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α-Sulfonyl Carbanions: Combined Kinetic, Thermodynamic, and NMR Approaches for the Study of the Ionization of Benzyltriflones in Me_2SO and H_2O-Me_2SO Mixtures

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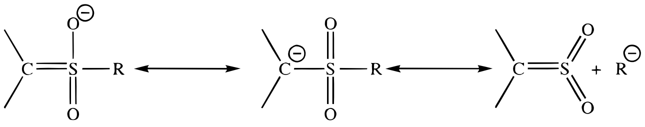
Abstract: The ionization of a series of benzyltriflones $ArCH_2SO_2CF_3$ (Ar = C_6H_5, 4-CNC_6H_4, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$, 2,4,6-$(NO_2)_3C_6H_2$) has been studied kinetically and thermodynamically as well as by ^{1}H, ^{13}C, and ^{19}F NMR in H_2O-Me_2SO mixtures and/or Me_2SO. The findings that the acidity of the triflones is enhanced on going from hydroxylic solvents to Me_2SO and that their deprotonation is associated with high Marcus intrinsic reactivities are two major results indicating the presence of a large polarizable charge density at C_α of the carbanionic species. Comparison of the results obtained with those for related arylnitromethane and arylacetonitrile compounds strongly supports this conclusion. NMR data add to the evidence that polarization rather than d−p π-resonance or negative hyperconjugation is the dominant factor in accounting for the capability of the strongly electron withdrawing SO_2CF_3 group to stabilize negative charge. Altogether, our results lead to a structural picture of the triflone carbanions in solution which does not totally fit the conclusions reached on the basis of solid-state or computed gas-phase studies.

Carbanions that are stabilized by carbonyl, cyano, nitro, and sulfonyl or sulfoxide groups have received wide use in synthesis, and some of them are important biochemical intermediates.[1] Considerable evidence has been accumulated that carbanions α to nitro and carbonyl groups derive much of their stability by rehybridization from sp^3 to sp^2, thus allowing delocalization of charge to the more electronegative atoms.[1a−c] In contrast, it has been less clear how conjugative effects are important in determining the stability of carbanions adjacent to cyano or sulfur groups.[1d−h] Recently, a number of studies have appeared which convincingly support the view that the polar effect of the cyano group is the main factor governing the stability of α-cyanocarbanions.[2−4] The finding that nitriles are carbon acids exhibiting much higher intrinsic Marcus reactivities ($\log k_0 \approx 7$) than carbonyl ($\log k_0 \approx 3-4$) or nitro ($\log k_0 < 2$) compounds was very revealing in this regard.[4]

The situation for α-sulfur-stabilized carbanions, especially α-sulfonyl carbanions has long been a subject of much debate.[1d−h] The enhanced stability of α-sulfonyl carbanions has been first explained in terms of a substantial d−p π-bonding between the carbanion lone pair and sulfur 3d orbitals, as depicted in **1**.[5−8] However, this resonance effect has been questioned by theoretical studies and carbanion stabilization by simple charge polarization effects has been favored, i.e., **2**.[7,9−15] In more recent years, negative hyperconjugation has also been suggested as an important contributing mechanism, i.e., **3**, especially in fluorinated carbanions such as triflone carbanions (R = CF_3).[7,14,16−19]



1 2 3

In as much as the intrinsic reactivity (in the Marcus sense) of a carbon acid is closely related to the extent of the structural and solvational reorganization that is needed to form the conjugate carbanion, a measure of this parameter for some α-sulfonyl derivatives should help clarify the mode of action

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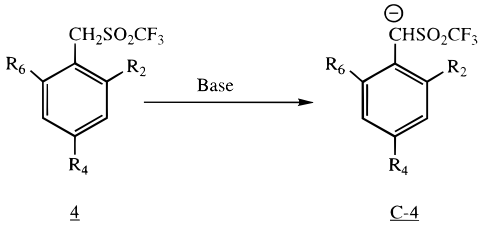
of the SO_2R group.[4,20,21] Thus, if the charge delocalization mechanisms, i.e., **1** and **3**, and not the polarizability or inductive effects are important in determining the stability of conjugate carbanions, sulfones should exhibit relatively low intrinsic reactivities, comparable at least with those reported for carbon acid structures giving rise to moderately resonance-stabilized carbanions.[4] In this paper, we report a structural, thermodynamic, and kinetic study of the ionization of the various benzyltriflones **4a**−**e** to give the conjugate carbanions **C-4a**−**e** in Me_2SO and some H_2O-Me_2SO mixtures according to eq 1. Altogether, our results favor the idea that charge polarization effects are by far the most important mechanism contributing to the stabilization of **C-4a**−**e**, including in the picryl system. Implications of this conclusion with regard to the structures of the carbanions in solution are considered by comparison with solid-state and gas-phase data.[9,14−19,22]



(1)

(a) $R_2=R_4=R_6=H$; (b) $R_2=R_6=H$, $R_4=CN$;
(c) $R_2=R_6=H$, $R_4=NO_2$; (d) $R_2=R_4=NO_2$, $R_6=H$;
(e) $R_2=R_4=R_6=NO_2$

Results

Structural Studies. Addition of dilute tetramethylammonium hydroxide to $\sim 4 \times 10^{-5}$ M solutions of **4a**−**e** in H_2O-Me_2SO mixtures containing 30%, 50%, and 70% Me_2SO by volume results in the reversible and complete formation of species exhibiting intense absorption maxima at the following wavelengths: 286 nm (**C-4a**); 343 nm (**C-4b**); 473 nm (**C-4c**); 429 nm (**C-4d**); 437 nm (**C-4e**). Unambiguous evidence that base addition to **4a**−**e** actually affords the carbanions **C-4a**−**e** was obtained by carrying out a ^1H, ^{13}C, and ^{19}F NMR study of the ionization reactions in Me_2SO. Only the data required for discussion are given in Table 1. All chemical shift and coupling constant data are summarized in Supporting Information Tables S_1-S_3.[23]

Table 1. Effect of Ring Substituents on Chemical Shifts ($\Delta\delta H_\alpha$, $\Delta\delta C_\alpha$) and Coupling Constants ($\Delta^1J_{C\alpha H\alpha}$) upon Ionization of Benzyltriflones **4a**−**e** and Comparison with Picryl Ketones **8a,b**[a]

compd	δH_α	$\Delta\delta H_\alpha$	δC_α	$\Delta\delta C_\alpha$	$^1J_{C\alpha H\alpha}$	$\Delta^1J_{C\alpha H\alpha}$
4a	5.25		54.80		142.77	
C-4a	3.38	−1.87	55.02	0.22	163.89	21.12
4b	5.46		54.31		143.41	
C-4b	3.69	−1.77	60.20	5.89	167.42	24.01
4c	5.53		53.74		143.15	
C-4c	4.07	−1.46	65.72	11.98	168.02	24.87
4d	5.87		51.99		145.33	
C-4d	5.78	−0.09	72.25	20.26	176.98	31.65
4e	5.83		48.96		146.60	
C-4e	5.82	−0.01	73.46	24.43	172.26	25.66
8a[b]	4.43		42.59		132.3	
C-8a[b]	6.55	2.12	99.89	57.3	159.6	27.3
8b[b]	5.07		39.11		132.3	
C-8b[b]	7.26	2.19	95.32	56.21	158.9	26.6

[a] Solvent Me_2SO-d_6; δ in ppm relative to internal $SiMe_4$; J in hertz. [b] References 21 and 41d.

Table 2. pK_a Values for Benzyltriflones **4a**−**e** and Related Carbon Acids in Me_2SO and Various H_2O-Me_2SO Mixtures

compd	H_2O	30% Me_2SO	50% Me_2SO	70% Me_2SO	Me_2SO
4a[a]			15.10		14.62
4b[a]		12.82	12.00	11.02	10.70
4c[a]		11.75	10.57	9.55	9.46
4d[a]		7.98	6.94	5.61	5.05
4e[a]		6.87	6.16	4.40	4.47
5a	6.77[b]		7.93[b]	8.53[b]	12.32,[b] 12.20[c]
5b					9.31[d]
5c			6.02,[e] 6.00		8.62[d]
6b	13.45[f]		12.62[a]		12.36,[a] 12.30[i]
6c	9.91[g]		8.06[g]		6.00[g,h]
6d			12.17[g]		11.15[g,h]
6e			12.02[g]		11.03[g,h]
6f			10.71[g]		9.24[g,h]

[a] This work at 25 °C. [b] Reference 28 at 20 °C. [c] Reference 30 at 25 °C. [d] Reference 31 at 25 °C. [e] Reference 29 at 25 °C. [f] References 32−34 at 25 °C. [g] Reference 36 at 20 °C. [h] 90% Me_2SO−10% H_2O. [i] Bordwell's value quoted by Walters in ref 62c.

Equilibrium Measurements. Using appropriate buffers (carboxylic acids, phenols, and amines), the pK_a^{CH} values of **4a**−**e** were first determined in various H_2O-Me_2SO mixtures from observed absorbance variations at λ_{max} of **C-4a**−**e** obtained at equilibrium as a function of pH. These variations described regular acid−base equilibrations, as evidenced by Figure S_1, which shows that excellent straight lines with unit slopes were obtained on plotting the log values of the ratio of the concentrations of ionized to nonionized triflones as a function of pH (eq 2).[23] The pK_a^{CH} values thus obtained at 25 °C and constant ionic strength of 0.5 M (NMe_4Cl) are summarized in Table 2.

$$\log\frac{[\text{C-2}]}{[2]} = \text{pH} - pK_a^{CH} \tag{2}$$

The pK_a^{CH} values of **4a**−**e** in pure Me_2SO solution were measured as follows. In the case of **4a**, the ionization was found to occur in the same pH range as that for 2,4-dinitroaniline (pK_a

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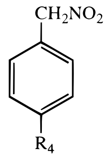
(23) See paragraph concerning Supporting Information at the end of this paper.

= 15.10) and 4,4′-dinitrodiphenylmethane (pK_a = 15.90).[24] Since these two compounds have conjugate bases exhibiting an intense visible absorption at $\lambda_{max} = 542$ nm ($\epsilon = 17\,320$ mol L^{-1} cm^{-1}) and $\lambda_{max} = 782$ nm ($\epsilon = 9.7 \times 10^4$ mol L^{-1} cm^{-1}), respectively, they were conveniently used as indicators to measure the pH of various buffer solutions made up from **4a** (Figure S_2).[23] Then, the pK_a^{CH} value of **4a** was readily obtained from eq 2.

In the case of the other triflones (**4b**−**e**), the ionization occurred in pH ranges covered by various amine buffers.[25−27] Accordingly, the pK_a^{CH} values of these triflones were determined according to the same procedure as that used in H_2O−Me_2SO mixtures. The results are also given in Table 2, together with similar data for the arylnitromethanes **5a**−**c**[28−31] and the arylacetonitriles **6a**−**f**.[32−36]



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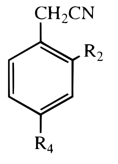
(a) R_4=H; (b) R_4=CN; (c) $R_4=NO_2$



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(a) $R_2=R_4$=H; (b) R_2=H, $R_4=NO_2$; (c) $R_2=R_4=NO_2$; (d) $R_2=NO_2$, R_4=Cl; (e) $R_2=NO_2$, R_4=Br; (f) $R_2=NO_2$, $R_4=CF_3$

Kinetic Measurements. We have found that rates of equilibration of **4a**−**e** with their conjugate bases **C-4a**−**e** according to eq 3 were too high to be accessible by stopped-flow spectrophotometry under most reasonable experimental conditions in buffer as well as NMe_4OH solutions in H_2O−Me_2SO mixtures. Only in the case of the 2,4-dinitrobenzyltriflone **4d** could some reliable kinetic measurements be carried out at 25 °C and constant ionic strength of 0.5 M (NMe_4Cl) in 50% H_2O−50% Me_2SO (v/v). Buffers made up from primary amines with pK_a^{BH} values close to the pK_a^{CH} value of **4d** were used, i.e., glycine ethyl ester, glycinamide, 2-methoxyethylamine, and aminoacetonitrile.[37] Experiments were performed under pseudo-first-order conditions with a large excess of the buffer reagents over the triflone concentration ($\approx 5 \times 10^{-5}$ M). Depending upon the pH studied, equilibrium 3 was approached either from the reactant side (pH ≥ pK_a^{CH}) or the product side (pH ≤ pK_a^{CH}), but in all instances, only one relaxation process was associated with the interconversion of **4d** and **C-4d**. The observed pseudo-first-order rate constants, k_{obsd}, measured in the various buffer systems employed are summarized in Table S_4.[23]

Table 3. Rate Constants for the Ionization of 2,4-Dinitrobenzyltriflone **4d** (pK_a^{CH} = 6.94) in 50% H_2O−50% Me_2SO (v/v)[a]

buffer (basic species B)	no.	pK_a^{BH}	k_p^B, M^{-1} s^{-1}	k_{-p}^{BH}, M^{-1} s^{-1}
aminoacetonitrile	1	5.26	10[b]	52000
glycine ethyl ester	2	7.24	6050	2900
glycinamide	3	8.01	9350	795[b]
2-methoxyethylamine	4	9.11	30600	206[b]

[a] $I = 0.5$ M (NMe_4Cl); $T = 25$ °C; experimental error in the rate constants: ±5%; in p$K_a^{BH}$and pK_a^{CH}: ±0.05 pK units; in the rate constants calculated from eq 5: ±15%; pK_a^{BH} values from ref 37. [b] Calculated from k_{-p}^{BH} or k_p^B via eq 5.

$$\mathbf{4a{-}e} \underset{k^{H}_{-p}[H^+] + k^{BH}_{-p}[BH] + k^{H_2O}_{-p}}{\overset{k_p^{H_2O} + k_p^{B}[B] + k_p^{OH}[OH^-]}{\rightleftarrows}} \mathbf{C\text{-}4a{-}e} \qquad (3)$$

$$k_{obsd} = k_p^B[B] + k_{-p}^{BH}[BH] = \left(k_p^B + \frac{k_{-p}^{BH}}{p}\right)[B] \qquad (4)$$

Analysis of the data in Table S_4 revealed that only the buffer pathways of eq 3 were important in determining k_{obsd} in the pH range of 5.26−8.81 covered in our experiments.[23] In agreement with the reduced eq 4, all plots of k_{obsd} vs free amine concentration ([B]), typically consisting of six to eight points at a given pH, i.e., at a given buffer ratio p = [B]/[BH], were linear with negligible intercepts. However, a pH dependence of the slopes was observed in buffers with pK_a^{CH} − 1 < pH < pK_a^{CH} + 1, i.e., the glycine ethyl ester buffers (Figure S_3).[23] In these instances, the individual rate constants k_p^B and k_{-p}^{BH} were determined from a standard treatment of the data obtained at three or more different buffer ratios. In other buffers, eq 4 simplified to either $k_{obsd} = k_p^B$[B] at high pH or $k_{obsd} = k_{-p}^{BH}$[BH] at low pH, allowing a facile determination of the k_p^B and k_{-p}^{BH} rate constants from the slopes of the various k_{obsd} vs [B] or [BH] plots. Then, the corresponding k_{-p}^{BH} or k_p^B values were calculated by means of eq 5. All k_p^B or k_{-p}^{BH} rate

$$\frac{k_p^B}{k_{-p}^{BH}} = \frac{K_a^{CH}}{K_a^{BH}} \qquad (5)$$

constants are summarized in Table 3. In the case of the 2,4,6-trinitrobenzyltriflone **4e** (pK_a^{CH}) = 6.16), a few measurements of the rates of equilibrium attainment according to eq 3 could be made at pH 5.56 and 5.74 in aminoacetonitrile buffers ([B]/[BH]) = 2 and 3, respectively). From the variations of the high k_{obsd} values thus obtained with the buffer concentration, an estimate of the corresponding k_{-p}^{BH} rate constant was obtained: $k_{-p}^{BH} \approx 9 \times 10^4$ mol^{-1} L^{+1} s^{-1}.

Discussion

Structures of the Carbanions. Although this approach has been largely used, determining the hybridization for carbon from an analysis of ^{13}C−H coupling constants is now known not to apply satisfactorily well for carbanions.[2,38−40] It is therefore through evaluation of the chemical shift variations brought about by the ionization of a carbon acid that reliable information on the structural reorganization which accompanies the formation

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Table 4. Changes in Chemical Shifts ($\delta\Delta H_\alpha$, $\delta\Delta C_\alpha$) and Coupling Constants ($\Delta^1 J_{C\alpha H\alpha}$) upon Ionization of α-Substituted Toluenes ($PhCH_2X$) in Me_2SO

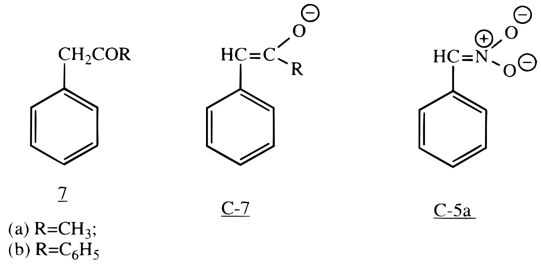
compd	X	$\Delta\delta H\alpha^c$	$\Delta\delta C\alpha^c$	ΔJ^c
5a	$NO_2{}^a$	0.99	29.9	29.2
7a	$COCH_3{}^a$	0.76	40.3	23
7b	$COC_6H_5{}^a$	0.98	45	20.7
6a	CN^a	−1.64	11	12.6
4a	$SO_2CF_3{}^b$	−1.87	0.22	21.1
4f	$SO_2CH_3{}^a$	−1.18	4.6	23
4g	$SO_2C_6H_5{}^a$	−1.14	3.6	20.7

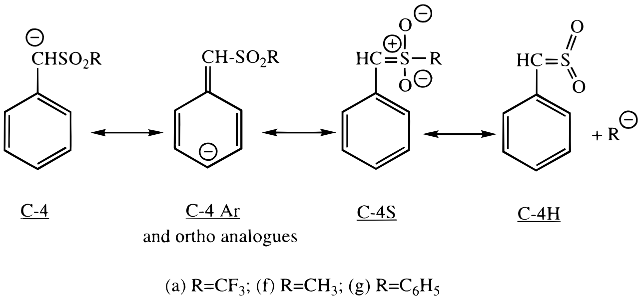
[a] Data taken from ref 2a. [b] This work. [c] $\Delta\delta$ in ppm; ΔJ in hertz.

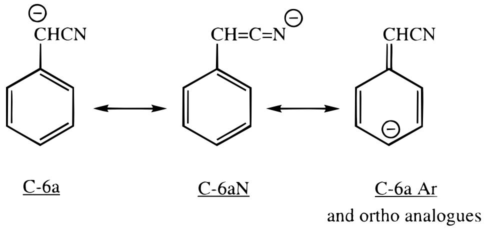
of the conjugate carbanion may be obtained. Such variations ($\Delta\delta$) are the result of two main opposing effects: (1) a high-field shift caused by the presence of negative charge and (2) a low-field shift caused by a possible $sp^3 \rightarrow sp^2$ rehybridization of the carbanionic center (C_α).[2,41] Significant upfield shifts of C_α and H_α resonances are actually the rule in reactions giving rise to sp^3-hybridized carbanions, e.g., the formation of alkyllithiums ($\Delta\delta C_\alpha = -13$ ppm for methyllithium).[38] In contrast, large downfield shifts in the range 40−60 ppm are typical for reactions where the rehybridization factor is predominant, e.g., the formation of fluorenyllithium in THF ($\Delta\delta C_\alpha = 43.6$)[38] and of the fluorenyl "carbanion" derived from (η^5-cyclopentadienyl)(η^6-fluorenyl)iron(II) cation in Me_2SO ($\Delta\delta C_\alpha = 49$; $\Delta\delta H_\alpha = 1.7$).[42] On the other hand, intermediate $\Delta\delta$ values are found in reactions giving rise to carbanions whose α-carbons are between sp^3 and sp^2 in hybridization, e.g., $\Delta\delta C_\alpha = 15.4$ ppm for formation of the unsubstituted benzyl anion.[39,43]

α-X-Substituted Toluene Anions ($PhCHX^-$). On the basis of the above reasoning, a comparison in Table 4 of the $\Delta\delta C_\alpha$ and $\Delta\delta H_\alpha$ values associated with the ionization of various α-substituted toluene carbon acids ($PhCH_2X$) is very informative regarding the structure of the resulting carbanions ($PhCHX^-$). As can be seen, large downfield shifts of the C_α and H_α resonances occur upon ionization of phenylnitromethane (**5a**; $\Delta\delta C_\alpha = 29.90$; $\Delta\delta H_\alpha = 0.99$) and the benzyl ketones **7a** ($\Delta\delta C_\alpha = 40.30$; $\Delta\delta H_\alpha = 0.76$) and **7b** ($\Delta\delta C\alpha = 45$; $\Delta\delta H\alpha = 0.98$) in Me_2SO.[2] Such $\Delta\delta$ values agree well with the traditional visualization of the related conjugate carbanions as the nitronate or enolate oxyanions **C-5a** and **C-7a,b**, respectively.[2a,4a] In contrast, the ionization of the benzyltriflone **4a** induces a very strong upfield shift of the H_α resonance: $\Delta\delta H_\alpha = -1.87$. Concomitantly, the C_α resonance moves negligibly to low field: $\Delta\delta C_\alpha = 0.22$.

Despite the much stronger electron-withdrawing effect exerted by the SO_2CF_3 group (vide infra), the situation closely resembles that observed in the ionization of benzylmethyl ($\Delta\delta C_\alpha = 4.60$; $\Delta\delta H_\alpha = -1.18$) and benzylphenyl ($\Delta\delta C_\alpha = 3.60$; $\Delta\delta H_\alpha = -1.14$) sulfones (**4f** and **4g**) as well as of benzylcyanide (**6a**; $\Delta\delta C_\alpha = 11.00$; $\Delta\delta H_\alpha = -1.64$).[2a] This suggests that a high negative charge density must be retained on the exocyclic carbon of the triflone carbanion (structure **C-4a**) and the two related sulfonyl anions (structures **C-4f**,**g**), as it does in the case of the nitrile anion (structure **C-6a**). It follows that both the resonance contributors **C-4S** and **C-4H** which imply significant C = S double-bond character as well as the aromatic contributor **C-4Ar** cannot be of appreciable importance in the stabilization of the three α-sulfonyl carbanions. Structures **C-6aN** and **C-6aAr** play similarly a minor role in the stabilization of **C-6a**.[2a,3]







Ionization of **4a** induces only a weak upshield shift of the fluorine resonance ($\Delta\delta F = -2.25$), supporting the idea that most of the negative charge of **C-4a** is not dispersed through the SO_2CF_3 group. On the other hand, the upfield shift of H_α increases in the order $SO_2C_6H_5 \sim SO_2CH_3 < CN < SO_2CF_3$, suggesting that in this series the possibility of having even a minor delocalization of charge through the phenyl ring decreases when the electron-withdrawing character of the exocyclic X group is increased. Interestingly, it has been shown that, with an sp^2-hybridized carbon and no steric restrictions of resonance, maximum charge delocalization onto the para carbon of a phenyl ring results in a maximum $\Delta\delta C_4$ value of about −25 ppm, while a purely inductive effect by an aromatic ring results in a negative para $\Delta\delta$ of < 10 ppm.[38] In the case of **C-4a**, a $\Delta\delta C_4$ value of − 12.76 ppm is found (Table S_2),[23] comparable with that reported for the phenylnitromethane anion **C-5a** ($\Delta\delta C_4 = -9.48$).[2a,44] This similarity is obviously consistent with a minor contribution of the structures **C-4Ar** to the stabilization of **C-4a**. For comparison, the upfield shift is $\Delta\delta C_4 = -21.6$ ppm for formation of the unsubstituted benzyl anion (as a lithium salt) despite the fact that this anion is not completely sp^2-hybridized.[38]

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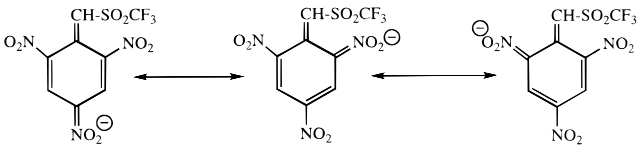
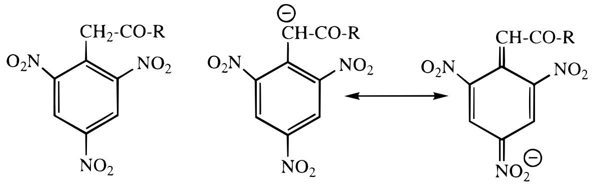
The $^1J_{C\alpha H\alpha}$ coupling constants for the various $PhCH_2X$ and $PhCHX^-$ species discussed above are included in Table 4. As can be seen, $^1J_{C\alpha H\alpha}$ is always much higher in the carbanion than in the parent toluene substrate with the ΔJ values being rather similar for the two ketone and the three sulfone compounds ($\Delta J \sim 21-23$ Hz). While similar ΔJ values for formation of α-sulfonyl and α-sulfoxide carbanions have been previously accounted for in terms of a notable sp^2 hybridization of the C_α carbon,[45] they are here clearly difficult to reconcile with the very different responses of the C_α and H_α resonances to the ionization of the CH_2X group.[46] This supports the aforementioned view that analysis of $^{13}C-H$ coupling constants may not afford clear-cut conclusions regarding hybridization and charge delocalization in carbanions.[2,38−40]

Ring-Substituted Benzyl Triflones. Table 1 shows that the effect of increasing the efficiency and the number of electron-withdrawing groups in the phenyl ring of the unsubstituted triflone **4a** is to reduce progressively the upfield shift of the H_α resonance from −1.87 to −0.01 ppm upon ionization. Concomitantly, $\Delta\delta C_\alpha$ increases from essentially zero to 24.4 ppm on going from **4a** to **4e**. These trends suggest a regular increase in the contribution of the activated phenyl ring to charge delocalization (structures **C-4Ar**$_{1,2,3}$ in the case of **C-4e**), with a rather similar situation in **C-4d** and **C-4e**, in accord with the idea that there is commonly some steric restriction to resonance due to the *o*-nitro groups in 2,4,6-trinitrocyclohexadienyl-type carbanions as compared with 2,4-dinitro analogues.[41b,47]



C-4 Ar1 C-4 Ar2 C-4 Ar3

A most noteworthy feature, however, is that the above highest $\Delta\delta H_\alpha$ and $\Delta\delta C_\alpha$ values do not compare at all with those associated to the ionization of ring α-substituted toluenes known to afford sp^2-hybridized cyclohexadienyl-type carbanions, e.g., $\Delta\delta H_\alpha = 1.96-2.31$, $\Delta\delta C_\alpha = 53.36-57.7$ ppm for the conversion of the picryl ketones **8a−d** to the anions **C-8a−d**.[21,41d,48] Such values are so much higher than those found for formation of **C-4e** that they provide clear, though indirect, support for a lesser importance of the aromatic resonance contributors in the stabilization of our triflone carbanions than in the related benzyl ketone carbanions. Also consistent with this conclusion is the observation that the visible spectrum of **C-4e** shows an absorption maximum at a much shorter wavelength ($\lambda_{max} = 437$ nm) than found for typical trinitrotoluene anions, including **C-8a−d** ($\lambda_{max} > 510$ nm).[21,41b,49] Then, we are left with the view that the negative charge of the carbanions **C-4a−e** is essentially retained at the C_α carbon, including in the picryl system.[50]



8 C-8 C-8 Ar1

(a) R=CH_3; (b) R=C_6H_5; (c) R=4-MeO-C_6H_4; (d) R=4-NO_2-C_6H_4

Equilibrium Acidities of 4a−e. Solvent Dependence of the Acidifying Effect of the SO_2CF_3 Group. Comparison in Table 5 of the pK_a value for ionization of the triflone **4a** with those previously reported for related α-substituted toluenes ($PhCH_2X$) shows that the acidifying effect of the SO_2CF_3 group is considerably larger than that of a carbonyl, a cyano, or a SO_2R group and almost as large as that of a NO_2 group in Me_2SO. This confirms previous observations made by Bordwell et al. in a study of the ionization of methane carbon acids (CH_3X) in this solvent.[5] That the $PhCH_2X$ compounds are all more acidic than the corresponding CH_3X compounds mainly reflects the acidifying inductive effect of a phenyl group.[55]

Examination of the effect of solvent on pK_a values is most informative regarding the relative acidifying behavior of the NO_2 and SO_2CF_3 substituents. As can be seen in Table 2, the acidity of the triflones **4a−e** tends to decrease while that of the arylnitromethane compounds (**5a**,**c**) strongly increases upon addition of increasing amounts of water to a Me_2SO solution. As a result, the SO_2CF_3 group is considerably less acidifying than a NO_2 group in aqueous solution as compared to Me_2SO. Thus, the acidity difference between **4a** and **5a** increases from 2.30 pK units to 7.17 pK units on transfer from Me_2SO to a 50% H_2O−50% Me_2SO mixture. Similarly, this solvent change strongly increases the difference in the pK_a values of the paranitro-substituted analogues **4c** and **5c**: $\Delta pK_a = 0.84$ in Me_2SO; $\Delta pK_a = 4.57$ in 50% Me_2SO.

In the case of nitroalkanes and arylnitromethanes, it is well recognized that the solvent dependence of the pK_a values reflects the favorable effect of hydrogen-bonding solvation on the

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[46] A reviewer has suggested that the sets of $\Delta\delta H_\alpha$, $\Delta\delta C_\alpha$, and ΔJ values associated with the ionization of **4a**, **4f**, and **4g** may be understood in terms of a rehybridization of the anionic C_α atom occurring with a minor charge transfer to the oxygen atoms of the SO_2R groups (structure **C-4S**). Since there is concomitantly convincing NMR evidence that the contribution of the aromatic ring to the charge transfer (structure **C-4Ar**) is negligible, a strong rehybridization of C_α upon ionization of **4a**, **4f**, and **4g** would imply that the negative hyperconjugation mechanism operates to a large extent in the stabilization of the conjugate carbanions **C-4a**, **C-4f**, and **C-4g** (structure **C-4H**). This situation is not borne out by ^{19}F NMR data since the ionization of **4a** does not result in a notable upfield shift of the fluorine resonance. Also, the kinetic and thermodynamic data obtained in H_2O−Me_2SO mixtures do not support this conclusion, emphasizing a rather similar behaviour of benzyl sulfones and benzylcyanides (vide infra). Interestingly no hyperconjugated form analogous to **C-4H** can be envisioned in the case of α-cyanocarbanions.

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[48] That the picryl ketone carbanions exist essentially in the form **C-8Ar$_1$** (or its *o*-nitro analogues) was evidenced in particular by the observation of a nonequivalence of the $H_{3,5}$ protons as well as of the $C_{2,6}$ and $C_{3,5}$ carbons of their picryl ring.[21.]

[49] All 2,4,6-trinitrotoluene carbanions exhibit rather similar λ_{max} values, presumably because steric restriction to resonance through the *o*-nitro groups favors the role of the paraquinoid structure in the delocalization of the negative charge, e.g. $\lambda_{max} = 514$ nm for 2,4,6-trinitrotoluene anion.[47b]

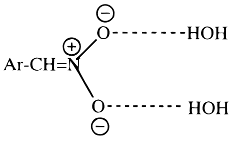
[50] An additional feature is worthy of comment. It has been shown experimentally and accounted for by theoretical calculations that delocalization of a negative charge through nitro-substituted phenyl as well as cyclohexadienyl rings results in large upfield shifts of the resonances of the nitro-bearing carbons ortho and/or para to the reaction site.[51−54] The corresponding $\Delta\delta$ (C_{ortho}) and $\Delta\delta$ (C_{para}) values lie commonly in the range −10, −17 ppm and −18, −30 ppm, respectively. As can be deduced from Table S_2, it is only for the picryl system that the $\Delta\delta(C_{2,6})$ and $\Delta\delta(C_4)$ values pertaining to the ionization of **4a−e** approach the lower limit indicated above: $\Delta\delta$ $(C_{2,6}) = -11.59$; $\Delta\delta(C_4) = -18.57$ ppm. Again, this result agrees well with the idea of an appreciable but certainly not predominant delocalization of negative charge through the activated phenyl ring of our triflone carbanions.

Table 5. Effect of the X Substituent on the Acidity of α-X-Substituted Toluenes and Related Methane Derivatives in Me_2SO^a

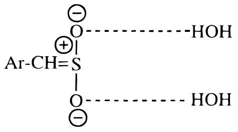
X	$pK_a^{PhCH_2X}$	$pK_a^{CH_3X}$
NO_2	12.32	17.20
SO_2CF_3	14.62	18.76
COC_6H_5	17.70	24.70
$COCH_3$	19.40	26.70
CN	21.90	31.20
$SO_2C_6H_5$	23.40	29.04
SO_2CH_3	25.40	31.1

[a] $T = 25$ °C; this work for $PhCH_2SO_2CF_3$; other pK_a values taken from refs 5, 30, 57b, and 59.

stabilization of the conjugate nitronate oxyanions in aqueous solution (structure $\mathbf{C\text{-}5_{solv}}$).[4,20,28,56−58] Should a canonical structure of this type notably contribute to the stabilization of the carbanions **C-4a−e**, as earlier suggested by Bordwell,[5] the hard negatively charged oxygen atoms of the SO_2CF_3 group should also be sensitive to hydrogen-bonding solvation, thereby leading to an enhanced acidity of the parent triflones in aqueous solution (structure $\mathbf{C\text{-}4S_{solv}}$). Obviously the experimental results do not fit this proposal. Instead, they agree with the idea that most of the negative charge of the triflone carbanions must reside at the C_α carbon, at least in the case of the unsubstituted species **C-4a**. Structure **C-4** is much more favorable than structures **C-4S** or **C-4H** in terms of polarizability of the negative charge of the carbanion, making it more susceptible to stabilization by Me_2SO than by water.[57−61] This would account for the enhanced acidity of the parent triflone in the dipolar aprotic solvent. Interestingly, Table 2 also reveals that the stabilizing effect of Me_2SO on the carbanions **C-4a−e** increases slightly, but regularly, with increasing the activation of the phenyl ring. Again, this finding can be readily reconciled with NMR results which have suggested that the contribution of the phenyl ring to the delocalization of the negative charge (structure $\mathbf{C\text{-}4Ar_\mathit{i}}$) increases to some extent from **C-4a** to **C-4e**. Because of this delocalization, the polarizable character of the carbanion and therefore its potential stabilization by Me_2SO increases.[21,57]

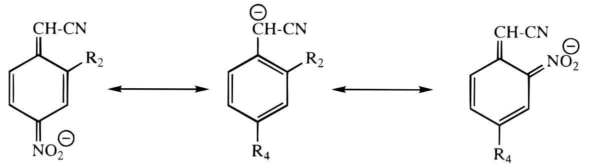


$C\text{-}5_{solv}$



$C\text{-}4S_{solv}$

In the NMR section, we have emphasized the similar electronic mode of action of the CN and SO_2R substituents in the stabilization of α-substituted carbanions. In this regard, it is interesting to note in Table 2 that the effect of adding Me_2SO to aqueous solution is to increase the acidity of the five benzyl cyanides **6b−f** in the same way at it does for the triflones **4a−e**.[35,36] In view of the much lower electron-withdrawing effect of a CN group compared to a SO_2CF_3 group, one might argue that the activating substituents in the aromatic ring induce a much more important transfer of negative charge through the phenyl moiety in the case of α-cyano than α-SO_2CF_3 carbanions. Thus, the enhancing effect of Me_2SO on the acidity of **6b−f** might be primarily viewed as the result of stabilization of the conjugate carbanions **C-6b−f** through resonance structures of type $\mathbf{C\text{-}6Ar_1}$ or $\mathbf{C\text{-}6Ar_2}$ rather than of type **C-6**. However, this explanation is not very attractive, at least in the case of the mononitro derivatives for the following reasons: (1) the observation that the ionization of **6b** results in a notable high-field shift of the H_α resonance ($\Delta\delta H_\alpha = -0.23$) leaves little doubt that an appreciable portion of the negative charge resides at the C_α carbon in the 4-nitrophenylacetonitrile anion[62] and (2) it is well-known that an *o*-NO_2 group is significantly less effective at resonance stabilization of negative charge than is a *p*-NO_2 group.[54] Since the para substituents of **6d−f** exert only an inductive effect, it seems reasonable to assume that the conjugate carbanions **C-6d−f** must also be primarily viewed as **C-6** rather than $\mathbf{C\text{-}6Ar_2}$. Our conclusion is therefore that the enhancing effect of Me_2SO on the acidity of **6b−f** must be, at least in part, a reflection of an increased stabilization of the carbanionic structures **C-6** by this dipolar aprotic solvent. Accordingly, the situation for benzylcyanides seems really comparable to that which prevails in the case of benzyltriflones, further favoring the view that both α-cyano and α-SO_2R carbanions have a large polarizable negative charge which is mostly localized at the α-carbon.



C-6 Ar1 C-6 C-6 Ar2

(b) R_2=H; (c) R_2=NO_2

(c) R_4=NO_2; (d) R_4=Cl; (e) R_4=Br; (f) R_4=CF_3

Intrinsic Reactivity of Benzyltriflones 4a−e. Figure 1 shows that a good Brönsted plot may be drawn on the basis of the measured rate constants k_p^B pertaining to the deprotonation of the 2,4-dinitrobenzyltriflone **4d** by primary amines in 50% Me_2SO. The corresponding β_B value is equal to 0.38, being very close to the range of 0.50 ± 0.10 commonly found for ionization of carbon acids of similar pK_a^{CH} values in this solvent.[4,21,28,35−37,56,61,63] Using the classical definition of the intrinsic rate constant, i.e., $k_0 = (k_p^B/q)$ when $pK_a^{CH} - pK_a^{BH} -$

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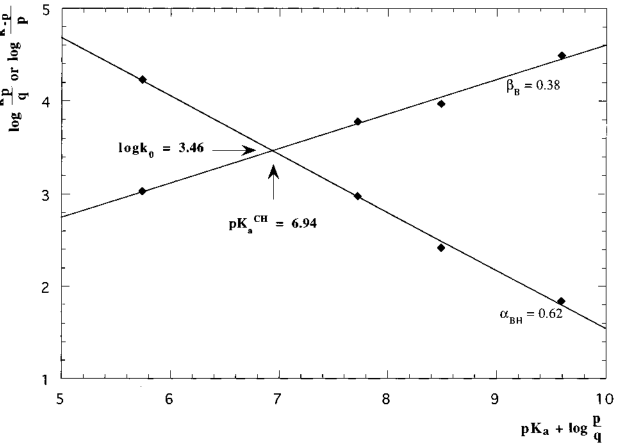

Figure 1. Brönsted plot for ionization of **4d** by primary amine buffers in 50% H_2O−50% Me_2SO (v/v): $T = 25$ °C, $I = 0.5$ M (NMe_4Cl). The numbering of the various catalysts is given in Table 3.

log $(p/q) = 0$, the log $k_0^{RNH_2}$ value for the ionization of **4d** was readily determined from Figure 1: log $k_0 = 3.46$.[4,20,56,64] Using the k_{-p}^{BH} rate constant ($k_{-p}^{BH} = 9 \times 10^4$ mol^{-1} L^{+1} s^{-1}) determined in aminoacetonitrile buffers and assuming $\alpha_{BH} = 0.50$, a rough value of log $k_0^{RNH_2}$ for the picryltriflone **4e** could also be estimated by means of eq 6: log $k_0 = 4.50 \pm 0.30$. On the other hand, the fact that the rates of deprotonation of **4a**−**c** by base reagents of pK_a^{BH}'s close to the related pK_a^{CH}'s are not accessible by stopped-flow spectrophotometry means that the intrinsic reactivity of these derivatives are higher than that of **4e**, i.e., log $k_0 \geq 5$.

$$\log k_0 = \log k_{-p}^{BH} + \alpha_{BH} \log \frac{K_a^{CH}}{K_a^{BH}} \qquad (6)$$

In the past decade, 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 which is required to form the conjugate carbanion.[4,20] 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.[4,20,21,35−37,56,58,63] Table 6 reveals a first significant result, namely that the log $k_0^{RNH_2}$ values measuring the intrinsic reactivity of **4a**−**e** are much higher than those associated with the ionization of carbon acids giving rise to strongly resonance-stabilized sp^2-hybridized nitronate and enolate carbanions. Representative examples of this category quoted in Table 6 include nitroalkanes such as phenylnitromethane **5a**, polynitrotoluene derivatives such as 2,4,4′-trinitrodiphenylmethane, *or* the picryl ketones **8a**−**d** as well as *β*-dicarbonyl compounds such as acetylacetone and 1,3-indandione. In these instances, low to very low log k_0 values are obtained because an enormous structural reorganization is required to form the conjugate bases, e.g., see structures **C-5a** and **C-8Ar**.[4,41b,63,65] Here, it is of particular interest to note that the intrinsic reactivities of the triflones **4a**−**e** are about 2 orders of magnitude higher than those of ketone carbon acids. Interestingly, Bunting and Wodzinski have found a similar difference in the reactivities of a number of structurally related sulfones and ketones but the exact log k_0 values could not be determined.[66]

Table 6. Comparison of Intrinsic Rate Constants for Deprotonation of Some Representative Carbon Acids by Primary and Secondary Amines in 50% H_2O−50% Me_2SO[a]

CH acid	log $k_0^{RNH_2}$	log $k_0^{RR'NH}$
$RCH(CN)_2$	∼7[b]	
4a−**c**	≥5[c]	
4e	∼4.5[c]	
9-cyanofluorene	3.76[d]	4.58[d]
4d	3.46[c]	
6b	3[e]	3.70[e]
1,3-indandione	2.44[f]	3.13[f]
6c	2.05[e]	2.75[e]
acetylacetone	2.06[f]	2.75[f]
8a	0.85[g]	
CH_3NO_2	0[h]	0.73[h]
2,4,4′-trinitrodiphenylmethane	−0.65[i]	−0.10[i]
$C_6H_5CH_2NO_2$ (**5a**)	−1[h]	−0.25[h]

[a] At 25 °C unless indicated otherwise; log $k_0^{RNH_2}$ and log $k_0^{RR'NH}$ refer to primary and secondary amines as deprotonating reagents, respectively. [b] Reference 4. [c] This work. [d] Reference 61 at 20 °C. [e] References 35 and 36 at 20 °C. [f] Reference 63. [g] Reference 21a. [h] Reference 28 at 20 °C. [i] Reference 65.

For a more complete understanding of the behavior of **4a**−**e**, it is once again interesting to compare the situation with that previously found for the four nitriles listed in Table 6. Thus, aliphatic nitriles, such as those of general structure $RCH(CN)_2$, have high intrinsic reactivities because they afford carbanions whose stabilization derives essentially from the polar effect of the cyano group.[4,35,36] Introduction of a R group such as a phenyl or a fluorenyl moiety provides a notable potentiality of resonance stabilization of the carbanion, as reflected by a decrease in log $k_0^{RNH_2}$ from about 7 to 3.76 for 9-cyanofluorene.[61] Introduction of nitro groups in the aromatic moiety further decreases the intrinsic reactivity. Thus, the log $k_0^{RNH_2}$ value of 3 measured for the ionization of 4-nitrophenylacetonitrile **6b** is understandable only if the nitrosubstituted ring contributes appreciably to the resonance stabilization of the carbanion **C-6b** (structure **C-6Ar$_1$**), even though it is also evident from NMR and pK_a results that a notable charge density remains located on Cα (vide supra).[35] On the other hand, the log k_0 value of 2.05 measured for 2,4-dinitrophenylacetonitrile **6c** is sufficiently low to suggest that delocalization through the activated ring must be in this instance the main factor contributing to the stabilization of the carbanion **C-6c**.[35] Going now to the triflone series, we note that the compound with the lowest log $k_0^{RNH_2}$ value, i.e., the 2,4-dinitro compound **4d** (log $k_0 = 3.46$), exhibits an intrinsic reactivity which is not only 30-fold higher than that measured for the cyanide analogue **6c** but also 3-fold greater than that for the mononitrosubstituted cyanide **6b**. More importantly, the four other triflones have log k_0 values which are located at a relatively high level, i.e., log $k_0 \geq 4$−5, in the intrinsic reactivity scale.[67] It seems to us that this situation is in itself most convincing evidence for a weak occurrence of charge delocalization and hence, a large predominance of the pyramidal carbanionic structure **C-4** rather than of the sp^2-hybridized

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(67) As suggested by a reviewer, the greater log k_0 value for **4e** than for **4d** is consistent with the evidence that the presence of the two *o*-NO_2 groups results in a notable steric inhibition to resonance in 2,4,6-trinitrotoluene carbanions.[4,41b,47]

canonical representations **C-4S**, **C-4H**, and **C-4Ar$_1$** in the stabilization of the α-SO_2CF_3 carbanions **C-4a−e**.

Conclusion

The three different approaches used in this work to study the ionization of the triflones **4a−e** lead to a unique structural picture of the resulting carbanions **C-4a−e**. On the basis of in particular our finding of high intrinsic reactivities for these compounds, it appears clearly that stabilization of a negative charge by the strong electron-withdrawing SO_2CF_3 group must be the result of polarization effects rather than of conjugative d−p π-bonding or negative hyperconjugation, at least in solution.[68] Interestingly, this situation is not fully in agreement with conclusions reached from high-level ab initio studies or crystal structure analyses.[7,17−19,22,23] These favor the view that α-sulfonyl carbanions with a C_α carbon bearing at least one aryl group are planar and that hypernegative conjugation operates significantly together with polarization effects in determining the stability of these species, especially in the case of SO_2CF_3 derivatives.[17−19] As pointed out by Streitwieser et al. in a recent study of the equilibrium acidities of some sulfones and sulfoxides in THF,[70] solid-state and computed gas-phase structures may not always be a perfect guide for structures and reactions in solution. This is apparently the case in the systems described in this work.

Experimental Section

Materials. Solvents were purified and solutions made up as described previously.[37,65] Buffers were purified commercial products. The synthesis of the various triflones **2a−e**, either by Hendrickson's method[71a] or a new methodology, was recently reported elsewhere.[71b]

Measurements. pH of buffer solutions in H_2O-Me_2SO mixtures [$I = 0.5$ M (NMe_4Cl)] were measured potentiometrically as described before.[37,65] In these solvents, the spectrophotometric determination of the pK_a^{CH} values of **4a−e** was facilitated by the fact that the anions **C-4a−e** exhibit a strong UV−visible absorption in regions of the spectrum where neither the parent triflones nor the required buffers absorb. Spectra were taken on a KONTRON-UVICON-930 spectrophotometer; λ_{max} values of **C-2a−e** were quoted in the Results.

The same spectrophotometric procedure was applied, using amine buffers, to measure the pK_a^{CH} values of **4b−e** in pure Me_2SO. In the case of the much less acidic unsubstituted triflone **4a**, the $pK_a^{Me_2SO}$ was determined with reference to two indicators i.e., 2,4-dinitroaniline and 4,4′-dinitrophenylmethane, for measuring the pH of buffer solutions made up from this triflone with [**C-4a**]/[**4a**] ratios equal to 1/3, 1/2, 1/1, 2/1, and 3/1. These solutions were prepared by addition of potassium dimsyl in Me_2SO so that the molarity of the anionic species **C-4a** was in all cases equal to 0.01 M. Under these experimental conditions, the pK_a^{CH} value of **4a** was calculated from eq 2 (see Results).

Kinetic measurements of the ionization of **4d**,**e** were carried out at 25 ± 0.2 °C with an Applied Photophysics stopped-flow spectrophotometer. NMR spectra were recorded on a Brucker AC300 spectrometer. Chemical shifts are reported in ppm (J values in hertz) with tetramethylsilane (^1H, ^{13}C) and $CFCl_3$ (^{19}F) as the internal references. The various triflones were dissolved in Me_2SO-d_6 (∼0.2 M), and the carbanions were generated in solution by adding an equimolar amount of methanolic potassium methoxide (∼5.5 M) to the above solutions. Under these experimental conditions, the stability of these species was sufficient as to provide not only well-resolved ^1H, ^{19}F, and noise proton-decoupled ^{13}C spectra but also proton-coupled ^{13}C spectra (Tables S_1−S_3).

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Supporting Information Available: Figure S_1 (variation of the ratio of ionized to un-ionized benzyltriflones **4** as a function of pH in 50% H_2O−50% Me_2SO (v/v); $I = 0.5$ M (NMe_4Cl)), Figure S_2 (ionization of 2,4-dinitroaniline in various benzyltriflone buffers in Me_2SO), Figure S_3 (effect of pH and buffer concentration on the observed rate constant, k_{obsd}, for deprotonation of 2,4-dinitrobenzyltriflone **4d** by primary amine buffers in 50% H_2O−50% Me_2SO (v/v); $T = 25$ °C, $I = 0.5$ M (NMe_4Cl)), Table S_1 (^1H and ^{19}F NMR data for benzyltriflones **4a−e** and related carbanions **C-4a−e**), Tables S_2 and S_3 (^{13}C NMR data for benzyltriflones **4a−e** and related carbanions **C-4a−e**), and Table S_4 (kinetic data; k_{obsd} values) (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[68] In response to a reviewer's comment, our results do not allow us to discriminate between polarizability and inductive/field effects, as has been done for various systems.[69]

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