

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 deadiationization 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

Edward M. Arnett,\* B. Chawla, Kent Molter, Kalyani Amarnath, and Marguerite Healy

Department of Chemistry, Duke University  
Durham, North Carolina 27706

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.

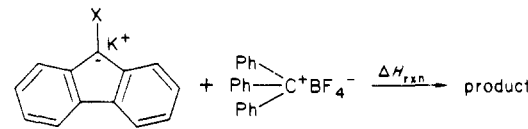
Recently we have reported several systems<sup>2,3</sup> involving resonance-stabilized carbocations and carbanions which react directly to produce covalent products by coordination. The energetics of such reactions are amenable to precise determination by standard equilibrium measurement (if the free 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.

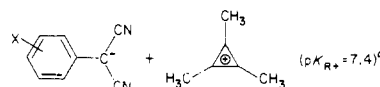
**Table I.** Heats of Reaction of 9-Substituted Fluorenyl Anions with Triphenylmethyl Cation in Benzonitrile at 25 °C



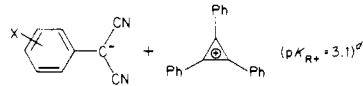
X	pK <sub>a</sub> <sup>a</sup>	$\Delta H_{\text{rxn}}$ , kcal/mol		
		exptl	calcd <sup>b</sup>	difference
<i>t</i> -C <sub>4</sub> H <sub>9</sub>	24.35	-48.74 ± 0.64	-48.42	+0.32
H	22.61	-45.82 ± 0.23	-46.37	-0.55
Ph	17.92	-42.91 ± 1.25	-40.86	+2.05
SC <sub>6</sub> H <sub>5</sub>	15.4	-39.94 ± 0.50	-37.90	+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> -CN	1.90 <sup>c</sup>	-5.78 ± 0.18	-5.49	+0.30
<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. I. <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.

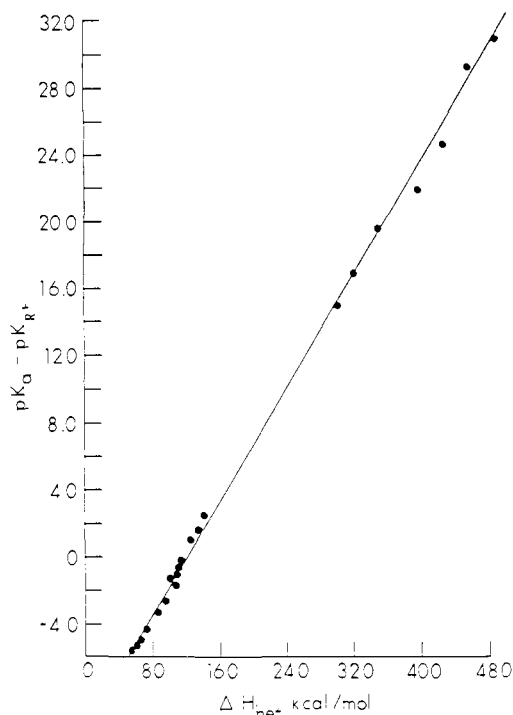


Figure 1. Correlation of combined data in Tables I and II using eq 3.

a simple "master equation" for heterolytic bond energies to produce resonance-stabilized ions in an inert polar medium

$$\Delta H_{\text{het}} = ApK_{R^+} + BpK_a + C \quad (1)$$

where the heterolytic bond energy ( $\Delta H_{\text{het}}$ ) is the negative of the measured heat of reaction between the carbocation whose free energy of formation from its carbinol in water is  $2.303RT$  (i.e.,  $1.36pK_{R^+}$ ) and the carbanion whose free energy of formation from a precursor carbon acid in  $\text{Me}_2\text{SO}$  at  $25^\circ\text{C}$  is  $1.36pK_a$  and  $A$ ,  $B$ , and  $C$  are constants.

Tables I and II test such a relationship using  $\Delta H_{\text{het}}$  for reaction of a variety of resonance-stabilized carbocations and carbanions in two solvents. Despite the variety of the ionic species and conditions, eq 1 has good correlative and predictive power for a given series of compounds. This implies at once quantitative validation of the simple approach to predicting heterolytic bond strengths in terms of the stabilities of the formed ions.

When both sets of data from Tables I and II are combined, one obtains eq 2: a master equation for all of the carbocation-

$$\Delta H_{\text{het}} = 11.98 - 1.178pK_{R^+} + 1.176pK_a \quad (2)$$

carbanion reactions we have studied so far. This equation was derived by a standard multiple regression analysis program for which the standard deviations of the constants are respectively in order:  $\pm 0.5383$ ,  $\pm 0.0651$ , and  $\pm 0.0536$  with a correlation coefficient  $r = 0.9981$ .

Comparison of the third and fourth columns of Table I shows that this equation reproduces the measured heats of reaction with an average difference of  $0.79$  kcal/mol even though most of the data from which 2 is derived were taken from the systems in Table II.

These results may be presented graphically with a single correlation line on Figure 1 by recasting 1:<sup>8</sup>

$$\Delta H_{\text{het}} = A + D(pK_a - pK_{R^+}) \quad (3)$$

Although there are clearly small differences between lines generated by each of the three data sets, it is remarkable that such a good correlation holds over such a wide range of structures and

energies. It is quite possible that a fortuitous cancellation of solvation and resonance effects is responsible for the extraordinary correlation of Figure 1 and it will be interesting to see how well this simple treatment holds up when a wider variety of ionic combinations are brought into reaction.

There is increasing interest in developing low-temperature processes for the cleavage of carbon-carbon bonds in macromolecules<sup>9-13</sup> especially as applied to the fossil fuel industries, where pyrolytic processes waste thermal energy and lead to tars. Heterolysis by treatment with strong acids or bases to yield ionic products are a promising alternative. The approach presented here may provide useful guidelines for predicting the most easily cleaved bonds in complex macromolecules.

**Acknowledgment.** We appreciate generous support from the donors of Petroleum Research Fund, administered by the American Chemical Society, the Gas Research Institute, and the Exxon Educational Foundation. Dr. Donald Chesnut provided the multivariate correlation program.

(9) (a) Larsen, J. W.; Kuemmerle, E. W. *Fuel* 1976, 55, 162 and references cited therein. (b) Larsen, J. W.; Yurum, Y.; Sams, T. L. *Fuel* 1983, 62, 476.

(10) Olah, G. A.; Bruce, M. R.; Edelson, E. H.; Husain, A. *Fuel* 1984, 63, 1130.

(11) (a) Heredy, L. A.; Neuwirth, M. B. *Fuel* 1962, 41, 221. (b) Heredy, L. A. *ACS Symp. Ser.* 1981, No. 192, 179-190.

(12) Darlage, L. J.; Weidner, J. P.; Block, S. S. *Fuel* 1974, 53, 54.

(13) Ouchi, K.; Imura, K.; Yamashita, Y. *Fuel* 1973, 52, 156.

### Intramolecular C-H Insertion: Synthesis of ( $\pm$ )-Pentalenolactone E Methyl Ester

Douglass F. Taber\*<sup>1</sup> and Jonathan L. Schuchardt

Department of Chemistry, University of Delaware  
Newark, Delaware 19716

Received December 26, 1984

We recently reported a general route to highly functionalized cyclopentanes, based on rhodium-mediated intramolecular C-H insertion.<sup>2</sup> There was some concern as to whether this reaction, facile with open-chain systems, would be as effective in sterically more constrained situations. Among other considerations, theoretical calculations<sup>3</sup> lead to the prediction that the activation energy for the insertion process will depend on the angle of approach of the intermediate Rh complex to the target C-H bond. We now report a simple route to the sesquiterpene antibiotic pentalenolactone E methyl ester (**1**) (Scheme I),<sup>4,5</sup> the key step of which is a rhodium-mediated intramolecular C-H insertion via a sterically constrained transition state.

Previous routes to **1**<sup>5</sup> (Scheme I) have dissected the angular lactone at "a", leading to a substituted bicyclo[3.3.0]octan-3-one such as **2**. An alternative analysis leads to a potentially more effective dissection, scission at "b". While **1** has three asymmetric centers, **3** has only one. Further, **3** should be readily available by spiroannulation of the symmetrical 4,4-dimethylcyclohexanone **4**, followed by carbonyl extrusion. Clearly, the key to such a retrosynthetic analysis lies in the *synthetic* step in which the

(1) Fellow of the A. P. Sloan Foundation, 1983-1987.

(2) (a) Taber, D. F.; Petty, E. H. *J. Org. Chem.* 1982, 47, 4808. (b) For other studies of intramolecular C-H insertion, see: Wenkert, E.; Davis, L. L.; Mylari, B. L.; Solomon, M. F.; daSilva, R. R.; Shulman, S.; Warnet, R. J.; Ceccherelli, P.; Curini, M.; Pellicciari, R. *J. Org. Chem.* 1982, 47, 3242 and ref 5b.

(3) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* 1984, 106, 2006.

(4) Isolation and structure: Cane, D. E.; Rossi, T. *Tetrahedron Lett.* 1979, 20, 2973.

(5) For previous syntheses of ( $\pm$ )-pentalenolactone E methyl ester, see: (a) Paquetté, L. E.; Annis, G. D.; Schostarez, H. *J. Am. Chem. Soc.* 1982, 104, 6646. (b) Cane, D. E.; Thomas, P. J. *J. Am. Chem. Soc.* 1984, 106, 5295. (c) Ohtsuka, T.; Shirahama, H.; Matsumoto, T. *Tetrahedron Lett.* 1983, 24, 3851.

(8) For precedents, see: (a) Chawla, B.; Mehta, S. K. *J. Phys. Chem.* 1984, 88, 2650. (b) Mashkovskii, A. A.; Odinkov, S. E. *Dokl. Akad. Nauk SSSR* 1972, 204, 1165. (c) Johnson, S. L.; Rumon, K. A. *J. Phys. Chem.* 1965, 69, 74.