Carbanion reactivity; studies of σ-adduct formation from benzyltriflone anions and 4-nitrobenzofurazan derivatives

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ABSTRACT: ^{1}H NMR studies in DMSO-d_6 of the reaction of benzyltriflones, **2**, with 4,6-dinitrobenzofuroxan, **4**, indicate the formation, with or without the presence of added base, of anionic σ-adducts. Spectra obtained from solutions of **2** and 4-nitrobenzofurazan, **6a**, in the presence of triethylamine are consistent with products formed by the elimination of trifluoromethylsulfinic acid from σ-adducts initially formed by carbanion attack at the 5-position of **6a**. Kinetic studies of the latter reaction in methanol allow the determination of rate constants for nucleophilic attack by the carbanions at the 5-position. The low value of β for these reactions together with the failure to observe reaction with 1,3,5-trinitrobenzene suggest that the benzyltriflone anions have unusually large steric requirements. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: carbanions; nucleophilic reactivity; sigma-adducts; elimination reactions; 4-nitrobenzofurazan

INTRODUCTION

There is current interest in comparing nucleophilicities,[1,2] particularly those of carbon nucleophiles. Mayr and co-workers have used the reactions with a series of benzhydryl cations to assess the nucleophilicities of carbanions stabilised by acyl, ester, cyano and nitro-groups.[3–5] Their results, although providing useful relationships, show that relative nucleophilicities may be strongly influenced by the solvent, e.g. methanol *versus* DMSO, and that often there is a poor correlation between nucleophilic reactivity and the pK_a values of the corresponding carbon acids.[3–5] In related fashion Terrier and co-workers have compared the electrophilicities of some neutral electrophiles, such as 1,3,5-trinitrobenzene and 4,6-dinitrobenzofuroxan, by measuring rate constants for their reactions with some standard carbon nucleophiles in acetonitrile.[6,7]

This paper is concerned with assessing the effects of a trifluoromethylsulfonyl group on carbanions in their σ-adduct forming reactions with nitrobenzofurazan derivatives. It is known that the SO_2CF_3 group is strongly electron-withdrawing and as judged by Hammett σ

values[8] is more effective than NO_2 as a ring substituent in stabilising anionic σ-adducts. Thus the adduct **1** is more stable by a factor of 10^6 than the trinitro analogue in methanol.[9]

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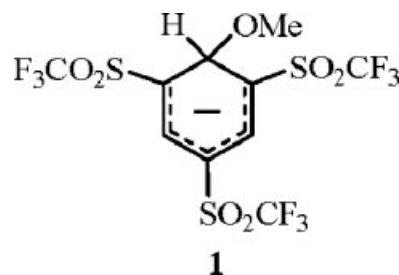
However, benzyltriflone has been shown[10] to be less acidic than phenylnitromethane by two pK_a units in DMSO and in water this difference is magnified mainly due to the excellent solvation of the nitronate ion by water.[11] Detailed studies[11–13] combining kinetic, thermodynamic and NMR methods have shown that in carbanions derived from benzyltriflones the negative charge remains largely on the exocyclic C_α carbon atom where it is stabilised by polarisation effects. The high intrinsic reactivity, in the Marcus sense,[14,15] associated with the ionisation process is compatible with low amounts of electronic and solvent re-organisation accompanying carbanion formation.

Here we report ^{1}H NMR studies in DMSO-d_6 of the σ-adduct forming reactions of the carbanion **3b** derived

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from the benzyltriflone **2b** with electrophiles **4**, **5** and **6a**. Kinetic results for the reactions of **3a,b,c** with nitrobenzofurazan derivatives **6a,b** were obtained in methanol to allow comparison of results with other carbanions.[16–19]


2 a R^1=H
   b R^1=CF$_3$
   c R^1=CN

3 a R^1=H
   b R^1=CF$_3$
   c R^1=CN

4

5

6 a R^2=H
   b R^2=Cl
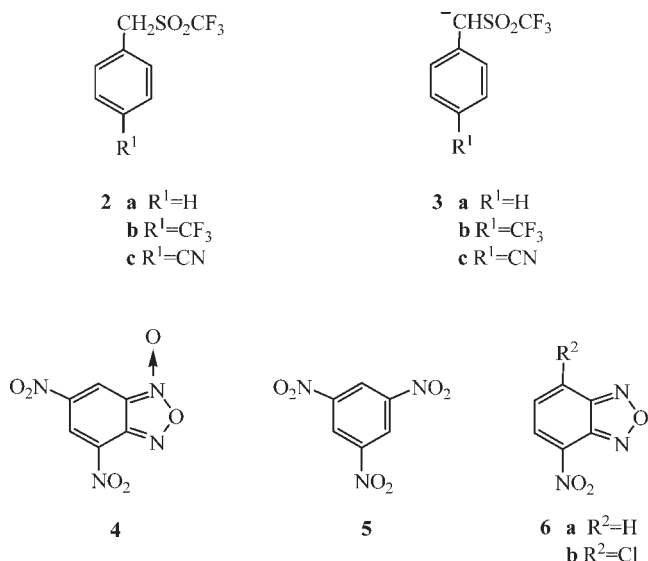
RESULTS AND DISCUSSION

^{1}H NMR studies

The strongly electrophilic character of 4,6-dinitrobenzofuroxan, **4**, and its ability to form σ-adducts with weakly nucleophilic carbon centres are well known.[20–26] Our spectra show that, even in the absence of added base, the reaction of **4**, 0.1 mol dm^{-3}, with **2b**, 0.025 mol dm^{-3}, in DMSO-d$_6$ resulted in the appearance over several days of new bands attributed to the anionic σ-adduct **7**. In **7**

there are two chiral centres[23] at C$_7$ and C$_\alpha$ and two sets of bands were observed in the intensity ratio 1.4:1 due to the diastereoisomers **7a** and **7b** (only one enantiomer is shown for each). Chemical shifts are shown in Table 1. The spectrum, in Fig. 1, of a solution containing **4**, 0.1 mol dm^{-3}, **2b** 0.05 mol dm^{-3} and triethylamine, 0.1 mol dm^{-3}, measured within 10 min of mixing showed that conversion of **2b** to **7a** and **7b** was largely complete. Little change in the spectrum occurred during 3 h and no new bands attributable to a possible product of elimination of trifluoromethylsulfinic acid were observed.

7a   **7b**
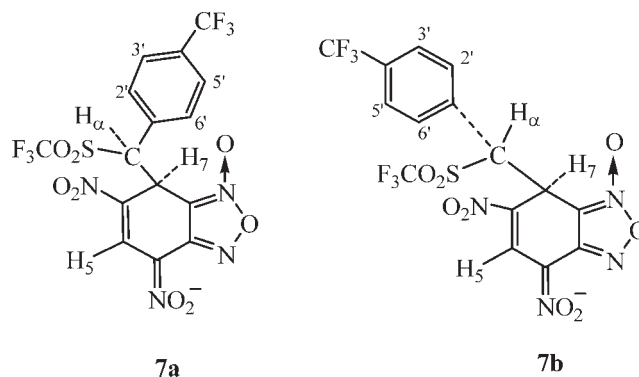
In contrast spectra of 1,3,5-trinitrobenzene, **5**, in DMSO-d$_6$ containing **2b** and triethylamine gave no evidence of strong interaction. After several hours only bands due to parent molecules were observed.

The spectrum of 4-nitrobenzofurazan, **6a**, 0.04 mol dm^{-3}, with **2b**, 0.05 mol dm^{-3}, and triethylamine, 0.1 mol dm^{-3}, measured within 15 min of mixing is shown in Fig. 2. Interestingly the spectrum does not correspond to that expected[19] for the σ-adduct, **8a**, but is attributable to **9a**; the product of elimination of trifluoromethylsulfinic acid from **8a**. Chemical shifts are shown in Table 2. Strong coupling $J = 10.4$ Hz is observed between H6 and H7

8a   **9a**
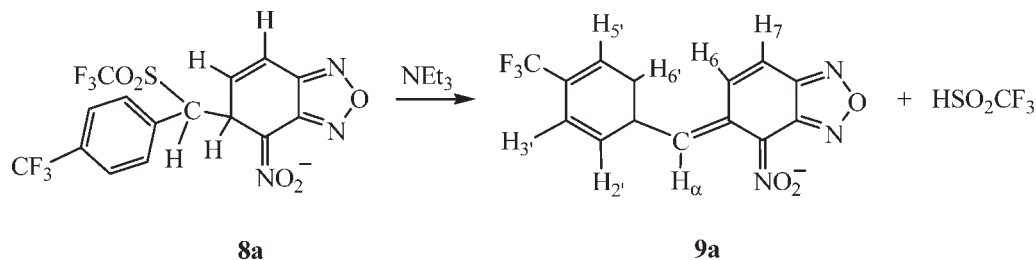
**Table 1.** ^{1}H NMR data[a] for **4**, **2b** and **7a,b** in DMSO-d$_6$

Compound	δ					J_{57}	J_{7-CH_α}	$J_{2',3'}$
	H$_7$	H$_5$	CH$_\alpha$	H$_{2',6'}$	H$_{3',5'}$			
4	9.26	8.95	—	—	—	2.0	—	—
2b	—	—	5.45	7.75	7.86	—	—	8.0
7a	5.40	8.36	5.65	7.49	7.73	<1.0	2.0	8.0
7b	5.28	8.39	5.57	7.53	7.78	<1.0	1.6	8.0

[a] J values are in Hz.
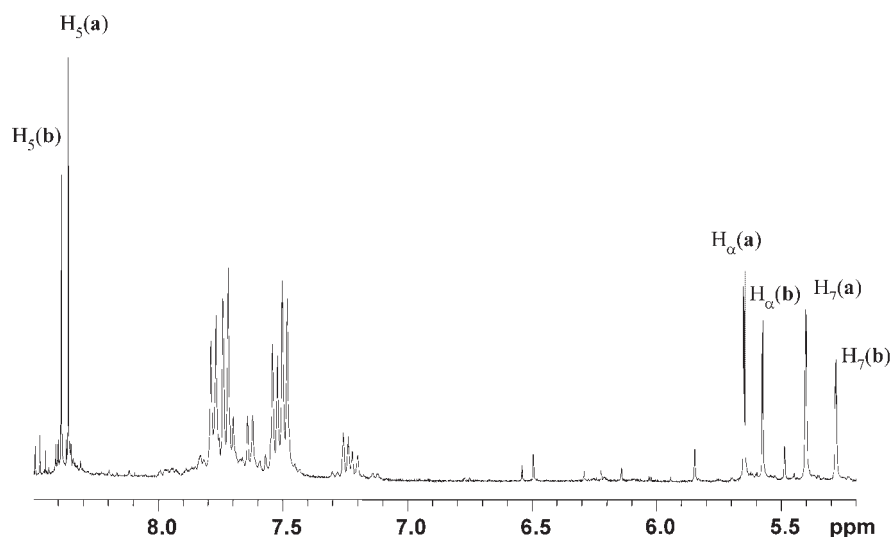
Figure 1. ^{1}H NMR spectrum of **4**, 0.1 mol dm^{-3}, **2b**, 0.05 mol dm^{-3}, and triethylamine, 0.1 mol dm^{-3}, in DMSO-d$_6$ measured 10 min after mixing. The numbering corresponds to structures **7a** and **7b**

while a weak interaction $^5H_{H_7H_\alpha} = 1.2$ Hz is observed between the hydrogens at the 7 and α positions. This is consistent with the long-range coupling associated with a coplanar zig-zag arrangement of bonds.[23] A weaker interaction $^4J_{H_6H_\alpha} = 0.8$ Hz is observed between H6 and Hα. The shifts of H6, H7 and Hα are similar to those[19] of the related alkene, **10**, formed by the elimination of nitrous acid from the nitroethane adduct of **6a**. Further justification that reaction occurs at the 5-position rather than the 7-position will be given later.


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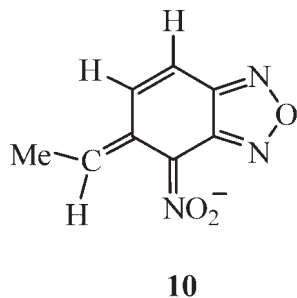
pK_a values in methanol

Since kinetic measurements were made in methanol it was necessary to determine pK_a values of the benzyl triflones in this solvent. Carbanions **3a,b,c** were generated from the benzyltriflones **2a,b,c** by reaction with sodium methoxide in methanol, as shown in Eqn. (1). Values of the ionisation ratio, IR, defined by Eqn. (2), were determined

$$\mathbf{2a, b, c} + MeO^- \overset{K}{\rightleftharpoons} \mathbf{3a, b, c} + MeOH \qquad (1)$$

$$IR = \frac{[\mathbf{3}]}{[\mathbf{2}]} \qquad (2)$$

spectrophotometrically using the strong UV absorbance of the benzyltriflone anions. Absorption maxima were at 290 nm for **3a**, 315 nm for **3b** and 340 nm for **3c**.

In the case of the cyano derivative, **2c**, ionisation could be achieved using solutions of sodium methoxide in
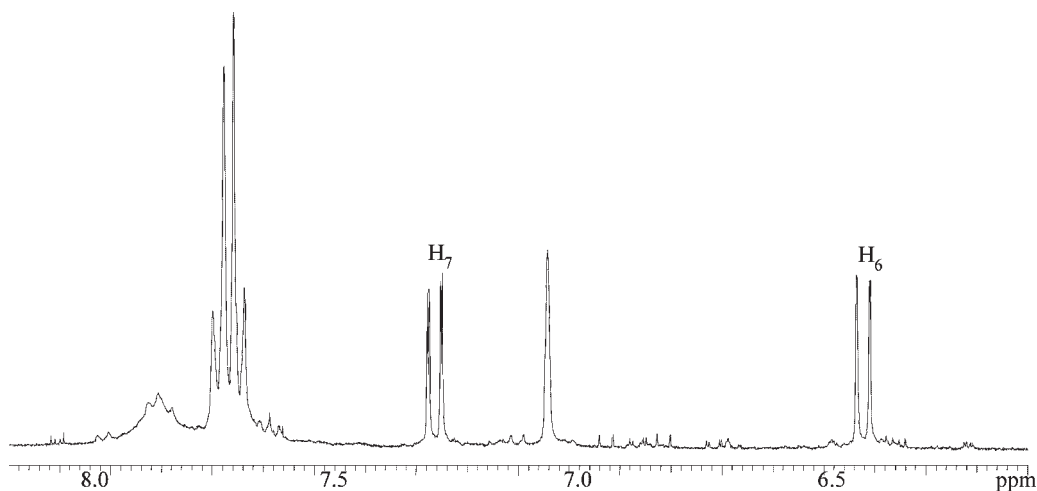
Figure 2. ^{1}H NMR spectrum, 400 MHz, of **9a** in DMSO-d$_6$. The small bands at δ 7.85 are due to unreacted **2b**

Table 2. ^{1}H NMR data^a for parent molecules, and **9a** and **10** in DMSO-d_6

| Compound | δ | | | | | | J_{56} | J_{67} | $J_{H_7H_\alpha}$ | $J_{H_6H_\alpha}$ | $J_{2',3'}$ |
	H_5	H_6	H_7	CH_α	$H_{2',6'}$	$H_{3',5'}$					
6a	8.70	7.85	8.61	—	—	—	7.2	8.8	—	—	—
2b	—	—	—	5.45	7.75	7.86	—	—	—	—	8.0
9a	—	6.44	7.30	7.08	7.70	7.73	—	10.4	1.2	0.8	8.8
10	—	6.71	7.23	7.65	—	—	—	10.0	—	—	—

^{a} J values are in Hz.

methanol. Absorbance measurements are given in Table 3. Since methoxide concentrations up to 0.5 mol dm^{-3} were used there is some deviation from ideal behaviour, so that basicities were represented by an acidity function. For **2c**, a value of p$K_a = 16.0 \pm 0.1$ was obtained using

$$pK_a = J_M - \log IR \qquad (3)$$

**Table 3.** Ionisation of **2c** in methanolic sodium methoxide^a

[NaOMe]/mol dm^{-3}	$J_M{}^b$	Abs,^{c} 340 nm	p$K_a{}^d$
0.0167	15.15	0.204	16.04
0.0333	15.46	0.384	16.03
0.0500	15.66	0.548	16.02
0.0833	15.90	0.724	16.07
0.117	16.09	0.953	16.04
0.167	16.32	1.13	16.09
0.250	16.45	1.17	15.94
0.333	16.58	1.49	15.89

^{a} Concentration of **2c** is 4.2×10^{-5} mol dm^{-3}.
^{b} From Ref. 27.
^{c} The limiting absorbance at high [NaOMe] is 1.80.
^{d} Calculated as J_M—log(Abs/1.80—Abs).

Table 4. Ionisation of **2b** (4.2×10^{-5} mol dm^{-3}) and **2a** (6.67×10^{-5} mol dm^{-3}) in methanol-DMSO mixtures containing sodium methoxide (0.025 mol dm^{-3})

| Mol % DMSO | $J_M{}^a$ | **2b** | | **2a** | |
		Abs, 315 nm	p$K_a{}^c$	Abs, 290 nm	p$K_a{}^c$
0	15.32	0.012	—	—	—
3.9	15.70	0.025	17.41	—	—
8.1	16.10	0.052	17.48	—	—
12.5	16.60	0.159	17.45	—	—
17.2	17.10	0.327	17.57	—	—
22.2	17.54	0.585	17.46	0.0156	19.60
33.3	18.45	—	—	0.114	19.62
36.3	18.72	1.19	—	—	—
39.4	19.02	—	—	0.520	19.41
46.1	19.64	—	—	1.160	19.40
53.3	20.19	1.30^b	—	1.59	—
61.0	20.88	—	—	1.80	—
67.0	21.42	—	—	1.80^b	—

^{a} Calculated from values in Ref. 28.
^{b} Taken as value for limiting absorbance at high basicity.
^{c} Calculated from Eqn. (3).

For **2a** and **2b** it was not possible to obtain high conversion into the respective carbanions using methanol alone. Here the basicity of the medium was increased using methanol-DMSO mixtures.[27] As before[18] the sodium methoxide concentration was kept constant at 0.025 mol dm^{-3} and the ratio of DMSO to methanol was varied. Both H_M values, relating to proton loss, and J_M values, relating to base addition, are available[27] for solutions of sodium methoxide in methanol-DMSO. The H_M values reported in the literature were measured using amine indicators, while the J_M values were obtained from the reaction, shown in Eqn. (4) of methoxide ions with α-cyanostilbenes.[28] This reaction involves formation of a carbanion which resembles those formed by the ionisation of the benzyltriflones. Hence these results were used to reflect the basicities of the media used in the present work. The results in Table 4 give a value of p$K_a = 17.5 \pm 0.1$ for **2b** and p$K_a = 19.5 \pm 0.1$ for **2a**.

$$(4)$$
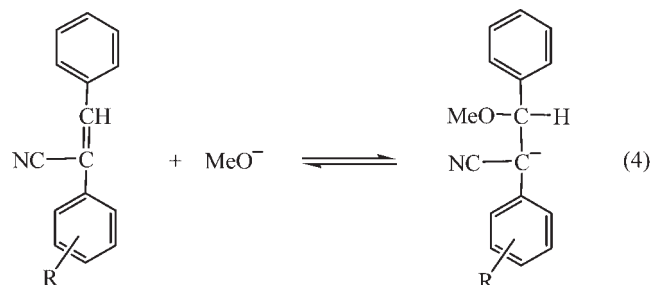
Kinetic measurements

These were made in methanol with 4-nitrobenzofurazan, **6a**, and its 7-chloro-derivative, **6b**, using carbanions generated by reaction of the benzyl triflones **2a,b,c** with methoxide ions. Since methoxide ions themselves will react with **6a** and **6b** to give σ-adducts,[29,30] and in the case of **6b** a substitution product,[30] the concentrations of methoxide were maintained at very low levels, $ca.$ 10^{-5} mol dm^{-3}, using bromophenol buffers.[19,31] Under these conditions the UV/visible spectra show that in the case of **6a** the absorbance of the parent at 320 nm, ε 9×10^3 dm^3 mol^{-1} cm^{-1}, is gradually replaced by a much stronger absorption band in the visible region. The absorption maxima of the products formed are with **3a** 400 nm, **3b** 409 nm and **3c** 420 nm with values ε
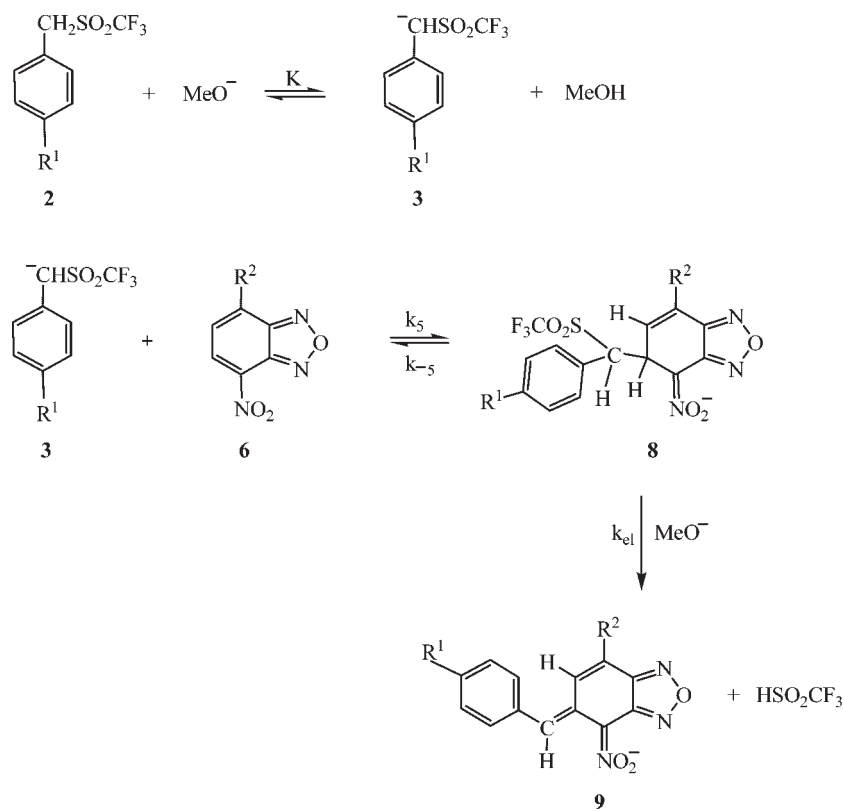
Scheme 1. Reactions of benzyltriflone anions with 4-nitrobenzofurazans in methanol

$2.5–3.0 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$. It is known that σ-adducts formed by either methoxide[29] or carbanion[18,19] attack at unsubstituted ring positions of **6a** have maxima at *ca.* 335 nm, ε $1.5 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$. Hence the new bands are not simply due to this process. The shift to longer wavelength and increase in absorbance are compatible with the increased possibilities of delocalisa-

tion in the products, **9**, of elimination of trifluoromethyl-sulfinic acid from the initially formed adducts, **8**. Hence we interpret our results in terms of Scheme 1.

Measurements at the absorption maxima of the products showed good first-order kinetics with values of rate constants, k_{obs}, given in Table 5. The amplitudes of the absorbance change did not depend on the carbanion

Table 5. Kinetic results for reactions of **6a**[a] with **3a,b,c** in methanol at 25°C

Benzyltriflone

$[2a]/mol\,dm^{-3}$	$[MeO^-]_{eq}{}^{b}/10^{-5}\,mol\,dm^{-3}$	$[3a]^{c}/10^{-9}\,mol\,dm^{-3}$	$k_{obs}/10^{-5}\,s^{-1}$	$k_5{}^{d}/10^4\,dm^3\,mol^{-1}\,s^{-1}$
0.053	5.5	7.6	9.8	1.3
0.033	5.5	4.8	7.8	1.6
0.053	2.6	3.6	5.9	1.6

$[2b]/mol\,dm^{-3}$	$[MeO^-]_{eq}{}^{b}/10^{-5}\,mol\,dm^{-3}$	$[3b]^{c}/10^{-7}\,mol\,dm^{-3}$	$k_{obs}/10^{-4}\,s^{-1}$	$k_5/10^3\,dm^3\,mol^{-1}\,s^{-1}$
0.012	5.5	1.7	7.5	4.4
0.007	5.5	1.0	4.7	4.7
0.012	2.6	0.82	3.6	4.4

$[2c]/10^{-4}\,mol\,dm^{-3}$	$[MeO^-]_{eq}{}^{b}/10^{-5}\,mol\,dm^{-3}$	$[3c]^{c}/10^{-7}\,mol\,dm^{-3}$	$k_{obs}/10^{-4}\,s^{-1}$	$k_5/10^3\,dm^3\,mol^{-1}\,s^{-1}$
5.7	5.5	2.6	3.6	1.4
3.3	5.5	1.5	2.3	1.5
5.7	2.6	1.2	1.9	1.6

[a] Concentration is $5 \times 10^{-5}\,mol\,dm^{-3}$.
[b] Equilibrium methoxide concentrations in bromophenol buffers.
[c] Calculated using pK_a values determined in this work.
[d] $k_{obs}/[3]$.

Table 6. Kinetic results for the reaction of **6b**[a] with **3b** in methanol at 25°C

[2b]/mol dm^{-3}	[MeO$^-$]$_{eq}$[b]/10^{-5} mol dm^{-3}	[3b][c]/10^{-8} mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	k_5[d]/10^4 dm^3 mol^{-1} s^{-1}
0.012	2.6	8.2	1.2	1.5
0.007	2.6	5.1	0.7	1.4
0.005	5.4	7.5	1.1	1.5

[a] Concentration is 5×10^{-5} mol dm^{-3}.
[b] Equilibrium methoxide concentration in bromophenol buffers.
[c] Calculated using pK_a = 17.5 for **2b**.
[d] k_{obs}/[3b].

concentration indicating that reactions went to completion. There is no spectroscopic evidence for build up in the concentration of the σ-adduct intermediates, **8**, and application of the steady-state principle leads to Eqn. (5). The results in Table 5 show that values of k_{obs} show a linear dependence on the equilibrium

$$k_{obs} = k_5[3] \cdot \frac{k_{el}[MeO^-]}{k_{el}[MeO^-] + k_{-5}} \qquad (5)$$

$$k_{obs} = k_5[3] \qquad (6)$$

concentrations of the carbanion present but are not directly dependent on the equilibrium methoxide concentrations. These dependences correspond to the condition $k_{el}[MeO^-] \gg k_{-5}$, so that Eqn. (5) reduces to Eqn. (6). This indicates that nucleophilic attack by carbanions on the nitrobenzofurazans is rate limiting so that the slopes of plots of k_{obs} versus [3] give values of k_5. We note that if elimination were rate determining values of k_{obs} would be expected to show dependences on both carbanion and methoxide concentrations, which is not the case. Also the reactions are first order in the benzofurazan concentration showing that formation of carbanions **3** from **2** and methoxide is not rate determining. If this were the case then a zero-order dependence on benzofurazan concentration would be expected.

7-chloro-4-nitrobenzofurazan, **6b**, shows an absorption maximum at 337 nm, ε 1.1×10^4 dm^3 mol^{-1} cm^{-1}. In buffered solutions containing the carbanion **3b** a new band slowly develops at 405 nm with an excellent isosbestic point at 360 nm. Kinetic data are shown in Table 6.

However in solutions containing 1,3,5-trinitrobenzene, **5**, methoxide and benzyltriflones there was no evidence for the formation of any species other than the methoxide adduct with λ_{max} 425, 495 nm.

Comparisons

Both the NMR spectra and the kinetic results for reaction of nitrobenzofurazans with **3** indicate that the elimination of trifluoromethylsulfinic acid from the initially formed σ-adduct intermediates is a relatively rapid process. Nevertheless, the kinetic data allow the determination of rate constants for nucleophilic attack and these are summarised in Table 7. The usual behaviour of 4-nitrobenzofurazan and its derivatives in reactions with nucleophiles is that 5-adducts are kinetically favoured while the isomeric 7-adducts are thermodynamically more stable.[18,19,29,30,32,33] The kinetic results in Table 7 are also in accord with reaction at the 5-position. Thus, the threefold faster reaction of carbanion **3b** with **6b** (where reaction is unlikely to be observed at the 7-position)[19,34] than with **6a** is consistent with the electronic effect of the 7-chloro substituent exerted at the 5-position.[19,30,32]

We have shown recently[19] that in reactions with nitroalkane anions in methanol the electrophilicities of 1,3,5-trinitrobenzene, **5**, and 4-nitrobenzofurazan, **6a**, are similar. Thus the lack of reaction of **5** with the carbanions **3** is surprising. It is likely to be due to the large bulk of benzyltriflone anions which would result in unfavourable steric interactions in adducts from **5** where reaction must

Table 7. Summary of kinetic and acidity data in methanol

		k_5/dm^3 mol^{-1} s^{-1}	
Carbanion	pK_a[a]	**6a**	**6b**
3a	19.5	1.5×10^4	—
3b	17.5	4.5×10^3	1.5×10^4
3c	16.0	1.5×10^3	—
11[b]	19.3	1.4×10^8	—
12[c]	15.6	300	—

[a] Values for corresponding acids.
[b] Data from Ref. 18.
[c] Data from Ref. 19.

occur at a ring carbon flanked by two nitro groups. Some steric strain has previously[19] been inferred in the adduct formed from **5** and the 2-nitropropenide anion. The 7-position of 4,6-dinitrobenzofuroxan, **4**, is likely to be more hindered than the 5-position of **6**, but the very high electrophilicity of **4** ensures that adduct formation with **3** is observed.

Further evidence for the high steric requirements of the benzyltriflone anions comes from a linear plot, not shown, of values in Table 7 of log k_5 *versus* pK_a. The slope, β, of the plot is 0.3 which is likely to indicate that bond formation in the transition state for reaction is not well advanced in what is likely to be a strongly favourable reaction. Our results do not allow the determination of the intrinsic reactivity,[14,15] in the Marcus sense, for reaction of the carbanions, **3**, with **6**. However, since the negative charge in **3** will not be strongly delocalised[11–13] values of intrinsic reactivity are likely to be relatively high. It is interesting to compare the values, in Table 7, of rate constants for reaction of **6a** with carbanions **3** with corresponding values for reaction with benzyl cyanide anions, **11**, and nitroalkane anions, **12**. The value of k_5 for reaction of the carbanion, **11**, form 4-cyanobenzylcyanide (pK_a 19.3 in methanol) is 10^4 times higher than the value for **3a**, pK_a 19.5. In both **3a** and **11** the negative
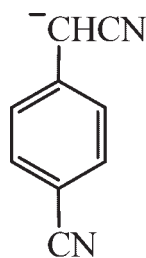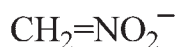
11   **12**

charge is likely to be localised at the carbon centre,[35] so the much lower reactivity of **3a** may be ascribed to steric factors. In fact the nucleophilicity of carbanions **3** is quite similar to that of the nitroalkane anions, such as **12**, whose reactivity is drastically reduced by strong solvation by methanol. These results show that both effects of solvation and steric factors need to be considered when interpreting nucleophilicities.

It is known that adducts formed form **4** and **6** with nitroalkane anions will form alkene derivatives by loss of nitrous acid.[19,23] The mechanism is likely to involve base-catalysed elimination[36] and some rate constants for methoxide catalysed reactions have recently been published.[19] Our results show that adducts **8** will similarly eliminate trifluoromethylsulfinic acid, HSO_2CF_3. Although our measurements do not allow the determination of rate constants for this process, the failure to observe the σ-adduct precursors suggests that elimination is a relatively facile process. There is likely to be some

correlation between the 'leaving group ability' of anions and the pK_a values of the corresponding acids—the lower the pK_a value the better the leaving group. Although the pK_a value of trifluoromethylsulfinic acid has not been determined it is likely to be considerably lower than that of nitrous acid, p$K_a = 3.3$ in water, confirming that $SO_2CF_3^-$ will be a 'good' leaving group.

The NMR results indicate that, in contrast to the adduct **8**, the adduct **7** is resistant to elimination. This may be due to steric congestion at the reaction centre in **7** which hinders the approach of the base present, triethylamine.

EXPERIMENTAL

Nitro-compounds **4**, **5**, **6a** and **6b** were available from previous work.[21,32] The benzyltriflones **2a**, **2b** and **2c** were prepared as previously reported[11,37,38] by refluxing the appropriately substituted benzylbromide with potassium triflinate in acetonitrile for 6 h using potassium iodide as a catalyst; **2a**, m.p. 100°C (literature value[37] 103°C) ^{1}H NMR (DMSO-d$_6$, 400 MHz) 5.25 (2H, s, CH$_2$), 7.47 (5H, m, C$_6$H$_5$), **2b**, m.p. 100°C (literature value[38] 95°C), ^{1}H NMR (DMSO-d$_6$, 400 MHz) 5.45 (2H, s, CH$_2$), 7.72 (2H, d, J 8.2 Hz, H2 and H6), 7.86 (2H, d, J 8.2 Hz, H3 and H5), **2c** m.p. 119°C, ^{1}H NMR (DMSO-d$_6$, 400 MHz) 5.52 (2H, s, CH$_2$), 7.75 (2H, d, 8 Hz, H2 and H6), 8.02 (2H, d, 8 Hz, H3 and H5). Solutions of sodium methoxide were prepared by dissolving clean sodium in AnalaR methanol under nitrogen. Solutions containing very low equilibrium concentrations of methoxide ions were prepared using buffers prepared from 4-bromophenol whose pK_a value[31] in methanol is 13.61. All other materials and solvents were the purest available commercial samples.

^{1}H NMR spectra in DMSO-d$_6$ were recorded at 22°C using a Bruker Avance-400 MHz instrument. UV-visible spectra and kinetic measurements were made at 25°C with a Shimadzu UV-2101 PC spectrophotometer. First-order rate constants, precise to $\pm5\%$ were evaluated using standard methods.

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