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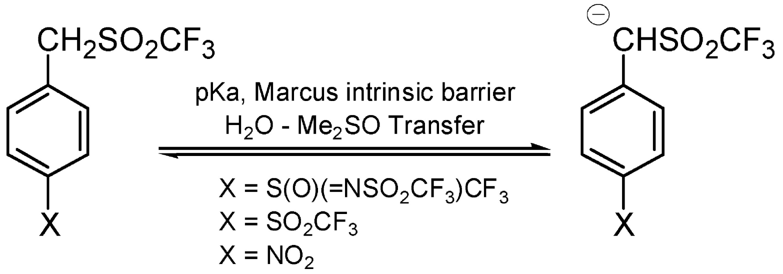

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Superacidifiers: Assessing the Activation and the Mode of Charge Transmission of the Extraordinary Electron-Withdrawing SO_2CF_3 and $S(O)(=NSO_2CF_3)CF_3$ Substituents in Carbanion Stabilization

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Abstract: We report on a structural (multinuclear NMR), thermodynamic (pK_a), and kinetic (Marcus intrinsic reactivity) study of the ionization of benzylic carbon acids activated by an exocyclic (α) SO_2CF_3 group and SO_2CF_3 or $S(O)(=NSO_2CF_3)CF_3$ in the para position of the phenyl ring. The latter exerts an enormous acidifying effect of ca. 8 pK units as compared with 4-H benzyltriflone in Me_2SO solution, (corresponding to remarkably high Hammett σ values $\sigma_p \approx 1.35$, $\sigma_{p-} \approx 2.30$). In considering the origin of this effect, important information was derived in comparing medium effects on pK_a's for NO_2, SO_2CF_3, and $S(O)(=NSO_2CF_3)$-CF_3 activated carbon acids. Highly contrasting behavior was thus induced by $H_2O \rightarrow Me_2SO$ transfer, with a large decrease in acidity of α-nitro activated carbon acids but a large increase in acidity of α-SO_2CF_3 analogues, leading to remarkable inversions in C−H acidity. These results support the view that in the case of the triflones the carbanion negative charge resides for the most part at the exocyclic Cα carbon, implying a major role of a polarizability effect. ^1H, ^{13}C, and ^{19}F NMR data fully support this proposal. Most importantly, the intrinsic reactivity (log k_0) positioning **9** and **10** on the Marcus scale for carbon acids could be kinetically measured in 50%H_2O−50%Me_2SO; for **9**, log $k_0 = 3.80$ and for **10**, log $k_0 = 4.20$. Such high log k_0 values correspond to low intrinsic barriers which can only be reconciled on the basis of minimum electronic and structural reorganization in formation of the conjugate carbanions. This further emphasizes polarization as the predominant mechanistic mode of charge stabilization in these species.

Introduction

Electron-withdrawing groups in molecules are prerequisite for enabling a variety of transformations in organic chemistry, including processes proceeding via carbanionic intermediates, nucleophilic substitutions, elimination reactions, and so forth.[1] The nitro group has traditionally been considered as an electron-withdrawing group *per excellence*, with a mode of action both inductive and through resonance.[2,3] Yet, in recent years, other structural moieties have been explored with the possibility of rivalling, or even exceeding, the electron-withdrawing capability of NO_2.[4−6] One avenue of approach, developed since the 1960s by Yagupol'skii and by Sheppard, was through modification of the sulfonyl (SO_2)R group via electron-withdrawing substituents as in SO_2CF_3.[7−11] In turn, these novel substituents have found utility in different realms of chemistry.[12−16]

Recently, we have reported on the ionization equilibria of a number of α-SO_2CF_3 activated carbon acids, including aliphatic and benzylic triflones.[17,18] Mainly through a combination of

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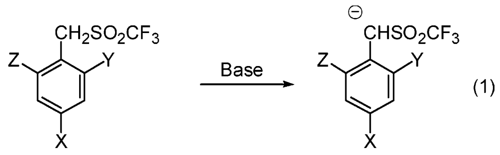
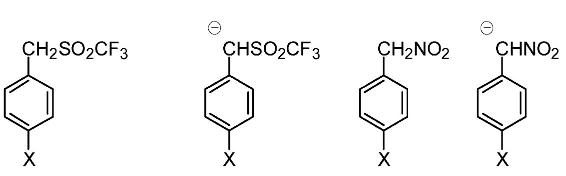
results of thermodynamic investigations with the structural information provided by NMR studies, the exceptional electron-withdrawing capability of the SO_2CF_3 group in carbanion stabilization was convincingly demonstrated. However, of equal importance perhaps was the discovery of a dominant solvent dependence of the carbon acidity, which was in marked contrast for the SO_2CF_3 group as compared with the well-recognized situation for the NO_2 group.[18a] Thus, going from water to Me_2SO strongly decreases the acidity of α-nitro activated carbon acids, in accord with the well-established nitronate structure of the conjugate carbanions.[3,14,19,20] In such species, negative charge is predominantly delocalized onto the oxygens of the NO_2 group, resulting in loss of H-bonding as the H_2O content of the medium is decreased. On the other hand, the same solvent transfer increases the acidity of α-SO_2CF_3 activated carbon acids.[18a] In the series of benzyltriflones **1**−**6**, it could be shown through substituent effects in the phenyl ring that the negative charge in the generated benzylic anions remains largely localized on the exocyclic carbon center, even in the case of a trinitro activation of the phenyl ring.[18b] Because of a predominance of polarization effects, a situation first recognized in a study of the ionization of dimethyl sulfone,[21] Me_2SO is thus rendered especially favorable in stabilizing charge through dispersion, thereby increasing the carbon acidity. A striking illustration of the contrasting response of α-nitro and α-SO_2CF_3 activated carbon acids to H_2O-Me_2SO transfer is the observation of inversions in relative acidities of these two classes of compounds, for example, nitromethane **7** is 1 order of magnitude more acidic than trifluoromethanesulfonylmethane **8** in water but it becomes 500-fold less acidic than **8** in pure Me_2SO.[18a] Such a clear reversal in the relative acidifying effects of the NO_2 and SO_2CF_3 groups within a family of structurally similar carbon acids was unprecedented and revealed further that Me_2SO is a solvent of choice in taking advantage of the mode of stabilization of negative charge by the SO_2CF_3 group and therefore of its acidifying potential.



1 X = Y = Z = H **C-1**
2 X = CF_3, Y = Z = H **C-2**
3 X = CN, Y = Z = H **C-3**
4 X = NO_2, Y = Z = H **C-4**
5 X = Y = NO_2, Z = H **C-5**
6 X = Y = Z = NO_2 **C-6**

CH_3NO_2 **7** $CH_3SO_2CF_3$ **8**

Recent efforts have been directed toward development of novel substituents that would be even more effective than the SO_2CF_3 group in charge withdrawal, and these substituents have been referred to as superacidifiers.[4−6] In the present work, we report on not only a structural (NMR) and thermodynamic study but also a kinetic study (Marcus intrinsic barrier) of the ionization of the two benzyltriflones **9** and **10** to give the conjugate carbanions **C-9** and **C-10** in pure Me_2SO solution and H_2O-Me_2SO mixtures of different compositions (eq 1). In these triflones, the effect of the exocyclic SO_2CF_3 group is opposed to the effect of para substitution of the phenyl ring by a $-S(O)(=NSO_2CF_3)CF_3$ group or a SO_2CF_3 group, respectively. As will be seen, our results will first emphasize the much stronger electron-withdrawing capability of the former fragment, not only with respect to a SO_2CF_3 group but also to a NO_2 group. Estimates of the Hammett σ_p and σ_{p-} constants for $S(O)(=NSO_2CF_3)CF_3$ could be obtained. Comparison of the data obtained for **9** and **10** with those previously reported for the ionization of the *para*-nitrobenzyltriflone **4** and two related carbon acids, namely the phenylnitromethanes **11** and **12**, will allow us to delineate the charge-transfer mechanism contributing to the stabilization of negative charge by the aforementioned CF_3 modified sulfonyl and sulfoximinyl groups. Of major importance for this discussion has been the successful positioning of **9** and **10** on the Marcus intrinsic reactivity scale for carbon acids.[3,20,22] Such a ranking is in itself a significant result since it has thus far proved to be very difficult to determine accurately the intrinsic reactivity of α-sulfur substituted carbon acids.[17,23]



9 X = $S(O)(=NSO_2CF_3)CF_3$ **C-9** **11** X = H **C-11**
10 X = SO_2CF_3 **C-10** **12** X = NO_2 **C-12**

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Table 1. Changes in Representative Chemical Shifts ($\Delta\delta H_\alpha$, $\Delta\delta C_\alpha$, $\Delta\delta C_4$, $\Delta\delta_F$) and Coupling Constants ($\Delta^1J_{C\alpha H\alpha}$) upon Ionization of Substituted Benzyltriflones (**1**, **4**, **9**, **10**) and Related Phenylnitromethanes (**11**, **12**)[a]

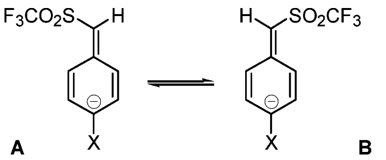
carbon acid	δH_α	$\Delta\delta H_\alpha$	δC_α	$\Delta\delta C_\alpha$	$^1J_{C\alpha H\alpha}$	$\Delta^1J_{C\alpha H\alpha}$	δC_4	$\Delta\delta C_4$	$\delta_F(\alpha\text{-}SO_2CF_3)$	$\Delta\delta_F$
1[b]	5.25		54.8		142.8		129.6		−79.1	
C-1[b]	3.38	−1.87	55.0	0.2	163.9	21.1	116.9	−12.8	−80.8	−1.7
4[b]	5.53		53.7		143.2		148.1		−79.8	
C-4[b]	4.07	−1.46	65.7	12.0	168.0	24.8	131.5	−16.6	−81.3	−1.5
9	5.45		53.7				127.5		−72.1	
C-9	4.37	−1.08	70.4	16.7			102.2	−25.3	−74.8	−2.7
10[c]	5.56		53.8		143.0		130.5		−72.0	
C-10[c]	4.06	−1.50	65.2	11.4	169.0	26.0	110.1	−20.4	−75.0	−3.0
11[d]	5.71		79.3		146.0		132.5			
C-11[d]	6.70	0.99	109.2	29.9	175.2	29.2	123.0	−9.5	–	–
12[d]	5.95		77.6		149.1		148.0			
C-12[d]	6.84	0.89	109.8	32.2	180.1	31.0	140.1	−7.9	–	–

[a] In $Me_2SO\text{-}d_6$. [b] Reference 17. [c] Reference 24. [d] Reference 27.

Results

Structural Studies. Addition of dilute tetramethylammonium hydroxide to $\sim 5 \times 10^{-5}$ M solutions of **9** and **10** in H_2O-Me_2SO mixtures containing 30, 50, and 70% Me_2SO by volume resulted in the reversible and complete formation of species exhibiting intense absorption maxima at the following wavelengths: 384 nm, $\epsilon = 30\,000$ M^{-1} cm^{-1} (**C-9**), and 359 nm, $\epsilon = 42\,000$ M^{-1} cm^{-1} (**C-10**) in 50% Me_2SO. Use of sodium hydride as the base reagent induced a similar interconversion in pure Me_2SO solutions.

That the addition of base to **9** and **10** afforded the carbanions **C-9** and **C-10** was unambiguously demonstrated by carrying out a ^1H, ^{13}C, and ^{19}F NMR study of the ionization reactions in Me_2SO. Because of an observable exchange between the two conformers A and B at probe temperature, the chemical shifts given in Table 1 refer to spectra recorded at temperatures where the process of eq 2 was found to be fast on the NMR time scale, that is, $T = 366$ K for **9** and $T = 362$ K for **10**. Note that a detailed investigation of the rotational isomerism of eq 2 for X $= SO_2CF_3$ has been made at different temperatures in Me_2SO as well as in acetone and acetonitrile. The results of this dynamic NMR study have been recently reported.[24]



(2)

X = SO_2CF_3, $S(O)(=NSO_2CF_3)CF_3$

pK_a Measurements. Using mostly aliphatic and alicyclic amine buffers (i.e., aminoacetonitrile, glycine ethyl ester, glycinamide, morpholine, 2-methoxyethylamine, butylamine, and piperidine), we determined the pK_a^{CH} values of **9** in H_2O and in H_2O-Me_2SO mixtures containing 10, 30, 50, and 70% Me_2SO as well as in pure Me_2SO from observed absorbance variations at λ_{max} of **C-9** obtained at equilibrium as a function of pH. These variations described regular acid−base equilibrations, as illustrated in Figure S1, which shows that excellent straight lines with unit slopes were obtained on plotting the log value of the ratio of the concentration of the ionized to un-ionized triflone as a function of pH (eq 3). The pK_a^{CH} values thus obtained together with those previously measured for **10** as well as other carbon acids of eq 1 are given in Table 2.

Table 2. pK_a Values for **9** and **10** and Related Benzyltriflones (**1**−**4**) and Phenylnitromethanes (**11**, **12**) in H_2O, Me_2SO, and Various H_2O-Me_2SO Mixtures[a]

carbon acid	H_2O	30% Me_2SO	50% Me_2SO	70% Me_2SO	Me_2SO
9	9.70[b]	8.55	7.60	7.15	6.45
10[c]	11.60	10.65	9.77	8.67	8.85
4[c]	–	11.75	10.57	9.55	9.46
3[c]	–	12.82	12.00	11.02	10.70
2[c]	–	13.82	13.30	–	11.95
1[c]	–	–	15.10	14.80	14.62
12[d]	5.89	–	6.02	–	8.62
11[e]	6.77	–	7.93	8.53	12.32 (12.20)

[a] $T = 25$ °C; % Me_2SO by volume. [b] 90%H_2O−10%Me_2SO. [c] Reference 18b. [d] Reference 27. [e] Reference 20.

$$\log \frac{[\textbf{C-9}]}{[\textbf{9}]} = \mathrm{pH} - \mathrm{p}K_a^{\mathrm{CH}} \tag{3}$$

Kinetic Measurements. Rates of equilibration of **9** and **10** with the respective conjugate bases **C-9** and **C-10** according to eq 4 were found to be rather high but nevertheless accessible by stopped-flow spectrophotometry provided that the kinetic experiments be carried out in buffers made up from primary amines (B) with pK_a^{BH} values close to the pK_a^{CH} value. Kinetic data were obtained at constant ionic strength of 0.5 M (Me_4NCl) and 25 °C in 50%H_2O−50%Me_2SO (v/v). Buffers used were aminoacetonitrile, glycine ethyl ester, glycinamide, and 2-methoxyethylamine for **9**, and glycinamide, 2-methoxyethylamine, and butylamine for **10**. All experiments were performed under pseudo-first-order conditions with a large excess of the buffer reagents over the concentration of **9** or **10** ($\sim 5 \times 10^{-5}$ M). Depending on the pH studied, equilibrium (4) was approached from either the reactant side (pH > pK_a^{CH}) or the product side (pH ≤ pK_a^{CH}), but in all instances, a sole relaxation process was associated with the interconversion of the carbon acid and the carbanion.

$$\textbf{9}\ (\text{or}\ \textbf{10}) \underset{k_{-p}^{H}[H^+] + k_{-p}^{BH}[BH] + k_{-p}^{H_2O}}{\overset{k_p^{H_2O} + k_p^{B}[B] + k_p^{OH}[OH^-]}{\rightleftharpoons}} \textbf{C-9}\ (\text{or}\ \textbf{C-10}) \tag{4}$$

$$k_{obsd} = k_p^{B}[B] + k_{-p}^{BH}[BH] = \left(k_p^{B} + \frac{k_{-p}^{BH}}{r}\right)[B] \tag{5}$$

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Table 3. Rate Constants for the Ionization of the Benzyltriflones **9** (pK_a = 7.60) and **10** (pK_a = 9.77) in 50%H_2O−50%Me_2SO (v/v)[a]

carbon acid			9		10	
buffer basic species B	N°	pK_a^{BH}	k_p^B, M^{-1} s^{-1}	k_{-p}^{BH}, M^{-1} s^{-1}	k_p^B, M^{-1} s^{-1}	k_{-p}^{BH}, M^{-1} s^{-1}
aminoacetonitrile	1	5.26	550[b]	1.2×10^5	–	–
glycine ethyl ester	2	7.24	9500	2.1×10^4	–	–
glycinamide	3	8.01	1.6×10^4	6830	4000[b]	2.3×10^5
2-methoxyethylamine	4	9.11	7.7×10^4	2400[b]	1.6×10^4	5.9×10^4
butylamine	5	9.99	–	–	3.5×10^4	1.5×10^4

[a] I = 0.5 M NMe_4Cl; experimental error in the rate constants in the range 5−10% for **9** and **10**, pK_a^{BH} values taken from refs 17 and 26. [b] Calculated from k_p^B or k_{-p}^{BH} via eq 6.

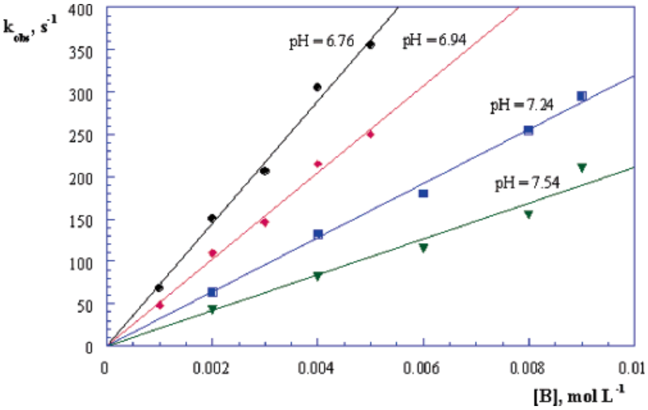

Figure 1. Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for the ionization of **9** in glycine ethyl ester buffers in 50%H_2O−50%Me_2SO (v/v): T = 25 °C, I = 0.5 M (NMe_4Cl).

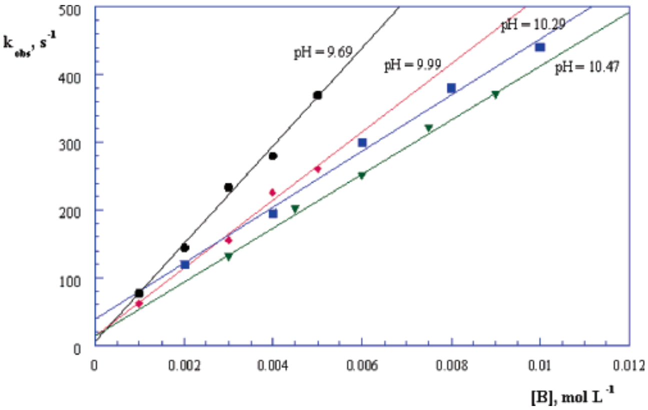

Figure 2. Effect of buffer concentration and pH on the observed rate constant, k_{obsd}, for the ionization of **10** in butylamine buffers in 50%H_2O−50%Me_2SO (v/v): T = 25 °C, I = 0.5 M (NMe_4Cl).

Analysis of the data pertaining to the interconversion of **9** and **C-9** indicated that only the buffer pathways of eq 4 were important in determining k_{obsd} in the pH range of 5.26−9.11 covered in our measurements. In agreement with the reduced eq 5, all plots of k_{obsd} versus free amine concentration ([B]) were linear with negligible intercepts. However, a pH dependence of the slopes was observed in buffers with p$K_a^{CH} - 1 <$ pH $<$ p$K_a^{CH} + 1$, namely the glycine ethyl ester and glycinamide buffers. In these instances, the individual rate constants k_p^B and k_{-p}^{BH} (r = [B]/[BH]) were determined from a standard treatment of the data obtained at three or more different buffer ratios (Figure 1).

In other buffers, eq 5 simplified to either $k_{obsd} = k_p^B$ [B] at high pH (2-methoxyethylamine buffers, Figure S2) or $k_{obsd} = k_{-p}^B$ [BH] at low pH (aminoacetonitrile buffers, Figure S3), allowing a facile determination of the k_p^B and k_{-p}^{BH} rate constants from the slopes of the k_{obsd} versus [B] or [BH] plots. Then, the corresponding k_{-p}^{BH} or k_p^B values were calculated by means of eq 6, where K_a^{CH} and K_a^{BH} represent the acidity constants of the carbon acid (CH) and the amine (BH), respectively. All k_p^B and k_{-p}^{BH} rate constants for equilibrium attainment between **9** and **C-9** are given in Table 3.

$$\frac{k_p^B}{k_{-p}^{BH}} = \frac{K_a^{CH}}{K_a^{BH}} \qquad (6)$$

In accord with a higher pK_a value, the interconversion of **10** and **C-10** has been kinetically studied in a more basic pH range (i.e., 8.01−10.47) than the one employed for **9**. Although this process proceeds with somewhat higher rates than that found for the equilibrium **9** $\rightleftarrows$ **C-9**, the related k_p^B and k_{-p}^{BH} rate constants could be derived with sufficient accuracy from the k_{obsd} values measured in the three primary amine systems studied. While the data pertaining to the glycinamide and 2-methoxyethylamine buffers (pH ≤ 9.59) fit eq 5 satisfactorily (Figures S4, S5), the k_{obsd} versus [B] plots pertaining to the four butylamine buffers at hand are characterized by non-negligible and pH-dependent intercepts (Figure 2), suggesting that the k_p^{OH} pathway of eq 4 begins to compete with the k_p^B and k_{-p}^{BH} pathways at pH ≥ 9.7 in 50%H_2O−50%Me_2SO. From these intercepts, which are subject to large errors, only a rough estimate of the rate constant k_p^{OH} could be obtained: $k_p^{OH} \approx 10^7$ M^{-1} s^{-1}.[25]

Discussion

Superacidifiers. S(O)(=NSO_2CF_3)CF_3 versus SO_2CF_3. In our quest to investigate novel substituents with extremely strong electron-withdrawing properties, which we have termed superacidifiers,[4−6,17] we report on a combined NMR, kinetic, and equilibrium study of the ionization of carbon acids **9** and **10** which include substitution by =NSO_2CF_3. The results have allowed us to evaluate the electron-withdrawing capability of this latter fragment in aqueous and Me_2SO solutions as well as to gain insights into the mode of electronic action of the overall S(O)(=NSO_2CF_3)CF_3 moiety.

The outstanding electron-withdrawing capability of the *para*-S(O)(=NSO_2CF_3)CF_3 substituent becomes strikingly apparent on examination of the pK_a values collected in Table 2. As can be seen, an enormous pK_a change of 8 pK units accompanies the substitution of 4-H in the unsubstituted benzyltriflone **1** by the S(O)(=NSO_2CF_3)CF_3 group in pure Me_2SO. Also apparent

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(25) From the value of k_p^{OH}, the rate constant $k_{-p}^{H_2O}$ can be calculated as $k_p^{OH} K_s/K_a^{CH}$ with K_s being the autoprotolysis constant of the 50:50 (v/v) H_2O−Me_2SO mixture (pK_s = 15.83 at 25 °C).[26] One thus obtains: $k_{-p}^{H_2O} \approx 7$ s^{-1}, a value which is actually too low to give rise to meaningful intercepts in the k_{obsd} versus [B] plots pertaining to the glycinamide and 2-methoxyethylamine buffers.

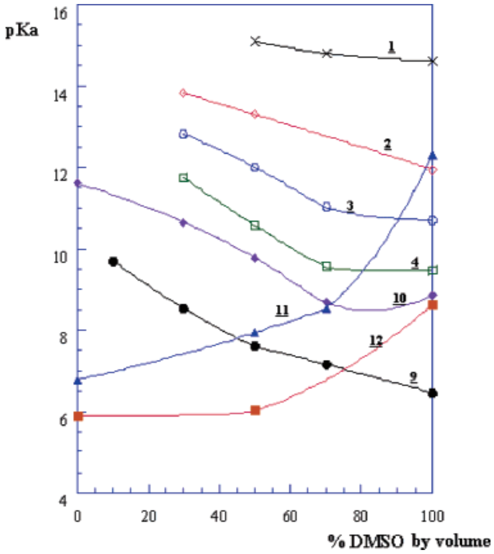


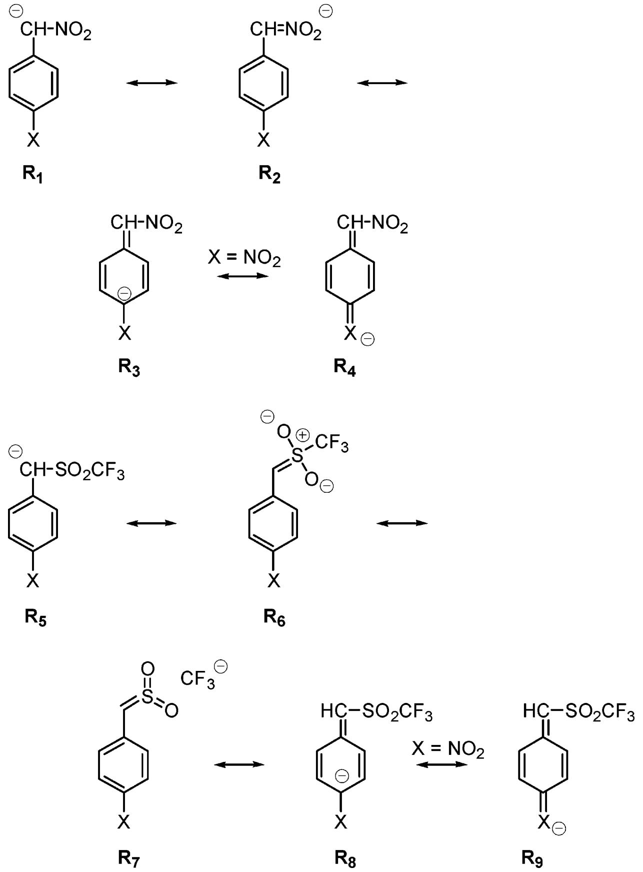
Figure 3. Effect of H_2O-Me_2SO transfer on the acidity of benzyltriflones (**1**−**4**, **9**, and **10**) and related phenylnitromethanes (**11**, **12**). See text for structural identification.

is that the activation brought about by this substituent surpasses the effect exerted by a *para*-SO_2CF_3 group by 2.4 p*K* units as well as that of a *para*-NO_2 group (compound **4**) by 3 p*K* units in Me_2SO solution. Interestingly, the 2.4-p*K*-unit difference between **9** and **10** can be regarded as a measure of the gain in activation incurred by substitution of one of the two oxygens of a SO_2CF_3 group by the $=N-SO_2CF_3$ fragment. In a recent study, Koppel et al. measured the effect of substituting an oxygen of a SO_2NH_2 group by the $=N-SO_2CF_3$ fragment on the acidity of a series of 4-X substituted arenesulfonamides.[6a] In that instance, the acidity enhancement brought about by this substitution which occurs immediately adjacent to the ionization site was very large, amounting to 8.3 pK_a units in Me_2SO solution. More related to our system is the finding of a 5-pK_a-unit increase in the acidity of the anilino NH_2 group on going from 4-trifluoromethanesulfonylaniline to the 4-$S(O)(=NSO_2CF_3)CF_3$ substituted aniline in the same solvent.[6a] In this case, the two activating substituents act through a phenyl ring in a conjugative manner. Even though the conjugate situation extends to the carbanions **C-9** and **C-10** (but not in the parent acids), it is reasonable to anticipate that the acidifying effect of the 4-X-substituent will become attenuated because the exocyclic α-SO_2CF_3 group acts in juxtaposition with the para substituent in determining the acidity.

Interestingly, pertinent information on the mode of electronic transmission in carbanions **C-9** and **C-10** can be derived from further analysis of the trends in pK_a values that are revealed in Table 2.

Medium Effects on Acidity as Evidence of Charge-Transfer Mechanism. Figure 3 illustrates the effect of medium composition on pK_a values of the α-SO_2CF_3 (**1**−**4**, **9**, **10**) and the α-NO_2 (**11**,**12**) substituted carbon acids.

It is apparent that, for the triflones, the medium change from highly aqueous to Me_2SO-rich is accompanied by a continuous increase in acidity. This increase amounts to ca. 3.25 p*K* units for the sulfoximine **9**. A similar trend, noted earlier, is observed for the *para*-SO_2CF_3 and *para*-NO_2 analogues **10** and **4** as well as for the parent unsubstituted triflone **1**.[17,18b] This is in marked contrast with the situation that prevails for the two phenylnitromethanes **11** and **12**, the pK_a values of which increase regularly on going from water to Me_2SO.[20,27] Striking evidence of this opposite behavior is that the phenylnitromethane molecule **11** is more acidic than the triflones **9** and **10** in aqueous solution but much less acidic in Me_2SO.



In the case of α-nitro substituted carbon acids such as **11** and **12**, it has been recognized that the resonance structure ***R*₂** with the charge essentially delocalized on the nitronate oxygen is by far the main contributor to stabilization of the conjugate carbanions, including when $X = NO_2$ (**C-11** and **C-12**).[20,27] It follows that, on changing from water to Me_2SO, there ensues a loss of H-bonding on this nitronate moiety and, hence, a decrease in the stability of the carbanion structure.[28] This explains the observed decrease in acidity of α-nitro activated carbon acids in general and of compounds **11** and **12** in the context of Figure 3 in particular.

Interestingly, the increase in acidity that is observed with the sulfoximine **9** as well as with the other triflones (**1**−**4**, **10**) suggests that the primary factor in stabilization of the derived carbanions is through polarizability effects. In this regard, a major feature of these compounds is that the ease of ionization is governed by combination of the electron-withdrawing effects of the α-SO_2CF_3 substituent and the *para*-X substituent ($X =$ H, CF_3, CN, NO_2, SO_2CF_3, $S(O)(=NSO_2CF_3)CF_3$). In the case of **10**, it is noteworthy that the $\Delta H^{\ddagger}$ value measured for the rotational conversion of eq 2 is much less than the average of

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(26) Terrier, F.; Lelièvre, J.; Chatrousse A. P.; Farrell, P. G. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1479.

(27) Moutiers, G.; Thuet, V.; Terrier, F. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1479.

(28) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219.

those reported for internal rotation in many benzylic carbanions. This indicates that the π-order of the $C_{Ar}-C_\alpha$ bond in **C-10** is not very high and that the presence of the *para*-SO_2CF_3 group has a relatively minor effect in inducing transfer of negative charge from the exocyclic α-SO_2CF_3 substituted carbanion center to the phenyl ring.[24] Indeed, the experimental evidence is in accord with predominance of the resonance structure $\mathbf{R_5}$ to stabilization of the carbanion **C-10**, as well as the carbanions **C-1**-**C-4**.[18,24] While resonance structures ($\mathbf{R_8}$, $\mathbf{R_9}$) implying charge delocalization through the ring contribute to a minor extent when X is strongly electron-withdrawing, in all cases those involving charge delocalization through the exocyclic SO_2-CF_3 group ($\mathbf{R_6}$, $\mathbf{R_7}$) play a negligible role.

As further elaborated below, in the case of the sulfoximine **9**, the pK_a value data are also explicable in terms of the polarizability phenomena of carbanion stabilization invoked to account for the behavior of **1**−**4** and **10**. The NMR and kinetic data discussed below will provide complementary information on this matter.

At this stage, however, an important point can be addressed, namely the possibility of getting an estimate of the Hammett σ_p and σ_{p-} values of the $S(O)({=}NSO_2CF_3)CF_3$ substituent.[29] Even though charge delocalization through the 4-X substituted phenyl ring is a minor factor contributing to the stabilization of the carbanions **C-1**,**4**, **C-9**, and **C-10**, the evidence from the pK_a data in Table 2 is that the acidity of the related carbon acids increases regularly with increasing the electron-withdrawing effect of the X substituent. Plotting the pK_a values measured in a given solvent (e.g., 50%H_2O−50%Me_2SO), versus the known σ_p (or σ_{p-}) parameters for H, CF_3, CN, NO_2, and SO_2CF_3[30] gives rise to reasonable and meaningful linear correlations, with a better fit to the data when using σ_{p-} instead of σ_p. This is shown in Figure S6, which refers to the data obtained in 50%H_2O−50%Me_2SO. On the basis of these relationships, the following estimates of the σ_p and σ_{p-} values for the $S(O)({=}NSO_2CF_3)CF_3$ substituent can be obtained: $\sigma_p = 1.35 \pm 0.1$, $\sigma_{p-} = 2.30 \pm 0.1$. Interestingly, the σ_p value is in accord with a previous estimate derived by Yagupolskii from a ^{19}F NMR study of 4-X substituted chlorobenzenes.[11c] As to the previously unknown σ_{p-} value, it highlights nicely the super electron-withdrawing character of the $S(O)({=}NSO_2CF_3)CF_3$ substituent.

NMR Evidence for Polarizability Effects. As can be seen in Table 1, the ionization of **9** is accompanied by a significant upfield shift of the H_α resonance ($\Delta\delta H_\alpha = -1.08$ ppm), and concomitantly the C_α resonance moves moderately to low field ($\Delta\delta C_\alpha = 16.75$ ppm). This has to be compared with the strong downfield shifts of the H_α and C_α resonances which are commonly found in ionization reactions giving rise to pure sp^2 hybridized cyclohexadienyl carbanions (e.g., $\Delta\delta H_\alpha \approx 2-2.2$ ppm; $\Delta\delta C_\alpha \approx 50-60$ ppm for carbanions **C-13a**,**b**).[31] Also, the ionization of **9** induces only a weak upfield shift of the fluorine resonance ($\Delta\delta F = -2.70$ ppm). Altogether, these results clearly indicate that a high charge density must be retained on the C_α carbon of the carbanion **C-9**, supporting the above conclusion that both the cyclohexadienyl structures $\mathbf{R_8}$ and $\mathbf{R_9}$ as well as the structures implying d−p π-bonding ($\mathbf{R_6}$) and negative hyperconjugation ($\mathbf{R_7}$) do not play a primary role in the stabilization of **C-9**.

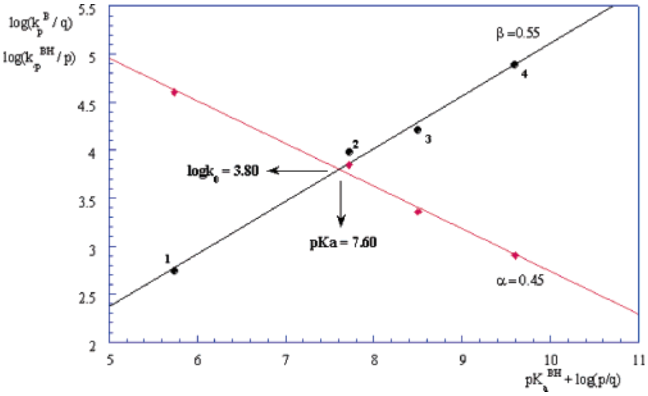
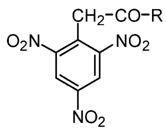
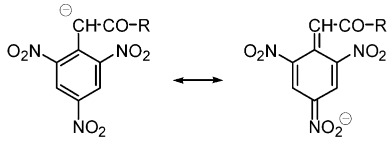


Figure 4. Brønsted plot for the ionization of **9** by primary amine buffers in 50%H_2O−50%Me_2SO (v/v): T = 25 °C, I = 0.5 M (NMe_4Cl). The numbering of the various catalysts is given in Table 3.



13 (a) R = CH_3; (b) R = C_6H_5



C-13

Table 1 reveals, however, that there is a clear trend in the $\Delta\delta H_\alpha$ values becoming less negative along the α-SO_2CF_3 series **1** → **4** → **10** → **9** as well as in the corresponding $\Delta\delta C_\alpha$ values which increase progressively in magnitude in this series. These trends are in agreement with the idea that charge transfer to the phenyl ring, even though it is not a dominant factor, is increasing to some extent on increasing the activating effect of the 4-X substituent. In other words, the contribution of the two cyclohexadienyl structures $\mathbf{R_8}$ and/or $\mathbf{R_9}$ is not totally negligible when the 4-X substituent is strongly electron-withdrawing, in agreement with the observation of rotational isomerism in **C-9** and **C-10** (vide supra).[24]

In this regard, it can be noted in Table 1 that there is a greater shielding of the C_4 carbon of the phenyl ring upon ionization of the 4-$S(O)({=}NSO_2CF_3)CF_3$ and 4-SO_2CF_3 triflones **9** and **10** than of the 4-NO_2 triflone **4**; $\Delta\delta C_4 = -25.3$ ppm for **9**; $\Delta\delta C_4 = -20.4$ ppm for **10**; $\Delta\delta C_4 = -16.69$ ppm for **4**. These data can be understood in terms of a preferred contribution of the resonance structure $\mathbf{R_8}$ in the accommodation of negative charge by the 4-SO_2CF_3 and the 4-$S(O)({=}NSO_2CF_3)CF_3$ groups at the para position of the phenyl ring. This is in accord with our above conclusions that the preferred mode of electronic action of these groups is in terms of polarizability effects.

Kinetic Evidence. Marcus Intrinsic Reactivity of 9 and 10. Figure 4 shows that a satisfactory Brønsted plot may be drawn on the basis of the measured rate constants k_p^B and k_{-p}^{BH} pertaining to deprotonation of the 4-$S(O)({=}NSO_2CF_3)CF_3$ substituted benzyltriflone **9** by primary amines in 50%H_2O−50%Me_2SO eq 4. Although it is based on the results obtained with three primary amines, a similar Brønsted plot can be drawn for the 4-SO_2CF_3 substituted benzyltriflone **10** (Figure 5). The corresponding β_B values are equal to 0.55 and 0.48 for **9** and

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(29) We thank a reviewer for raising the question of the σ_p (σ_{p-}) determinations.

(30) Exner, O. In *Correlation in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978.

(31) (a) Moutiers, G.; El Fahid, B.; Goumont, R.; Chatrousse A. P.; Terrier, F. *J. Org. Chem.* **1996**, *61*, 1978. (b) Edlund, U.; Buncel, E. *Prog. Phys. Org. Chem.* **1993**, *19*, 225.

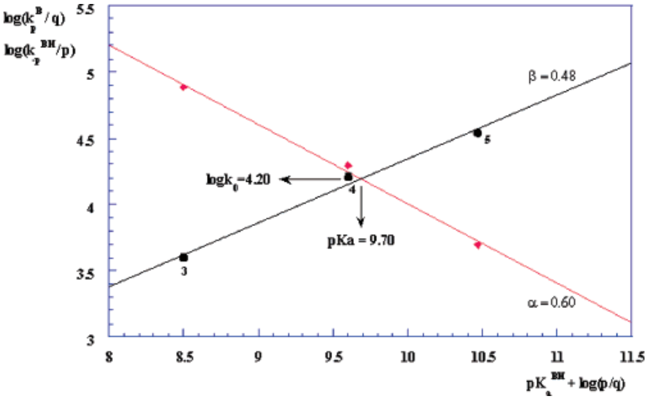


Figure 5. Brønsted plot for the ionization of **10** by primary amine buffers in 50%H_2O−50%Me_2SO (v/v): $T = 25$ °C, $I = 0.5$ M (NMe_4Cl). The numbering of the various catalysts is given in Table 3. Due to the high rates of ionization, the log k_0 and α and β values are subject to some uncertainty accounting in particular for $\alpha + \beta > 1$.

10, respectively, being in the range of 0.50 ± 0.10 commonly found for ionization of carbon acids of similar pK_a^{CH} values in that solvent.[3,17,20,26,27,31] Using the classical definition of the intrinsic rate constant (i.e., $k_0 = k_p^B/q$ when $pK_a^{CH} - pK_a^{BH} - \log(p/q) = 0$),[3] we readily determined the log $k_0^{RNH}2$ value for the ionization of **9** and **10** from the intersection of the two lines in Figures 4 and 5: log $k_0 = 3.80$ for **9**; log $k_0 = 4.20$ for **10**. Importantly, these values are comparable with the estimates previously reported for the benzyltriflones **1**, **3**, **4** (log $k_0 \geq 5$), **5** (log $k_0^{RNH}{}_2 \approx 3.4$), and **6** (log $k_0^{RNH}{}_2 \approx 4.5$).[17]

In the past few years, it has been recognized that there is commonly an inverse relationship between the intrinsic reactivity of a carbon acid and the extent of the structural and solvational reorganization that is required to form the conjugate carbanion.[3,17,20,32−34] The greater the resonance stabilization and therefore the sp^2-hybridized character of the resulting carbanion, the greater in general are the structural and solvation changes involved in the ionization process and the lower the intrinsic reactivity.

The situation for **9**, **10**, and related triflones can be appropriately discussed in terms of Table 4, which summarizes the intrinsic reactivities (log $k_0^{RNH_2}$) measured for a number of carbon acids in 50%H_2O−50%Me_2SO. As can be seen, α-nitro and α-carbonyl carbon acids exhibit low intrinsic reactivities, reflecting the formation of conjugate carbanions which can be structurally identified to the respective sp^2-hybridized nitronate and enolate structures.[1c,3,19,20] This is exemplified by the formation of the carbanions **C-7** (log $k_0 = 0$) and **C-11** (log $k_0 = -2$) of nitromethane (**7**) and phenylnitromethane (**11**), respectively, as well as the formation of the carbanions **C-14** (log $k_0 = 2.06$) and **C-15** (log $k_0 = 2.44$) of acetylacetone (**14**) and 1,3-indandione (**15**), respectively.[20a,35] Similarly, low to very low intrinsic reactivities characterize the ionization of polynitrotoluene and related derivatives where an enormous structural reorganization is required to form the resulting sp^2-hybridized cyclohexadienyl carbanions, for example, log $k_0 = 0.85$ for the formation of **C-13a** from the picryl ketone **13a** (vide supra) and log $k_0 = -2.15$ for the formation of **C-16** from 4,6-dinitro-7-methylbenzofuroxan (**16**).[31,36]

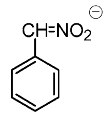
Table 4. Intrinsic Rate Constants for Deprotonation of Some Representative Carbon Acid Structures in 50%H_2O−50%Me_2SO[a]

carbon acid	log k_0
$RCH(CN)_2$[b]	~7
1, **3**, **4**[c]	≥5
6[c]	~4.5
10[d]	4.2
9[d]	3.84
9-cyanofluorene[e]	3.76
5[c]	3.46
18[f]	3
1,3-indandione[g]	2.44
19[f]	2.05
acetylacetone[h]	2.06
13a[i]	0.85
CH_3NO_2[j]	0
phenylnitromethane (**11**)[j]	−1
4,6-dinitro-7-methylbenzofuroxan[k]	−2.15

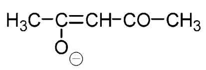
[a] At 25 °C unless indicated otherwise; log k_0 refers to ionization by primary amines. [b] Reference 3. [c] Reference 17. [d] This work. [e] Reference 31b at 20 °C. [f] References 20b,c at 20 °C. [g] Reference 35a at 20 °C. [h] Reference 35b at 20 °C. [i] Reference 30. [j] Reference 20a at 20 °C. [k] Reference 36; log k_0 refers to ionization by carboxylate bases.

$CH_2{=}NO_2^{\ominus}$

C-7

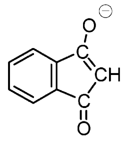


C-11

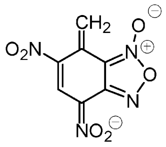


$H_3C{-}C(O^{\ominus}){=}CH{-}CO{-}CH_3$

C-14



C-15



C-16

Contrasted with nitro and carbonyl groups, a CN group derives most of its electron-withdrawing character from a polar effect.[3,18a,27,37−39] Accordingly, the ionization of α-cyano activated carbon acids proceeds with very little structural reorganization, accounting for the finding of high intrinsic reactivities for compounds of general structure RCH_2CN or $RCH(CN)_2$ (log $k_0 \approx 7$).[3] Interestingly, the introduction of an additional α-activating group with even moderate π-acceptor character provides an appreciable potentiality of resonance stabilization of the carbanion, as reflected by a marked decrease in log k_0 from about 7 to 3.76 for 9-cyanofluorene (**17**).[40] More important decreases in log k_0 occur upon introduction of nitro substituted phenyl rings with log k_0 values of 3 and 2.05 for the ionization of 4-nitrophenylacetonitrile (**18**) and 2,4-dinitrophenylacetonitrile (**19**), respectively.[3,20b,c] In these instances, the nitro substituted rings contribute markedly to the resonance stabilization of the conjugate carbanion (structures **C-18a** and **C-19a,b**),

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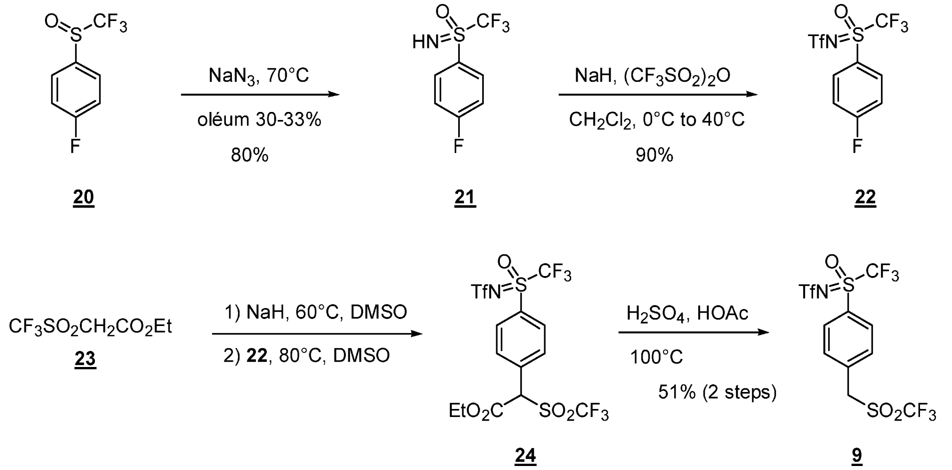
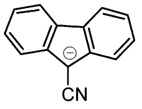
(32) (a) Bernasconi, C. F.; Bunnell, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 2900. (b) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115.
(33) Buncel, E.; Dust, J. M. In *Carbanion Chemistry*; Oxford University Press: Oxford, 2003; Chapter 2.
(34) Richard, J. P.; Williams, G.; O'Donoghue, A.-M. C.; Amyes, T. L. *J. Am. Chem. Soc.* **2002**, *124*, 2957
(35) (a) Bernasconi, C. F.; Paschalis, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2969. (b) Bernasconi, C. F.; Bunnell, R. D. *Isr. J. Chem.* **1985**, *26*, 420.
(36) Terrier, F.; Croisat, D.; Chatrousse, A. P.; Pouet, M. J.; Hallé J.-C.; Jacob, G. *J. Org. Chem.* **1992**, *57*, 3684.
(37) Richard, J. P.; Williams, G.; Gao, J. *J. Am. Chem. Soc.* **1999**, *121*, 715.
(38) (a) Bradamante, S.; Pagani, G. A. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1035. (b) Abbotto, A.; Bradamante, S.; Pagani, G. A. *J. Org. Chem.* **1993**, *58*, 449.
(39) Wiberg, K. B.; Castejon, H. *J. Org. Chem.* **1995**, *60*, 6327.
(40) Bernasconi, C. F.; Terrier, F. *J. Am. Chem. Soc.* **1987**, *109*, 7115.

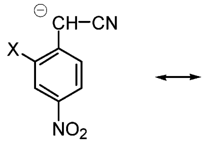
Scheme 1. Synthesis of *N*-Trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-4-(trifluomethylsulfonylbenzyl)-sulfoximine **9**



accounting for the finding of intrinsic reactivities that approach those of α-carbonyl carbon acids.[3]

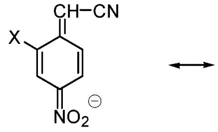


C-17



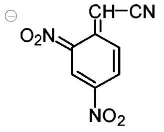
C-18 X = H

C-19 X = NO_2



C-18a

C-19a



C-18b

C-19b

A result of first significance is revealed in Table 4, namely that the benzyl triflone with the lowest log k_0 value, namely the 2,4-dinitro compound **5** (log $k_0 = 3.46$), exhibits an intrinsic reactivity that is not only 30-fold higher than that mesured for the 2,4-dinitrobenzylcyanide analogue **19** but also 3-fold greater than that for the mononitro substituted benzylcyanide **18**. More importantly, all other triflones, especially the 4-SO_2CF_3 and 4-S(O)(=NSO_2CF_3)CF_3 derivatives **9** and **10** and the 2,4,6-trinitrobenzyltriflone **6**, have log k_0 values that are located at a higher level than 9-cyanofluorene **17** in the intrinsic reactivity scale. Such high log k_0 values provide evidence that no major structural changes occur upon ionization of **9** and **10** and related substrates. This implies first that d−p π-bonding and negative hyperconjugation (resonance structure $\mathbf{R_6}$ and $\mathbf{R_7}$) do not contribute appreciably to stabilization of the conjugate carbanions. Here, this also implies that charge transfer from the exocyclic α-SO_2CF_3 substituted carbon to the phenyl ring occurs at a lower extent in the triflone carbanions than in the benzylcyanide carbanions, despite the presence of much stronger activating groups in the ring of the former compounds. Overall, the situation fully confirms the evidence reached above from NMR and pK_a data that polarizability effects are predominant in governing the accommodation of negative charge by SO_2R groups, with the best structural picture of the carbanions **C-9** and **C-10** being in terms of canonical structures of type $\mathbf{R_5}$.

Experimental Section

Materials. All solvents were distilled prior to use. In particular, dimethyl sulfoxide was refluxed over calcium hydride and distilled, collecting the fractions of 32−35 °C (under 2 mmHg), which were stored under nitrogen. Only freshly prepared solutions were used in the spectrophotometric studies carried out in pure Me_2SO. H_2O-Me_2SO solutions were prepared as described previously.[17,18,26] Buffers were purified commercial products. Chemicals were purchased from Fluka or Aldrich Company. NMR spectra were recorded in $CDCl_3$ or Me_2SO-d_6 solutions on a Bruker AC-300 spectrometer. Reported coupling constants and chemicals shifts were based on a first-order analysis. Internal reference was tetramethylsilane for ^1H (300 MHz), central peak of $CDCl_3$ (77 ppm referred to TMS) for ^{13}C (75 MHz) NMR spectra, internal $CFCl_3$ (0 ppm) for ^{19}F (282 MHz) NMR spectra. The synthesis of the 4-SO_2CF_3 substituted benzyltriflone **10** was recently reported.[41]

Scheme 1 depicts the strategy used to synthesize the *N*-trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-4-(trifluomethylsulfonylbenzyl)-sulfoximine **9**. Following a previous report from our laboratory of a new and very efficient synthetic route to 4-fluorophenyltrifluoromethyl sulfoxide **20**,[42] the sulfoximines **21** and **22** were prepared in good yields using the reagents and experimental conditions described by Yagupol'skii et al.[9a,11c] Then, the sulfoximine **9** was obtained in 51% yield through a two-step process consisting of a nucleophilic aromatic substitution of the fluorine atom with the carbanion of ethyl trifluoromethanesulfonyl acetate **23**[41] with subsequent decarboxylation of the resulting substituted product **24** in acidic medium. Because of the low stability of the fluorinated sulfoximine group in basic medium, the substitution step has to be carried out with a very careful control of the experimental conditions, as detailed below.

***S*-Trifluoromethyl-*S*-*p*-fluorophenyl-sulfoximine 21.** Sodium azide (3.83 g, 59.0 mmol) was slowly added under argon at 0 °C to a solution of 4-fluorophenyltrifluoromethyl sulfoxide (5 g, 23.6 mmol) in oleum 27−33% (23.5 mL). Then, the reaction was heated for 1.5 h at 70 °C under a slight pressure of argon. The crude mixture was added to ice. After filtration, a white solid of *S*-trifluoromethyl-*S*-*p*-fluorophenyl-sulfoximine[9a] (4.56 g, 80%) was obtained without further purification. mp 48.2 °C, δ_H(300 MHz, $CDCl_3$) 8.17 (2H, m, H_{Aro}), 7.30 (2H, m, H_{Aro}), 3.80 (1H, bs, NH); δ_F(282 MHz, $CDCl_3$) −79.4 (3F, s, SCF_3), −110.9 (1F, s, F_{Aro}); δ_C(77 MHz, $CDCl_3$) 167.1 ($C_{Aro}F$, d, *J* 258.9), 133.6 ($2C_{Aro}H$, d, *J* 10.3), 127.3 ($C_{Aro}S$), 125.1 (CF_3, q, *J* 331.3), 116.9 ($2C_{Aro}H$, d, *J* 22.9); *m*/*z*: (CI NH_3) 245.

***N*-Trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-*p*-fluorophenyl-sulfoximine 22.** A solution of *S*-trifluoromethyl-*S*-*p*-fluorophenyl-

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[41] Goumont, R.; Faucher, N.; Moutiers, G.; Tordeux M.; Wakselman, C. *Synthesis* **1997**, 691.

[42] Wakselman, C.; Tordeux M.; Freslon, C.; Saint-Jalmes, L. *Synlett* **2001**, 550.

sulfoximine (5 g, 22 mmol) in CH_2Cl_2 (100 mL) was cooled to 0 °C, and NaH (1.14 g, 28.6 mmol) was added portionwise under argon. The reaction was stirred for 2 h at room temperature and cooled again to 0 °C. Triflic anhydride (7.78 mL, 46.2 mmol) was added dropwise, and the mixture was refluxed for 8 h and added to ice. The aqueous phase was extracted three times with diethyl ether, and the organic layers were mixed, washed three times with 5% NaOH and water, dried, and concentrated. *N*-Trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-*p*-fluorophenyl-sulfoximine[9a] (7.14 g, 90%) was obtained without further purification. δ_H(300 MHz, $CDCl_3$) 8.17 (2H, m, H_{Aro}), 7.49 (2H, m, H_{Aro}); δ_F(282 MHz, $CDCl_3$) −75.8 (3F, s, NSO_2CF_3), −78.9 (3F, s, SCF_3), −94.5 (1F, s, F_{Aro}); δ_C(77 MHz, $CDCl_3$) 168.8 ($C_{Aro}F$, d, *J* 265.1), 133.9 ($2C_{Aro}H$, d, *J* 11.9), 124.4($C_{Aro}S$, d, *J* 4), 119.9 (CF_3, q, *J* 327.2), 118.9 (CF_3, q, *J* 320.4), 118.6 ($2C_{Aro}H$, d, *J* 23.2); *m*/*z*: (EI) 290 (100%, M − CF_3), 143(39), 95(90), 69(66).

***N*-Trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-4-(trifluomethylsulfonylbenzyl)-sulfoximine 9.** Sodium hydride (0.9 g, 22.2 mmol) was added slowly to a solution of ethyl (trifluoromethanesulfonyl) acetate[41,43] (4.19 g, 22.2 mmol) in DMSO (13 mL). The mixture was heated for 1 h at 60 °C and cooled to ambient temperature. A solution of *N*-trifluoromethylsulfonyl-*S*-trifluoromethyl-*S*-*p*-fluorophenyl-sulfoximine (4 g, 11.1 mmol) in DMSO (10 mL) was added under argon to the preformed anion, and the reaction was heated for 15 h at 80 °C. A saturated solution of NH_4Cl (20 mL) was added, and the mixture was extracted three times with diethyl ether. The organic layers were washed three times with a solution of $NaHCO_3$ 5%, dried, and evaporated. The resulting compound **24** was heated for 12 h at 100 °C in a solution of sulfuric acid (12.5 mL), acetic acid (25 mL), and water (25 mL). Water was added, and the aqueous phase was extracted three times with diethyl ether. The organic layers were washed three times with a solution of 5% $NaHCO_3$, dried, evaporated, and purified by column chromatography on silica using ethyl acetate/pentane 1/9, and then ethyl acetate/pentane 5/5 as eluent to give the desired compound **9** (2.76 g, 51%) as a white solid. mp 41 °C (Found: C, 24.39; H, 1.37; N, 2.95. $C_{10}H_6F_9NS_3O_5$ requires C, 24.64; H, 1.24; N, 2.87%). δ_H(300 MHz, $CDCl_3$) 8.24 (2H, d, H_{Aro}, *J* 8.5), 7.87 (2H, d, H_{Aro}), 4.65 (2H, s, CH_2); δ_F(282 MHz, $CDCl_3$) −75.0 (3F, s, NSO_2CF_3), −76.7 (3F, s, SO_2CF_3), −78.8 (3F, s, SCF_3); δ_C(77 MHz, $CDCl_3$) 134.4 (C_{Aro}), 133.4 ($C_{Aro}H$), 131.2 ($C_{Aro}H$), 130.8 (C_{Aro}), 119.8 (CF_3, q, *J* 328.9), 119.4 (CF_3, q, *J* 327.8), 118.8 (CF_3, q, *J* 320.4), 55.2 (CH_2); *m*/*z*: (CI NH_3) 505 (M + 18).

Kinetic and Spectrophotometric Measurements. All aliphatic and alicyclic amine buffers (see Results) used to study the thermodynamics and the kinetics of the ionization of **9** and **10** in H_2O and H_2O-Me_2SO mixtures as well as pure Me_2SO were previously calibrated by potentiometry or spectrophotometry.[23,25,44] In these solvents, the spectrophotometric determination of the pK_a^{CH} values of **9** and **10** was facilitated by the fact that the anions **C-9** and **C-10** exhibit a strong absorption in the visible region where neither the parent molecules nor the required buffers absorb UV−visible spectra. Spectra were taken on a HP 8453 spectrophotometer; λ_{max} values of **C-9** and **C-10** were quoted in the Results.

Kinetic measurements of the ionization of **9** and **10** in 50%H_2O−50%Me_2SO were carried out at 25 ± 0.2 °C with an Applied Photophysics SX.18MV stopped-flow spectrophotometer.

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Supporting Information Available: Variation of the ratio of ionized to un-ionized benzyl triflone **9** as a function of pH in 90%H_2O−10%Me_2SO, 70%H_2O−30%Me_2SO, and 100%Me_2SO (v/v) (Figure S1); Effect of pH and buffer concentration on the observed rate constant, k_{obsd}, for the ionization of **9** in 2-methoxyethylamine buffers in 50%H_2O−50%Me_2SO (v/v) (Figure S2); Effect of pH and buffer concentration on the observed rate constant, k_{obsd}, for the ionization of **9** in aminoacetonitrile buffers in 50%H_2O−50%Me_2SO (v/v) (Figure S3); Effect of pH and buffer concentration on the observed rate constant, k_{obsd}, for the ionization of **10** in glycinamide buffers in 50%H_2O−50%Me_2SO (v/v) (Figure S4); Effect of pH and buffer concentration on the observed rate constant, k_{obsd}, for the ionization of **10** in 2-methoxyethylamine buffers in 50%H_2O−50%Me_2SO (v/v) (Figure S5); Plots of the pK_a values for the triflones versus the Hammett σ_p (top) and σ_{p-} (bottom) constants in 50%H_2O−50%Me_2SO (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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