating **3** by solvolysis, in superacidic media and in the gas phase, are in progress.

**Acknowledgment.** We thank Dr. T. Sonoda for communicating his results prior to publication. This research was partially supported by the Technion V.P.R. Fund—New York Metropolitan R. Fund.

**Note Added in Proof.** While this paper was in press an important paper on the magnitude and origin of the  $\beta$ -silicon effect on carbenium ions was published.<sup>20</sup> The reader is referred to this paper for a more complete discussion (than possible in a communication) on the hyperconjugative stabilization by silicon. The conclusions of Jorgensen et al. regarding the magnitude and the effect of correlation on the  $\beta$ -silicon effect are similar to ours.

Registry No. **1a**, 17333-73-2; **1c**, 97521-77-2; **3**, 97521-78-3.

(18) Apeloig, Y.; Arad, D., manuscript in preparation.

(19) The  $C_1$ - $C_2$  bond length remains essentially unchanged, and the  $C_6$ - $C_7$  distance is shortened by 0.05 Å.

(20) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.

## A First Example of Generating Aryl Cations in the Solvolysis of Aryl Triflates in Trifluoroethanol<sup>1</sup>

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Received January 28, 1985

The solvolytic generation of aryl cations has long been an unrealized goal. The method of generating these cations in solution so far is restricted (except for a novel example of the solvolysis of dienynyl triflates<sup>2</sup>) to the dediazonation of arenediazonium ions.<sup>3</sup> Several research groups have attempted to generate these cations in the solvolysis of aryl substrates by using various “super”

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(1) Presented at the VII IUPAC Conference on Physical Organic Chemistry, Auckland, New Zealand, August 1984, Abstr. A17.

(2) (a) Hanack, M.; Michel, U. *Angew. Chem.* **1979**, *91*, 928. (b) Hanack, M.; Holweger, W. *J. Chem. Soc., Chem. Commun.* **1981**, 713.

(3) Reviews: (a) Hegarty, A. F. In “The Chemistry of Diazonium and Diazo Groups”; Patai, S., Ed.; Wiley: London, 1978; p 511. (b) Zollinger, H. In “The Chemistry of Triple-Bonded Functional Groups”; Patai, S.; Rappoport, Z., Eds.; Wiley: London, 1983; Suppl. C, p 603.

(9) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. “Vinyl Cations”; Academic Press: New York, 1979.

(10) The calculations hold strictly only in the gas phase. However, numerous studies have shown the existence of a linear correlation between the free enthalpies (or rates) of solvolysis and the gas-phase stabilities (either experimental or calculated) of the corresponding cations. E.g.: Mayr, H.; Schneider, R.; Wilhelm, D.; Schleyer, P. v. R. *J. Org. Chem.* **1981**, *46*, 5336.

(11) Himeshida, Y.; Kobayashi, H.; Sonoda, T., following paper in this issue.

(12) Fleming, I. In “Frontier Orbitals and Organic Chemical Reactions”; Wiley: New York, 1976; pp 80-85.

(13) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901. Apeloig, Y.; Schreiber, R. *Tetrahedron Lett.* **1978**, 4555.

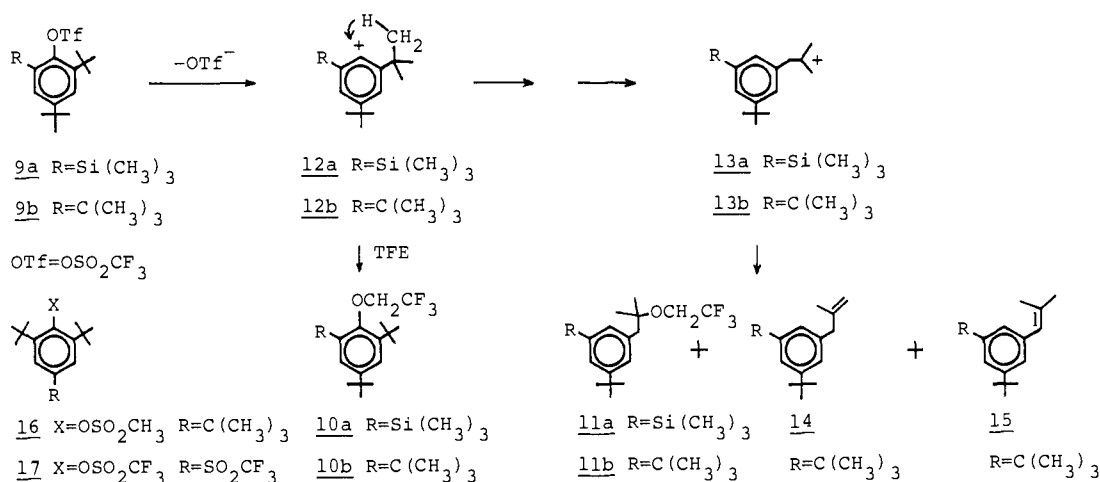
(14) The ability of  $\beta$ -silyl substituents to stabilize carbenium ions is known but the degree of stabilization has not yet been evaluated quantitatively. See: Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020 and references therein.

(15) The relief of ground-state strain upon solvolysis of 2,6-bis(trimethylsilyl)phenyl triflate is probably small. However, this factor may be more important in other 2,6-disubstituted aryl triflates.

(16) Cauletti, C.; Furlani, C.; Granozzi, G.; Sebal, A.; Wrackmeyer, B. *Organometallics* **1985**, *4*, 290.

(17) (a) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197. (b) Gleiter, R.; Jahne, G.; Oda, M.; Iyoda, M. *J. Org. Chem.* **1985**, *50*, 678.

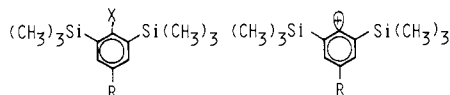
Scheme I



leaving groups,<sup>4</sup> but no one has succeeded.

We wish to report here a first example of the generation of aryl cations in the solvolysis of aryl trifluoromethanesulfonates (triflates) by introducing trimethylsilyl and/or *tert*-butyl group(s) as the ortho substituent(s) in the aryl groups.

When heated in trifluoroethanol (TFE) buffered with potassium carbonate (5 equiv) or 2,6-lutidine (**2**) (1.5 equiv) at 120 °C for 24 h 2,6-bis(trimethylsilyl)phenyl triflate (**1a**)<sup>5</sup> gave trifluoroethyl



$1a$	$X = \text{OSO}_2\text{CF}_3$	$R = \text{H}$	$6a$	$R = \text{H}$
$1b$	$X = \text{OSO}_2\text{CF}_3$	$R = \text{CH}_3$	$6b$	$R = \text{CH}_3$
$1c$	$X = \text{OSO}_2\text{CH}_3$	$R = \text{H}$		
$3a$	$X = \text{OCH}_2\text{CF}_3$	$R = \text{H}$		
$3b$	$X = \text{OCH}_2\text{CF}_3$	$R = \text{CH}_3$		
<b>4</b>	$X = \text{OH}$	$R = \text{H}$		
$5a$	$X = \text{SCH}_2\text{CH}_3$	$R = \text{H}$		
$5b$	$X = \text{SCH}_2\text{CH}_3$	$R = \text{CH}_3$		
<b>7</b>	$X = \text{CO}_2\text{CH}_2\text{CF}_3$	$R = \text{H}$		
<b>8</b>	$X = \text{CO}^+$	$R = \text{H}$		

ether (**3a**)<sup>6</sup> quantitatively. The solvolysis of **1a** obeyed a first-order kinetics:  $k_1 = 1.36 \times 10^{-4} \text{ s}^{-1}$  with **2** in TFE at 100 °C;  $\Delta H^\ddagger = 26.5 \text{ kcal mol}^{-1}$  (80–100 °C);  $\Delta S^\ddagger = -5.5 \text{ cal deg}^{-1} \text{ mol}^{-1}$  at 100 °C. The rate was independent of the concentration of **2**. Similarly **1b**<sup>5</sup> gave **3b**<sup>6</sup> as a sole product. A GC/MS analysis of the solvolysis products of **1a** in 80% aqueous TFE by using <sup>18</sup>O-enriched H<sub>2</sub>O (49.2 atm % <sup>18</sup>O) indicated <sup>18</sup>O-incorporation in the phenolic products, 2,6-bis(trimethylsilyl)phenol (**4**) and 2-(trimethylsilyl)phenol, which is produced by protodesilylation of **4** under the solvolytic conditions. Namely, aryl-oxygen cleavage of **1a**

is occurring in the solvolysis. The solvolysis of **1a** and **1b** in TFE (137 equiv) in the presence of ethanethiol (50 equiv) and **2** (5 equiv) gave ethyl thioethers **5a** (56%) and **5b** (57%) in addition to **3a** (44%) and **3b** (43%), respectively.

These kinetic data and the low selectivity toward external nucleophiles<sup>8</sup> support an S<sub>N</sub>1 mechanism for the solvolysis of **1a** and **1b** via aryl cations **6a** and **6b**, respectively, and exclude the S<sub>N</sub>Ar mechanism. Additional support for the intermediacy of **6a** came from the production of the carboxylic acid ester **7** (10%)<sup>6,7</sup> in addition to **3a** (87%)<sup>7</sup> in the trifluoroethanolysis of **1a** with **2** (2 equiv) under 255 atm of carbon monoxide at 100 °C. **7** is presumably derived from the benzoyl cation **8**, a product in the reaction of **6a** with carbon monoxide.<sup>9</sup>

On the other hand, the trifluoroethanolysis of triflate **9a**<sup>5</sup> with **2** at 100 °C gave a mixture of two trifluoroethyl ethers **10a** (66%)<sup>6,7</sup> and **11a** (27%)<sup>6,7</sup>. The formation of **11a** suggests the intramolecular 1,4-hydride shift to the aryl cation **12a** followed by 1,2-aryl shift to give rise to the stabilized cation **13a** which is eventually attacked by TFE. Similarly the trifluoroethanolysis of **9b**<sup>5</sup> with **2** at 100 °C gave a mixture of products via the aryl cation **12b**. The major products were trifluoroethyl ether **11b** (75%)<sup>7</sup> and olefins **14** and **15** (7%),<sup>7</sup> presumably derived from the rearranged cation **13b**.<sup>10</sup> Trifluoroethyl ether **10b** (3%),<sup>7</sup> a product from the reaction of **12b** with TFE, was also obtained.

Changes of the leaving group to mesylate ( $k_{\text{OTf}}/k_{\text{OMs}} > 10^4$ )<sup>5b</sup> and of the para substituent to trifluoromethylsulfonyl group ( $\sigma_p$ : -0.20 for *t*-Bu; 0.93 for CF<sub>3</sub>SO<sub>2</sub>)<sup>11</sup> induce a drastic change in the solvolytic behavior of aryl sulfonates. Heating of mesylates **1c**<sup>5</sup> and **16**<sup>5</sup> and triflate **17**<sup>5</sup> with potassium carbonate or **2** in TFE resulted in the exclusive but sluggish formation of the corresponding phenols by the nucleophilic attack of the solvent at the sulfur atom: S-O bond cleavage of the mesylate and triflate groups occurred.<sup>4</sup>

The presence of trimethylsilyl and/or *tert*-butyl group(s) at both ortho positions is essential for the S<sub>N</sub>1 solvolysis. The triflates of 2-(trimethylsilyl)phenol<sup>5a</sup> and 2,4- and 3,5-di-*tert*-butylphenols are stable upon heating with **2** in TFE at 150 °C.<sup>12</sup> The relative solvolysis rates ( $k_{\text{rel,TFE,100}^\circ\text{C}}$ : 5.0 for **1a**; 2.0 for **9a**; 1.0 for **9b**) indicate that two factors are essential for the S<sub>N</sub>1 solvolysis of the aryl triflates: (1) hyperconjugative stabilization of the phenyl

(4) For previous approaches to this problem, see: (a) Su, T. M.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386. (b) Streitwieser, A., Jr.; Dafforn, A. *Tetrahedron Lett.* **1976**, 1435. (c) Subramanian, L. R.; Hanack, M.; Chang, L. W. K.; Imhof, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099. (d) Laali, K.; Szele, I.; Yoshida, K. *Helv. Chim. Acta* **1983**, *66*, 1710.

(5) Aryl triflates **1a** (bp 104 °C (0.65 mmHg)), **1b** (mp 51–53 °C), **9a** (mp 67–68 °C), **9b** (mp 77–78 °C), and **17** (mp 138 °C) are quite stable under atmosphere and prepared by treating the corresponding phenol or trimethylsilyl ether compounds with butyllithium and triflic acid anhydride in ether at -78 °C. Aryl mesylates **1c** (mp 152 °C) and **16** (mp 125 °C) are prepared similarly with methanesulfonyl chloride. See: (a) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211. (b) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 15. Details of the preparation will be shown elsewhere with X-ray analysis of these triflates.

(6) Elemental and spectroscopic analysis of the isolated products gave satisfactory results.

(7) Detection and characterization of products are done by GC/MS and <sup>1</sup>H and <sup>19</sup>F NMR of the reaction mixture.

(8) Reference 3a, p 522.

(9) A similar reaction in the dediazonation of benzenediazonium ions in TFE under high pressure of carbon monoxide has been shown to proceed via a phenyl cation intermediate. See: Bergstrom, R. G.; Landells, R. G. M.; Wahl, G. H., Jr.; Zollinger, H. *J. Am. Chem. Soc.* **1976**, *98*, 3301.

(10) Formation of **14** and **15** has been shown in the dediazonation of 2,4,6-tri-*tert*-butylbenzenediazonium ions. See: Barclay, L. R. C.; Briggs, A. G.; Briggs, W. E.; Dust, J. M.; Gray, J. A. *Can. J. Chem.* **1979**, *57*, 2172.

(11) Stang, P. J.; Anderson, A. G. *J. Org. Chem.* **1976**, *41*, 781.

(12) Similarly triflates of 2,4,6-triisopropylphenol and 2,4,6-tricyclopropylphenol have been reported unreactive to S<sub>N</sub>1 solvolysis.<sup>4c</sup>

cations,<sup>13</sup> especially by the C-Si  $\sigma$  bond of the *o*-trimethylsilyl groups;<sup>14</sup> (2) relief of the ground-state steric strain among the triflate group and the two ortho substituents, especially in the case of the *tert*-butyl groups.<sup>15</sup>

Further investigation on this first example of aryl cation generation via the solvolysis of aryl triflates is now under progress.

**Acknowledgment.** We are grateful to Professor Y. Apeloig for generously informing us of their results. Sincere thanks are also due to Professors H. Zollinger, M. Hanack, and R. Tanaka and Drs. S. Kobayashi and I. Szele for their valuable discussions.

**Registry No.** 1a, 97391-18-9; 1b, 97391-19-0; 1c, 97391-20-3; 3a, 97391-21-4; 3b, 97391-22-5; 4, 97391-23-6; 5a, 97391-24-7; 5b, 97391-25-8; 7, 97391-26-9; 9a, 97391-27-0; 9b, 97391-28-1; 10a, 97391-31-6; 11a, 97391-32-7; 11b, 97391-33-8; 14, 72215-85-1; 15, 72215-86-2; 16, 97391-29-2; 17, 97391-30-5.

(13) The importance of hyperconjugative stabilization in phenyl cations and vinyl cations has been demonstrated in the large secondary  $\beta$ -deuterium kinetic isotope effects in the deadiation of benzenediazonium ions and in the solvolysis of vinyl triflates. See: (a) Swain, C. G.; Sheats, J. E.; Gorenstein, D. G.; Harbison, K. G. *J. Am. Chem. Soc.* 1975, 97, 791. (b) Stang, P. J.; Hargrove, R. J.; Dueber, T. E. *J. Chem. Soc., Perkin Trans. 2* 1974, 843. (c) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979; p 278.

(14) The hyperconjugative stabilization of phenyl cations by *o*-silyl groups is demonstrated in an ab initio calculation by Apeloig and his colleague. See the preceding paper in this issue. See also: Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* 1985, 107, 1496 and references cited therein.

(15) Effective van der Waals radii derived from rotational barriers in biphenyl ring-ring rotation indicate that a trimethylsilyl group is not so "large" as a *tert*-butyl group. See: Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* 1980, 102, 5618. Bödecker, H. O.; Jonas, V.; Kolb, B.; Mannschreck, A.; Köbrich, G. *Chem. Ber.* 1975, 108, 3497.

## Toward a Master Equation for Predicting Heterolysis Energies of Carbon-Carbon Bonds in Solution

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Received May 24, 1985

Fragmentation of organic molecules by carbon-carbon bond cleavage may occur through homolysis to produce a pair of free radicals or heterolytically to yield a carbanion, a carbocation, and/or an unsaturated system. Homolytic bond dissociation energies have been well studied and are predictable<sup>1</sup> and of considerable practical value for high-temperature pyrolytic processes. We report here preliminary results which offer promise of putting many heterolytic reactions in solution on a predictable thermodynamic basis.

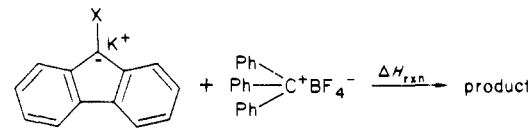
Recently we have reported several systems<sup>2,3</sup> involving resonance-stabilized carbocations and carbanions which react directly to produce covalent products by coordination. The energetics of such reactions are amenable to precise determination by standard equilibrium measurement (if the free energy of reaction is not too far from zero) or, more generally, by reaction calorimetry. Heats of heterolysis ( $\Delta H_{\text{het}}$ ) are available immediately from such calorimetric heats of reaction ( $\Delta H_{\text{rxn}}$ ) of carbocation solutions

(1) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(2) (a) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.* 1984, 106, 6726. (b) Arnett, E. M.; Troughton, E. B. *Tetrahedron Lett.* 1983, 24, 3299. (c) Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* 1983, 105, 6172.

(3) Note also: Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* 1985, 173. This paper reports the first hydrocarbon salt to be formed through a carbocation-carbanion coordination reaction.

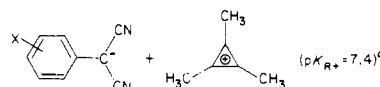
**Table I.** Heats of Reaction of 9-Substituted Fluorenyl Anions with Triphenylmethyl Cation in Benzonitrile at 25 °C



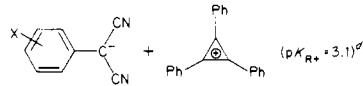
X	pK <sub>a</sub> <sup>a</sup>	$\Delta H_{\text{rxn}}$ , kcal/mol		
		exptl	calcd <sup>b</sup>	difference
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	24.35	-48.74 ± 0.64	-48.42	+0.32
H	22.61	-45.82 ± 0.23	-46.37	-0.55
Ph	17.92	-42.91 ± 1.25	-40.86	+2.05
SC <sub>6</sub> H <sub>5</sub>	15.4	-39.94 ± 0.50	-37.90	+2.04
N=NC <sub>6</sub> H <sub>4</sub> Cl- <i>o</i>	12.95	-35.02 ± 0.46	-34.96	+0.06
CO <sub>2</sub> Me	10.35	-31.99 ± 0.55	-31.96	+0.03
CN	8.3	-29.89 ± 0.47	-29.43	+0.46
av 0.79				

<sup>a</sup>References 5 and 7. <sup>b</sup>Calculated using the equation  $\Delta H_{\text{rxn}} = -11.98 + 1.178\text{p}K_{\text{R}^+} - 1.176\text{p}K_{\text{A}}$  and  $\text{p}K_{\text{R}^+} = -6.63$  for trityl cation.<sup>6</sup>

**Table II.** Experimental and Calculated Heats of Reaction between Resonance-Stabilized Carbocations and Carbanions in Acetonitrile at 25 °C



X	pK <sub>a</sub> <sup>a</sup>	$\Delta H_{\text{rxn}}$ (exptl), kcal/mol	$\Delta H_{\text{rxn}}$ <sup>b</sup> , (calcd), kcal/mol	difference
<i>m</i> -CF <sub>3</sub>	2.18 <sup>c</sup>	-6.17 ± 0.24	-5.82	+0.35
<i>m</i> -Cl	2.54 <sup>c</sup>	-6.47 ± 0.16	-6.25	+0.22
<i>p</i> -Cl	3.14	-7.34 ± 0.3 <sup>e</sup>	-6.95	+0.39
H	4.24	-8.63 ± 0.3 <sup>e</sup>	-8.25	+0.38
<i>p</i> -CH <sub>3</sub>	4.85	-9.57 ± 0.3 <sup>e</sup>	-8.96	+0.61
<i>p</i> -OCH <sub>3</sub>	5.67	-10.91 ± 0.3 <sup>e</sup>	-9.93	+0.98
av 0.46				



<i>m</i> -CN	1.90 <sup>c</sup>	-10.01 ± 0.10	-10.56	-0.55
<i>m</i> -CF <sub>3</sub>	2.18 <sup>c</sup>	-10.63 ± 0.11	-10.89	-0.26
<i>m</i> -Cl	2.54 <sup>c</sup>	-10.94 ± 0.05	-11.31	-0.37
<i>p</i> -Cl	3.14	-11.30 ± 0.3 <sup>e</sup>	-12.02	-0.72
H	4.24	-12.20 ± 0.3 <sup>e</sup>	-13.31	-1.11
<i>p</i> -CH <sub>3</sub>	4.85	-13.40 ± 0.3 <sup>e</sup>	-14.03	-0.63
<i>p</i> -OCH <sub>3</sub>	5.67	-14.00 ± 0.3 <sup>e</sup>	-14.99	-0.99
av 0.66				

<sup>a</sup> Bordwell, F. G., private communication. <sup>b</sup> Calculated by using eq 2. <sup>c</sup> This work. <sup>d</sup> "Carbonium Ions—General Aspects and Methods of Investigation", Olah, G. A., Schleyer, P. V. R., Eds.; Wiley Interscience: 1968; Vol. 1. <sup>e</sup> Reference 2a.

with carbanions merely by changing the sign ( $\Delta H_{\text{het}} = -\Delta H_{\text{rxn}}$ ).

Solvation has a remarkably small effect on the relative free energies or enthalpies of formation of delocalized carbocations<sup>4</sup> or carbanions.<sup>5</sup> Even in the gas phase, the differential values for ionic stabilities ( $\delta\Delta G^\circ$ ) are virtually the same as are measured by  $\text{p}K_{\text{R}^+}$ 's for carbocations in aqueous sulfuric acid<sup>6</sup> or by  $\text{p}K_{\text{A}}$ 's for carbanions in dimethyl sulfoxide.<sup>7</sup>

Since free energies and enthalpies of formation for both types of ionic species are closely correlated, it is attractive to propose

(4) Wolf, J. F.; Abboud, J. L. M.; Taft, R. W. *J. Org. Chem.* 1977, 42, 3316.

(5) Taft, R. W.; Bordwell, F. G. private communication.

(6) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* 1983, 105, 2889.

(7) Arnett, E. M.; Venkatasubramanian, K. G. *J. Org. Chem.* 1983, 48, 1569 and earlier references cited therein.