atom moves back and forth by 0.38 Å along the N–S–N line 9 times a second at 0 °C, i.e., the bond switching.

There can be several types of monoprotonated species as shown in Scheme I, however, the real entity that effects the ring transformation should be **2**-$\alpha$-H$^+$-ii ($\equiv$ **2**-$\beta$-H$^+$-ii), since the N–S bond is weakened by protonation at nitrogen 2 of the ring and allows the sulfur atom to accept an electron from the unprotonated amidino nitrogen. Although an exact estimate is difficult, equilibrium ratios (**2**-$\alpha$-H$^+$-i/**2**-$\alpha$-H$^+$-ii) can be assumed to be in the range from $10^{3.5}$ ($10^{4.9-1.4}$) to $10^{5.4}$ ($10^{4.9+0.5}$). Thus, the real rate of ring transformation (4) should be in the range of $9 \times 10^{3.5}$ to $9 \times 10^{5.4}$ s$^{-1}$ at 0 °C, and $\Delta G^{\ddagger}_{273}$ can be calculated to be from 8.0 to 10.3 kcal mol$^{-1}$. Such a low barrier of the ring transformation can be attributed to the stability of the intermediate $\pi$-sulfurane(s) and also to the essential weakness of the hypervalent N–S$^{IV}$–N bond.

**Registry No. 2**, 72212-82-9.

**Supplementary Material Available:** Kinetic parameters of the ring transformation of **2** in methanol-$d_4$ in the presence of less than 1 equiv of TFA (1 page). Ordering information is given on any current masthead page.

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(9) Partial support of this work was provided by a Grant-in-Aid for Scientific Research (No. 57430006) administered by the Ministry of Education, Science and Culture of Japanese Government.

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# Regioselectivity and Rearrangement upon Addition of Nucleophiles to (Diene)iron Complexes

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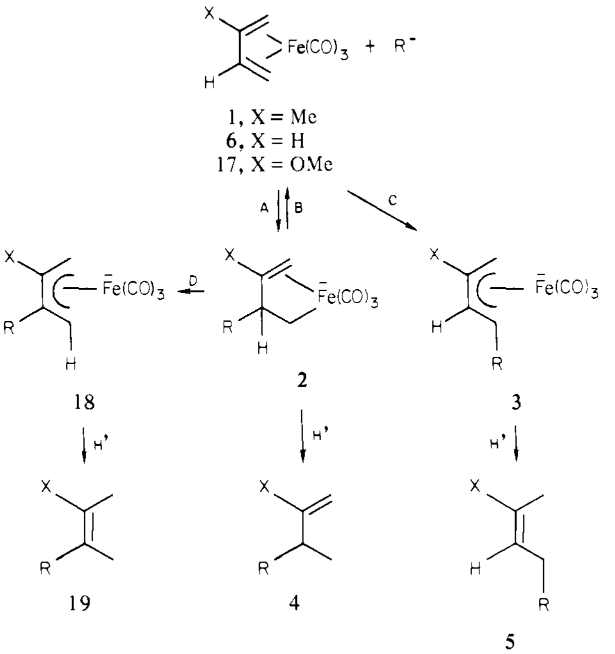
The regioselectivity in addition of nucleophiles to metal-coordinated polyene systems is of interest both for practical synthesis[1] and theory.[2,3] While the theoretical analyses assume kinetically controlled reactions, this assumption is seldom established by experiment and may often be inappropriate.[4] With $\eta^4$-1,3-diene ligands, even the simplest example (1,3-butadiene) offers two sites of attack (terminal or internal). The only published prediction suggests preferential addition at a terminal position for cationic $\eta^4$-1,3-diene complexes,[2] and a few isolated examples are in harmony.[5,6] Here we describe a systematic study of selectivity with ($\eta^4$-1,3-diene)tricarbonyiron complexes which demonstrates that kinetically controlled addition at −78 °C is strongly preferred at an unsubstituted internal position but that reversal of the initial addition can be rapid below 0 °C. Formation of the more stable $\eta^3$-allyl complexes then occurs, via nucleophile addition at a terminal position (substituted terminal preferred over unsubstituted) and, in special cases, via hydride migration (Scheme I).

Scheme I. Reaction Pathways



a, X = Me; R = CMe$_2$CN. b, X = Me; R = CHPh$_2$.
c, X = OMe; R = CHPh$_2$. d, X = H; R = CHPh$_2$.

Table I. Reactions of Anions with (Isoprene)tricarbonyliron[a]

| entry | R$^-$ | conditions,[a] °C/h | product ratio 4/5 | combined yield |
|---|---|---|---|---|
| 1 | CMe$_2$CN | −78/0.5 | 100/0 | 88% |
| 2 | CMe$_2$CN | 25/2 | 0/100 | 70% |
| 3 | CHPh$_2$ | −78/0.5 | 81/19 | 73% |
| 4 | CHPh$_2$ | −78/2 | 85/15 | b |
| 5 | CHPh$_2$ | 0/0.5 | 52/48 | b |
| 6 | CHPh$_2$ | 0/2 | 11/89 | b |
| 7 | CHPh$_2$ | 25/2 | 0/100 | 61% |

[a] The anions were generated at −78 °C in THF-HMPA, and the diene complex was added slowly, on an 8-10 mmol scale. After the specified time/temperature, the mixture at −78 °C was treated with excess trifluoroacetic acid, allowed to stir for 30 min without warming, and then added to aqueous sodium bicarbonate. Isolation by the usual extraction procedures gave the crude product. The products were separated by chromatography on silver nitrate-silica gel and weighed. [b] The yield was not determined; the product ratio is the peak area ratio by analytical GLPC.

Reactions of ($\eta^4$-isoprene)tricarbonyliron (**1**) have been studied in greatest detail. While anionic intermediates of type **2** and **3** from anion addition to ($\eta^4$-1,3-cyclohexadiene)tricarbonyliron have been characterized spectroscopically,[7] for the present study we chose to analyze the product distribution (**4** and **5**)[8] after

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(1) Questions of regioselectivity have figured strongly in the development of methodology involving nucleophilic addition to the following. (a) (Alkene)metal complexes: Hegedus, L. S.; McGuire, M. A. *Organometallics* **1982**, *1*, 1175–1178 and references therein. Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122 and references therein. (b) (Allyl)palladium complexes: Trost, B. *Ibid.* **1980**, *13*, 385 and references therein. Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310–1312. Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193–5196. (c) (Cyclohexadienyl)iron(II) complexes: Birch, A. J. *et. al Tetrahedron, Suppl. 9* **1981**, *37*, 289 and references therein. (d) (Arene)metal complexes: Semmelhack, M. F.; Garcia, J. L.; Cortês, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467–469 and references therein. Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207–221 and references therein.

(2) A comprehensive tabulation and general theoretical rationalization has been presented: Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(3) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320.

(4) For example, while the addition of nucleophiles to ($\eta^2$-1,3-diene)(cyclopentadienyl)dicarbonyliron(II) occurs at C-2 (internal), parallel additions to ($\eta^4$-1,3-diene)palladium(II) complexes are preferred at C-1 (terminal). The latter selectivity may be the result of thermodynamic control (more stable $\eta^3$-allyl product). (a) For the CpFe(CO)$_2$–diene case, see: Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) For the diene–Pd(II) case, see: Bäckvall, J.-E. *Ibid.* **1983**, *16*, 343. Recent results have demonstrated regiochemical equilibration during nucleophilic addition to certain (arene)chromium complexes: (a) Kundig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6962–6965. (b) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.*, in press.

(5) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365.

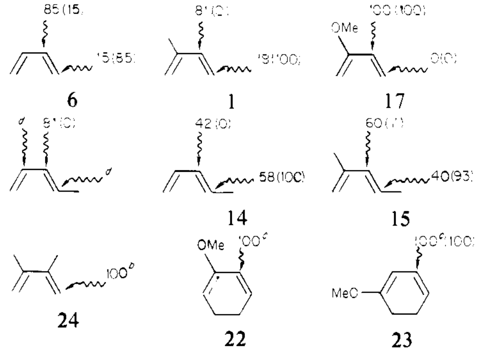
(6) (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400–409. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858–4860.

(7) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.*, in press.

(8) For earlier examples of acid cleavage of the iron intermediates, see: Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. The geometry of the alkenes is not always established, but a single isomer is obtained unless otherwise noted. In addition, double-bond positional isomers of **4** and **5** appear in minor amounts in certain cases. They have been characterized and included in the yields quoted for **4** and **5**.[9]

0002-7863/84/1506-2715$01.50/0

Table II. Selectivity in Addition of $LiCHPh_2$ to (Diene)tricarbonyliron Complexes



[a] The numbers are the percentage of the Anion–diene adducts from addition of the anion at the indicated position. The numbers not in parenthesis are the results from reaction at −78 °C/0.5 h (kinetic control). The numbers in parenthesis refer to product distribution after equilibration (25 °C/2 h). [b] It has not been established that the product from short reaction time is the result of kinetic control. [c] This reaction was carried out at −78 °C under an atmosphere of CO as trapping agent for the first-formed intermediate (see ref 12 and supplementary material). The product is a 3-acyl derivative. [d] Addition at C-2 and C-4 cannot be distinguished by the observations so far.

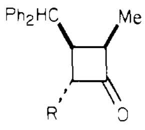
quenching with trifluoroacetic acid. The results are presented in Table I.[9] With both $LiCHPh_2$ and $LiC(CH_3)_2CN$, addition is complete within a few minutes at −78 °C and strongly favors addition at C-3 (Scheme I, step **A**; products **4a** and **4b**). During warming to 0 °C, rearrangement to **3** begins to occur and is complete after 2 h at 25 °C. The half-time for rearrangement is 0.5–1 h/0 °C. Three sets of crossover experiments establish that simple reversal of anion addition (step B) and readdition at a terminal position (step C) can account for the rearrangement:

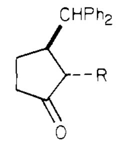
(a) When $LiCHPh_2$ is added to a solution of **2a** at −78 °C, quenching at −78 °C gives **4a**, as before, but upon warming the mixture of **2a** and $LiCHPh_2$, anion exchange occurs, and the product from cleavage of **3b** appears (products are **5a** and **5b**, in the ratio 26:74).[9]

(b) No anion exchange of **3a** with $LiCHPh_2$ has been observed; **3a** is formed irreversibly at 25 °C.

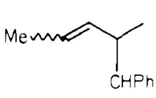
(c) Addition of ($\eta^4$-1,3-butadiene)tricarbonyliron (**6**) to a solution of **2b** results in transfer of the anion unit from **2b** to **6**, at approximately the same rate as positional isomerization of the anion unit (**2a** → **3a**).[9] At −78 °C (2 h), no transfer occurs and acid quenching produces only **4b** and **5b** (86:14). At 0 °C, both isomerization of **2b** and anion transfer occur; quenching after 2.0 h produces **4b** (30%), **5b** (39%), and the product from addition to C-1 of butadiene (**5d**, 31%). At 25 °C, equilibration is complete; quenching after 2.0 h gives **5b** (48%) and **5d** (52%).

The results of similar addition/equilibration/quenching studies are summarized in Table II. The quenching products are simple (analogous to **4** and **5**)[8] with all diene complexes in the table except for **6** and ($\eta^4$-2,4-pentadiene)tricarbonyliron (**7**). With complexes **6** and **7**, CO insertion complicates the mixture of low-temperature quenching products. Reaction of $LiCHPh_2$ with **6** at −78 °C for 0.5 h followed by excess trifluoroacetic acid at −78 °C produces cyclobutanone **8** (51% yield) and cyclopentanone **9** (9% yield)[9,10] along with the usual type of olefin product (**5d**) from addition to the terminal position (14%). Under the same conditions, **7** produces **10** (42%) and **11** (16%) along with **12** (13%).[11] After

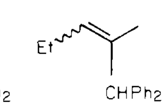




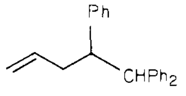
**8**, R = H **9**, R = H
**10**, R = Me **11**, R = Me



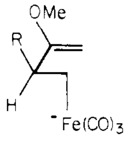
**12**



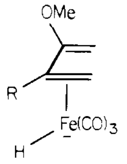
**13**



**16**



**20**



**21**

addition/equilibration at 25 °C/2 h followed by acid quenching, no CO insertion products were detected from either **6** or **7**; the only product from **6** is 5d (terminal addition), while **13** (47%) and **12** (11%, *E*/*Z* mixture) are obtained from **7**.[11] With complexes **14** and **15** (Table II) bearing substituents in a terminal position, kinetic addition at both internal and terminal positions is important; simple olefinic products are obtained. Anion equilibration occurs below 25 °C and leads to products (e.g., **16** from **14**) from addition exclusively at the more substituted terminus.[9]

The anionic intermediate from addition to ($\eta^4$-2-methoxy-1,3-butadiene)tricarbonyliron (**17**) equilibrates by a different mechanism. Under the usual conditions for kinetic control, the usual type of product (**4c**, Scheme I) is obtained (80% yield). Isomerization of the anionic intermediate occurs upon warming, apparently via hydride transfer, to give allyl complex **18c** (Scheme I, step D); after 2 h/25 °C, quenching produces exclusively **19c** (60% isolated). We view the hydride shift occuring via detachment of the alkene ligand (**20**), β-hydride elimination (**21**), and readdition to give **18**.

The complexes (**22** and **23**, Table II) from 1-methoxy-1,3-cyclohexadiene and 2-methoxy-1,3-cyclohexadiene show completely selective addition for an internal position during reaction with $LiCMe_2CN$ at −78 °C for 2 h.[9,12] At 25 °C, the anion unit still resides at C-3 of **23**; acid quenching and hydrolysis gives 3-(2-cyano-2-propyl)cyclohexanone.[9] Equilibration again appears to be occurring by a hydride shift rather than anion rearrangement. Only in the case of the 2,3-disubstituted diene (in **24**, Table II) was terminal addition favored at −78 °C.

These results, together with earlier trapping experiments with CO,[10,12] demonstrate that addition to ($\eta^4$-1,3-diene)tricarbonyliron complexes is generally favored at an unsubstituted internal position,[13] that initial addition is not controlled by product stability, and that equilibration to the more stable intermediate can occur rapidly at 0 °C.

**Acknowledgment.** We acknowledge financial support in the form of a research grant from the National Science Foundation (CHE 82-04399) and helpful discussion with Dr. J. W. Herndon. We are grateful to Mary Baum for assistance in obtaining and

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[9] Experimental details and full characterization data are presented in the supplementary material.

[10] The formation of cyclobutanones from protonation of **2d** can be rationalized but is not well precedented. A more complete study of this aspect will be reported in due course. Cyclopentanones are formed in high yield under modest CO pressure but not generally during acid quenching in the absence of CO: Semmelhack, M. F.; Herndon, J. W.; Liu, J. *Organometallics* **1983**, *3*, 1885.

[11] Compounds **12** and **13** could have arisen by addition at C-2 or C-4. Formation of **13** requires a hydride shift in any case.

[12] The kinetic addition product is trapped by insertion of CO and the cleavage with methyl iodide according to the procedure reported earlier: Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497.

[13] A set of detailed calculations would be helpful in analyzing the substituent effects on charge densities and orbital coefficients in diene ligands; data so far available suggest that the internal positions are relatively electron deficient compared to the terminal positions[14,15] and that the larger coefficients in the LUMO of the diene complexes appear at the terminal carbons.[15] A charge-controlled process can be suggested, consistent with the tendency toward attack at an internal position. Substituents such as methyl and phenyl in the terminal position may perturb the charge distribution so as to favor kinetic addition at the terminal site.

[14] (a) Connor, J. A.; Derrick, L. M. R.; Hall, M. P.; Hillier, I. H.; Guest, M. F.; Higgenson, B. R.; Llloyd, D. R. *Mol. Phys.* **1974**, *28*, 1193–1205. (b) El-Awady, A. A. *Inorg. Nucl. Chem.* **1979**, *36*, 2185–2190.

[15] Extended Hückel calculations carried out at Princeton by Andy Gray. See: Herndon, J. W. Ph.D. Thesis, Princeton University, 1983.

interpreting NMR spectral data and to the National Science Foundation for providing funds for the purchase of the NMR instrument.

**Supplementary Material Available:** Characterization data and general experimental procedures (10 pages). Ordering information is given on any current masthead page.

## Enhanced Substituent Solvation Assisted Resonance Effects in Dipolar Non-Hydrogen-Bond-Donor Solvents

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A recent analysis of gas- vs. aqueous-phase data has revealed that phenol acidities in water have significant and specific dependencies on hydrogen bonding to substituents.[1] Strong hydrogen-bond-acceptor (HBA) substituents give relatively increased acidities due to the hydrogen-bond-donor (HBD) properties of water, whereas strong HBD substituents give relatively decreased acidities due to the HBA properties of water. These hydrogen-bond interactions act to modify both the substituent field/inductive (F) and resonance (R) effects.[1,2] Thus for those +R substituents that are *both* $\pi$ electron and strong hydrogen-bond acceptors, the F effect is increased by hydrogen bonding in water about equally at the meta and para ring positions (we refer to these as specific substituent solvation assisted field (SSSAF) effects). The acidifying +R resonance effect is also significantly increased by substituent HBA hydrogen bonding (SSSAR), but *only* at the para position.[1,2]

We communicate here a preliminary report on the results of a complementary investigation of the effects of substituent solvation by $Me_2SO$ based upon comparisons of phenol acidities in the gas phase vs. $Me_2SO$ solution.[3,4] The inability of the $Me_2SO$ solvent to act as an HBD toward either the phenoxide ion center or substituents with strong HBA properties[5] was expected to cause at least three significant changes, relative to those observed for the aqueous solvent. (1) The absence of hydrogen-bond solvation of phenoxide ions by $Me_2SO$,[5] together with the relative ineffectiveness of electrostatic or Lewis acid solvation,[2] should cause a much smaller solvent attenuation of gas-phase acidities, i.e., a smaller slope for the plot of gas phase vs. $Me_2SO$ phenol acidities. (2) The absence of hydrogen-bond substituent solvation should cause SSSAF effects to be absent for all +R substituents at both meta and para positions in $Me_2SO$. (3) Enhanced acidity effects will be observed only for those +R para substituents that become sufficiently charge localized by their R effect as to cause electrostatic or nonprotonic Lewis acid solvation (SSAR[6] effect).

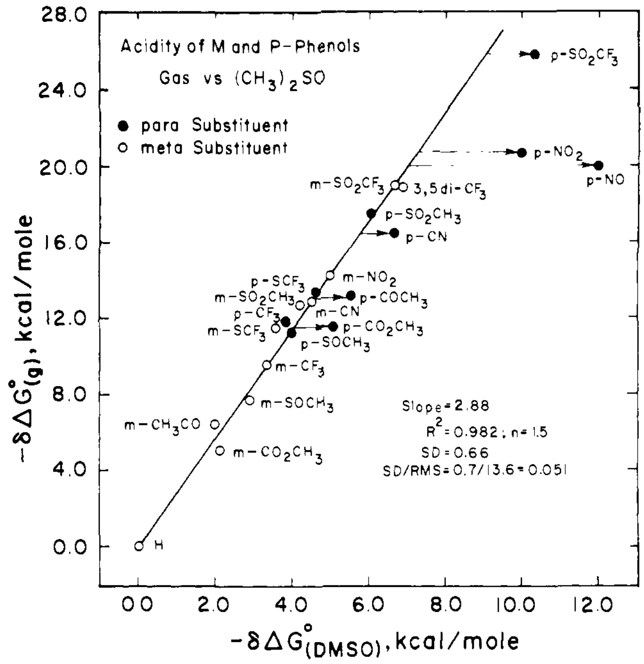

**Figure 1.** Relative acidities of meta- and para-substituted phenols: gas vs. $(CH_3)_2SO$ solution. Correlation statistics are as given. Ordinant: $-\delta\Delta G^\circ(g)$, kcal/mol. Abscissa: $-\delta\Delta G^\circ((CH_3)_2SO)$, kcal/mol.

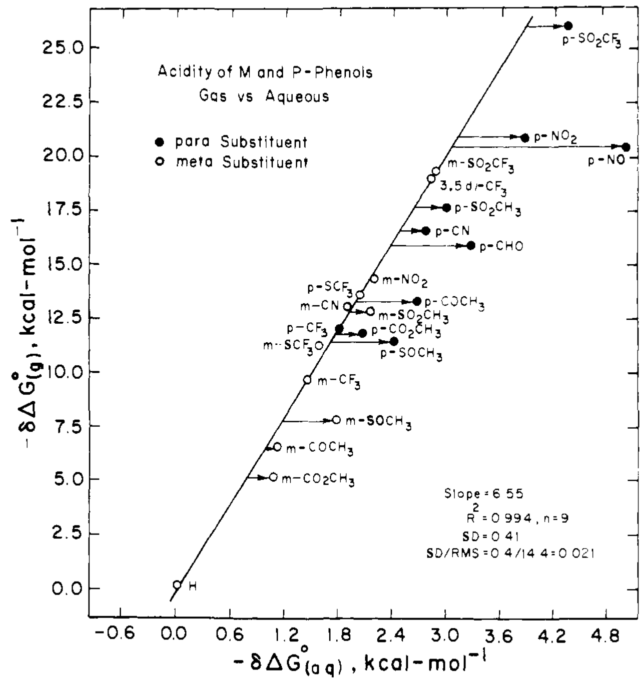

**Figure 2.** Relative acidities of meta- and para-substituted phenols: gas vs. aqueous solution. Correlation statistics are as given. Ordinant: $-\delta\Delta G^\circ(g)$, kcal/mol. Abscissa: $-\delta\Delta G^\circ(aq)$, kcal/mol.

The gas-phase acidities of an extended series of +R meta- and para-substituted phenols[1,7,8] are plotted in Figure 1 against the corresponding acidities of these phenols in dilute $Me_2SO$ solution (each relative to that for the unsubstituted phenol). Examination of Figure 1 confirms the changes anticipated: (1) the slope of the line in Figure 1 is 2.9 compared to 6.6 observed in water (Figure 2); (2) there is no significant deviation from a linear

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[1] Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017-4029.

[2] Taft, R. W. *Prog. Phys. Org. Chem.* **1983**, *14*, 305-346.

[3] The acidities of phenols in $Me_2SO$ were measured and corrected for homo-hydrogen bonding between the phenol and its conjugate base as previously described.[4]

[4] Bordwell, F. G.; McCallum, R. J.; Olmstead, W. N. *J. Org. Chem.* **1984**, *49* (in press).

[5] Cf.: Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877 and references therein.

[6] We omit the adjective "specific" for SSAR effects in $Me_2SO$ since at present there is no compelling evidence as to which type is involved. Specific solvation is defined as involving discrete solvent-solute (or Lewis acid-base) complexes as contrasted to nondiscrete many molecule electrostatic solvation.

[7] Our new $-\delta\Delta G_p{}^\circ$ values in kcal/mol for the following para substituents: p-$SCF_3$, 13.5; p-$SO_2CF_3$, 25.9; p-NO, 20.2. $-\delta\Delta G_m{}^\circ$ values: m-$SCF_3$, 11.7; m-$SO_2CF_3$, 19.1; 3,5-$(CF_3)_2$, 19.0.

[8] The meta and para $\pi$ electron-donor (−R) substituent points have been omitted from Figures 1 and 2. Substituent solvation effects for these functions will be discussed in a full paper now in preparation.