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ORIGINAL ARTICLE

# $^1\text{H}$ NMR and kinetics studies of the reaction of 4-methyl, 4-bromo and 3-trifluoromethyl benzyltriflones with aromatic nitro-compounds

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## KEYWORDS

4-Nitrobenzofurazan;  
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**Abstract** Rate measurements are reported for the reactions in methanol of carbanions derived from benzyltriflones, **2a–c**, with 4-nitrobenzofurazan derivatives, **4a** and **4b**, to give anionic  $\sigma$ -adducts.  $^1\text{H}$  NMR studies in  $\text{DMSO}-d_6$  of the reaction of benzyltriflones, **2**, and 4-nitrobenzofurazan, **4a**, in the presence of triethylamine are consistent with products formed by the elimination of trifluoromethyl sulfonic acid from  $\sigma$ -adducts initially formed by carbanion attack at the 5-position of **4a**. Evidence for the high steric requirements of the benzyltriflone anions come from the low value of  $\beta$ ; the slope of the linear plot of values of  $\log k_5$  versus  $\text{p}K_a$ .

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## 1. Introduction

There is considerable current interest in measuring quantitatively nucleophilic and electrophilic reactivities, particularly in carbon–carbon bond forming reactions (Mayr et al., 2001, 2003; Bug and Mayr, 2003). Mayr and coworkers have used the reactions with a series of benzhydryl cations to assess the nucleophilicities of carbanions stabilised by acyl, ester, cyano and nitro-groups (Berger et al., 2007; Bug et al., 2004; Phan and Mayr, 2006). Their results, although providing useful

relationships, show that relative nucleophilicities may be strongly influenced by the solvent, e.g. methanol versus DMSO (Berger et al., 2007; Bug et al., 2004; Phan and Mayr, 2006). Conversely the electrophilicities of some superelectrophiles including 4,6-dinitrobenzofuroxan, DNBF, have been determined by measuring the rate constants for their reactions with some standard nucleophiles, including *N*-methylpyrrole and indole, in acetonitrile (Terrier et al., 2004, 2005; Lakhdar et al., 2007).

This work is concerned with assessing the effects of a trifluoromethyl sulfonyl group on carbanions in their  $\sigma$ -adduct forming reactions with nitrobenzofurazan derivatives. It is known that the  $\text{SO}_2\text{CF}_3$  group is strongly electron-withdrawing and as judged by Hammett  $\sigma$  values (Exner, 1978) is more effective than  $\text{NO}_2$  as a ring substituent in stabilising anionic  $\sigma$ -adducts. Thus the adduct **1** is more stable by a factor of  $10^6$  than the trinitro analogue in methanol (Terrier et al., 1989). However, compared with phenylnitromethane, benzyltriflone has been shown (Bordwell et al., 1980) to be less acidic

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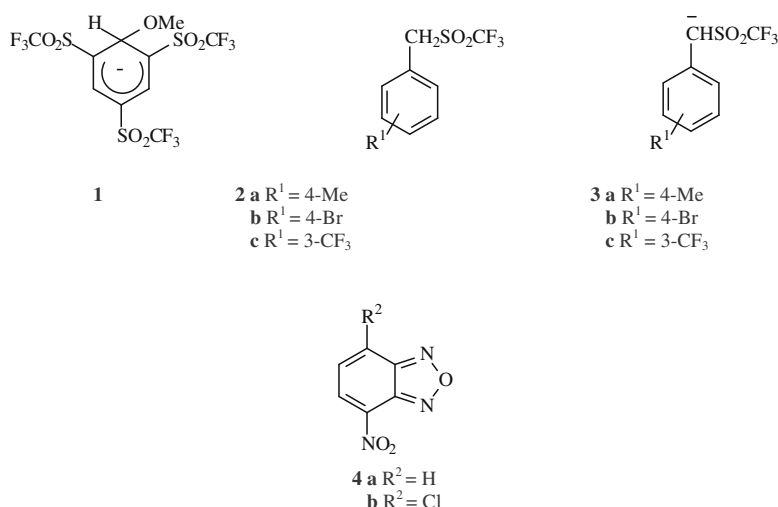


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by two  $pK_a$  units in DMSO. On the other hand, this difference is magnified in water due to the excellent solvation of the nitronate ion by water (Goumont et al., 2003). It was previously reported (Goumont et al., 2003; Terrier et al., 1998, 2005) from kinetic, thermodynamic as well as NMR studies that in carbanions derived from benzyltriflones the negative charge remains largely on the exocyclic  $C_\alpha$  carbon atom where it is stabilised by polarisation effects.

Very recently (Asghar et al., 2008) reactions of the carbanion from bis(phenylsulfonyl)methane were studied. Rate constants in methanol as a solvent were reported for formation of the initial  $\sigma$ -adducts with some 4-nitrobenzofurazan derivatives and with 4-nitrobenzofuroxan and also for the methoxide catalysed elimination of phenyl sulfinic acid.

Here, I report on the  $^1H$  NMR studies in DMSO- $d_6$  of the  $\sigma$ -adduct forming reactions of the carbanion **3b** derived from the benzyltriflone **2b** with electrophiles **4a**. The results of kinetic studies of the reactions in methanol of carbanions derived from ring-substituted benzyltriflone anions **3a–c** with nitrobenzofurazan derivatives **4a** and **4b** allow comparison of results with other carbanions (Cox et al., 1988; Crampton et al., 1986; Atherton et al., 1995; Asghar and Crampton, 2007a,b).



## 2. Experimental

### 2.1. Materials

Nitro-compounds **4a** and **4b** were available from previous work (Crampton et al., 2002, 1999). The benzyltriflones **2a–c** were prepared as previously reported (Goumont et al., 2003, 1997; Hendrickson et al., 1974) by refluxing the appropriately substituted benzylbromide with potassium triflate in acetonitrile for 6 h using potassium iodide as a catalyst.

Solutions of sodium methoxide were prepared by dissolving 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 (Rochester and Rossall, 1967) in methanol is 13.61. All other materials and solvents were the purest available commercial samples.

### 2.2. Spectroscopy data for benzyltriflones

**2a**, m.p. 94 °C, yield = 71%. The mass spectrum (EI) showed a line at 238 corresponding to  $C_9H_9SO_2F_3$  ( $M^+$ ).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz), 2.4 (3H, s,  $CH_3$ ), 5.20 (2H, s,  $CH_2$ ), 7.36 (2H, d,  $J$  8 Hz, H2 and H6), 7.26 (2H, d,  $J$  8 Hz, H3 and H5), **2b**, m.p. 104 °C, yield = 38%. The mass spectrum (EI) showed a line at 302 corresponding to  $C_8H_6SO_2F_3Br$  ( $M^+$ ).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz) 5.30 (2H, s,  $CH_2$ ), 7.45 (2H, d,  $J$  8.2 Hz, H2 and H6), 7.69 (2H, d,  $J$  8.2 Hz, H3 and H5), **2c**, m.p. 170 °C, yield = 65%. The mass spectrum (EI) showed a line at 292 corresponding to  $C_9H_6SO_2F_6$  ( $M^+$ ).  $^1H$  NMR (DMSO- $d_6$ , 400 MHz) 5.49 (2H, s,  $CH_2$ ), 7.88 (1H, s, H1), 7.81 (1H, d,  $J$  8 Hz, H2), 7.73 (1H, t,  $J$  8 Hz, H3), 7.86 (1H, d,  $J$  8 Hz, H4).

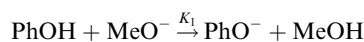
### 2.3. Instruments used

- Mass spectrum was recorded on Pegasus (III) Drive 2.15 Leco.
- $^1H$  NMR spectra in DMSO- $d_6$  were recorded at 24 °C using a Bruker Avance-400 MHz instrument.

- UV-visible spectra and kinetic measurements were made at 25 °C with SPE Cord Analytic Jena. First-order rate constants, precise to  $\pm 5\%$  were evaluated using standard methods.

### 2.4. Kinetic analysis (a specimen calculation)

In solutions containing bromophenol, represented as (PhOH), and methoxide ions in methanol the following equilibrium will exist:

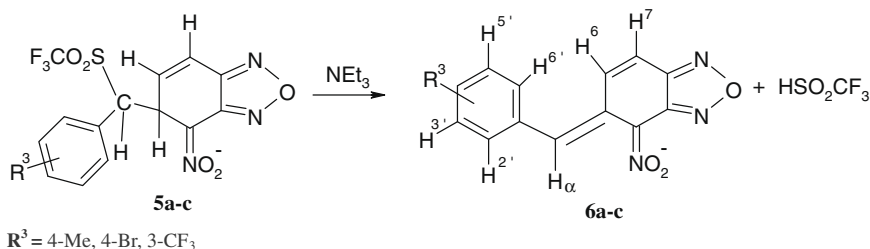


The equilibrium constant for this process is  $K_1$ , and the equilibrium methoxide concentration may be calculated using Eq. (1).

$$[\text{MeO}^-] = \frac{[\text{PhO}^-]}{[\text{PhOH}]} \frac{1}{K_1} \quad (1)$$

The value of  $K_1$  is related to the  $pK_a$  value of bromophenol, known to be 13.61 (Rochester and Rossall, 1967) in methanol, by Eq. (2). Here  $pK_m$  refers to the autoprotolysis constant of methanol Eq. (3) and has the value of  $pK_m = 16.92$  (Rochester, 1970). The value obtained for  $K_1$  is  $2040 \text{ dm}^3 \text{ mol}^{-1}$ .

$$\log K_1 = pK_m - pK_a \quad (2)$$



Since the value of  $K_1$  is relatively high, the equilibrium concentration of methoxide will be very low, and most of the base present will be converted to phenoxide. For example when  $[\text{PhOH}] = 0.038 \text{ mol dm}^{-3}$  and  $[\text{PhO}^-] = 0.002 \text{ mol dm}^{-3}$ , the equilibrium concentration of methoxide is  $2.58 \times 10^{-5} \text{ mol dm}^{-3}$ .

$$[\text{MeO}^-]_{\text{eq}} = \frac{0.002}{0.038} \frac{1}{2040} = 2.58 \times 10^{-5} \text{ mol dm}^{-3} \quad (4)$$

This is the equilibrium concentration of methoxide in the first run in Table 3. Since this concentration is buffered it will not be changed in the presence of the benzyltriflones.

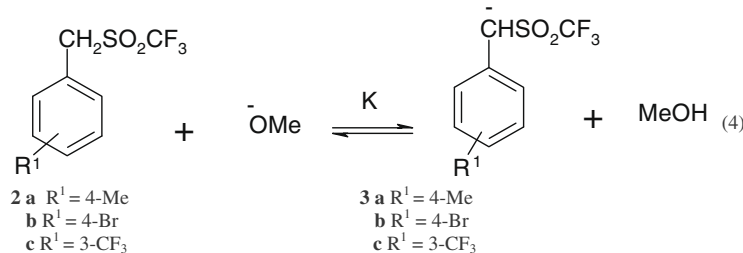
Interestingly the spectrum does not correspond to that expected (Asghar and Crampton, 2007a) for the  $\sigma$ -adduct **5a** but is attributable to **6a**; the product of elimination of trifluoromethyl sulfinic acid from **5a**.

Chemical shifts are shown in Table 1 for **4a** with **2a-c** in the presence of triethylamine. The shifts of H6, H7 and H $\alpha$  are similar to those (Asghar and Crampton, 2007a) of the related alkene formed by the elimination of nitrous acid from the nitroethane adduct of **4a**. Further justification that reaction occurs at the 5-position rather than the 7-position will be given later.

### 3.2. $pK_a$ values

Since kinetic measurements were made in methanol it was necessary to determine  $pK_a$  values of the benzyltriflones in this solvent. Carbanions **3a-c** were generated from the benzyltriflones **2a-c** by reaction with sodium methoxide in methanol, as shown in Eq. (4). Values of the ionisation ratio, IR, defined by Eq. (5), were determined spectrophotometrically using the strong UV absorbance of the benzyltriflone anions. It was found that the benzyltriflones **2a-c** showed UV absorbance maxima at ca. 261.

Absorption maxima were at 288 nm for **3a**, 294 nm for **3b** and 295 nm for **3c**.



For each of benzyltriflones the value obtained by dividing  $k_{\text{obs}}$  by [carbanion] was constant. The general expression for equilibration of carbanion and benzofurazan to give adduct **5** is Eq. (8).

## 3. Results and discussion

### 3.1. <sup>1</sup>H NMR results

The spectrum of 4-nitrobenzofurazan, **4a**,  $0.04 \text{ mol dm}^{-3}$ , with **2a-c**,  $0.05 \text{ mol dm}^{-3}$ , and triethylamine,  $0.1 \text{ mol dm}^{-3}$ , was measured within 25 min of mixing.

$$\text{IR} = \frac{[3]}{[2]} \quad (5)$$

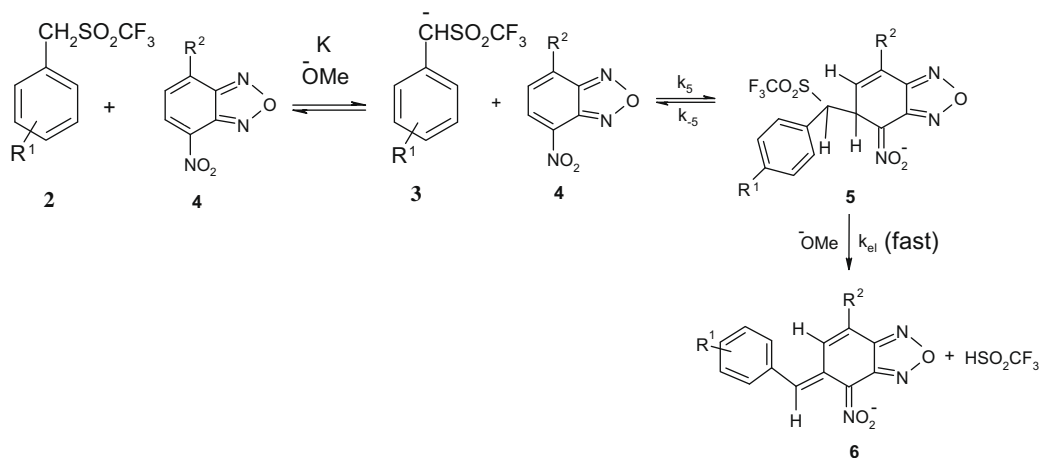
For **2a-c** it was not possible to obtain high conversion into the respective carbanions using methanol alone. Here the basicity of the medium was increased using methanol–DMSO mixtures (Rochester, 1970). As before (Atherton et al., 1995) the sodium methoxide concentration was kept constant at  $0.025 \text{ mol dm}^{-3}$  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 (Rochester, 1970) for solutions of sodium methoxide in methanol–DMSO. The  $H_M$  values reported in the literature were measured using amine

**Table 1**  $^1\text{H}$  NMR data<sup>A</sup> for **4a** with **2a–c** and **6a** in  $\text{DMSO-}d_6$ .

Compound	$\delta$										
	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	CH <sub>2</sub>	H <sub>2',6'</sub>	H <sub>3',5'</sub>	<i>J</i> <sub>5,6</sub>	<i>J</i> <sub>6,7</sub>	<i>J</i> <sub>H<sub>7</sub>H<sub>2</sub></sub>	<i>J</i> <sub>H<sub>6</sub>H<sub>2</sub></sub>	<i>J</i> <sub>2',3'</sub>
<b>4a</b>	8.70	7.85	8.61	–	–	–	7.2	8.8	–	–	–
<b>2a</b>	–	–	–	5.20	7.36	7.26	–	–	–	–	8.0
<b>6a</b>	–	6.20	7.07	6.80	7.31	7.22	–	10.2	1.2	0.8	8.8
<b>2b</b>	–	–	–	5.30	7.45	7.69	–	–	–	–	8.2
<b>6b</b>	–	6.33	7.19	6.98	7.40	7.63	–	10.4	1.2	0.8	8.8
<b>2c</b>				CH <sub>2</sub>	H <sub>2',H<sub>4'</sub>H<sub>5'</sub>H<sub>6'</sub></sub>						
				5.49	7.73–7.86						
<b>6c</b>				CH <sub>2</sub>	H <sub>2',H<sub>4'</sub>H<sub>5'</sub>H<sub>6'</sub></sub>				<i>J</i> <sub>6,7</sub>	<i>J</i> <sub>H<sub>6</sub>H<sub>2</sub></sub>	
	–	6.41	7.28	7.05	7.70–7.83			10.4	10.4	0.8	

<sup>A</sup> *J* values are in Hz.**Table 2** Ionisation of **2a–c** ( $4.2 \times 10^{-5}$  mol dm<sup>-3</sup>) in methanol DMSO mixtures containing sodium methoxide (0.025 mol dm<sup>-3</sup>).

Mol% DMSO	<i>J<sub>M</sub></i> <sup>A</sup>	<b>2a</b> , 4-Me		<b>2b</b> , 4-Br		<b>2c</b> , 3-CF <sub>3</sub>	
		Abs, 288 nm	p <i>K<sub>a</sub></i> <sup>C</sup>	Abs, 294 nm	p <i>K<sub>a</sub></i> <sup>C</sup>	Abs, 295 nm	p <i>K<sub>a</sub></i> <sup>C</sup>
0	15.32	–	–	–	–	–	–
3.9	15.70	–	–	0.0009	18.68	–	–
8.1	16.10	–	–	–	–	–	–
12.5	16.60	–	–	0.01	18.54	0.06	17.66
17.2	17.10	–	–	0.03	18.55	0.07	17.88
33.3	18.45	0.013	20.25	0.34	18.65	0.40	17.85
36.3	18.72	–	–	–	–	0.45	17.77
39.4	19.02	0.044	20.28	0.63	18.62	0.47	17.80
46.1	19.64	0.167	20.25	0.79	18.69	0.50 <sup>B</sup>	–
53.3	20.19	0.350	20.34	–	–	–	–
61.0	20.88	0.740	20.01	–	–	–	–
67.0	21.42	0.84 <sup>B</sup>	–	–	–	–	–
70.0	22.30	–	–	0.88 <sup>B</sup>	–	–	–

<sup>A</sup> Calculated from values in Crampton et al. (1999).<sup>B</sup> Taken as value for limiting absorbance at high basicity.<sup>C</sup> Calculated from Eq. (6).**Scheme 1** Reactions of 4-nitrobenzofurazan derivatives with carbanions benzyltriflones.

indicators, while the  $J_M$  values were obtained from the reaction of methoxide ions with  $\alpha$ -cyanostilbenes (Stewart and Kroeger, 1967). This reaction involves formation of a carban-

ion 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

of  $pK_a = 20.23 \pm 0.1$  for **2a**,  $18.62 \pm 0.1$  for **2b** and  $17.80 \pm 0.1$  for **2c** were obtained using Eq. (6) and summarized in Table 2.

$$pK_a = J_M - \log IR \quad (6)$$

### 3.3. Kinetic measurements

These were made in methanol with 4-nitrobenzofurazan, **4a**, and its 7-chloro-derivative, **4b**, using carbanions generated by reaction of the benzyltriflones **2a–c** with methoxide ions. Since methoxide ions themselves will react with **4a** and **4b** to give  $\sigma$ -adducts (Terrier et al., 1980; DiNunno et al., 1975) and in the case of **4b** a substitution product (DiNunno et al., 1975) the concentrations of methoxide were maintained at very low levels, *ca.*  $10^{-5}$  mol dm<sup>-3</sup>, using bromophenol buffers (Asghar and Crampton, 2007a; Rochester and Rossall, 1967). Under these conditions the UV-visible spectra show

that in the case of **4a** the absorbance of the parent at 320 nm,  $\epsilon = 2.9 \times 10^3$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, is gradually replaced by a much stronger absorption band in the visible region. The absorption maxima of the products formed are with **3a** 399 nm, **3b** 407 nm and **3c** 410 nm with values  $\epsilon = 1.5$ – $2.5 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>.

It is known that  $\sigma$ -adducts formed by either methoxide (Terrier et al., 1980) or carbanion (Atherton et al., 1995; Asghar and Crampton, 2007a) attack at unsubstituted ring positions of **4a** have maxima at *ca.* 335 nm,  $\epsilon = 1.5 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. 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 delocalization in the products, **6**, obtained from elimination of trifluoromethyl sulfinic acid from the initially formed adducts, **5**.

Hence we interpret our results in terms of Scheme 1. Measurements at the absorption maxima of the products

**Table 3** Kinetic results for reactions of **4a**<sup>A</sup> with **3a–c** in methanol at 25 °C.

[ <b>2a</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3a</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0107	$2.58 \times 10^{-5}$	$1.352 \times 10^{-10}$	$4.0 \times 10^{-6}$	$2.96 \times 10^4$
0.0087	$2.58 \times 10^{-5}$	$1.089 \times 10^{-10}$	$3.2 \times 10^{-6}$	$2.94 \times 10^4$
0.0070	$2.58 \times 10^{-5}$	$0.880 \times 10^{-10}$	$2.6 \times 10^{-6}$	$2.94 \times 10^4$
[ <b>2b</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3b</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0107	$2.58 \times 10^{-5}$	$5.507 \times 10^{-9}$	$5.5 \times 10^{-5}$	$9.99 \times 10^3$
0.0087	$2.58 \times 10^{-5}$	$4.457 \times 10^{-9}$	$4.5 \times 10^{-5}$	$10.10 \times 10^3$
0.0070	$2.58 \times 10^{-5}$	$3.603 \times 10^{-9}$	$3.6 \times 10^{-5}$	$9.99 \times 10^3$
[ <b>2c</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3c</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0107	$2.58 \times 10^{-5}$	$3.64 \times 10^{-8}$	$2.2 \times 10^{-4}$	$6.00 \times 10^3$
0.0087	$2.58 \times 10^{-5}$	$2.95 \times 10^{-8}$	$1.8 \times 10^{-4}$	$6.10 \times 10^3$
0.0070	$2.58 \times 10^{-5}$	$2.37 \times 10^{-8}$	$1.5 \times 10^{-4}$	$6.20 \times 10^3$

<sup>A</sup> Concentration is  $3.3 \times 10^{-5}$  mol dm<sup>-3</sup>.

<sup>B</sup> Equilibrium methoxide concentrations in bromophenol buffers.

<sup>C</sup> Calculated using  $pK_a$  values determined in this work.

<sup>D</sup>  $k_{\text{obs}}/[3]$ .

**Table 4** Kinetic results for reactions of **4b**<sup>A</sup> with **3a–c** in methanol at 25 °C.

[ <b>2a</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3a</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0110	$2.58 \times 10^{-5}$	$1.39 \times 10^{-10}$	$1.17 \times 10^{-5}$	$8.40 \times 10^4$
0.0110	$5.45 \times 10^{-5}$	$2.94 \times 10^{-10}$	$2.40 \times 10^{-5}$	$8.20 \times 10^4$
0.0066	$5.45 \times 10^{-5}$	$1.78 \times 10^{-10}$	$1.50 \times 10^{-5}$	$8.40 \times 10^4$
[ <b>2b</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3b</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0110	$2.58 \times 10^{-5}$	$5.66 \times 10^{-9}$	$1.85 \times 10^{-4}$	$3.27 \times 10^4$
0.0110	$5.45 \times 10^{-5}$	$11.96 \times 10^{-9}$	$3.90 \times 10^{-4}$	$3.26 \times 10^4$
0.0066	$5.45 \times 10^{-5}$	$7.24 \times 10^{-9}$	$2.38 \times 10^{-4}$	$3.29 \times 10^4$
[ <b>2c</b> ] (mol dm <sup>-3</sup> )	[MeO <sup>-</sup> ] <sub>eq</sub> <sup>B</sup> (mol dm <sup>-3</sup> )	[ <b>3c</b> ] <sup>C</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}/s^{-1}$	$k_5^D$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
0.0110	$2.58 \times 10^{-5}$	$3.75 \times 10^{-8}$	$7.0 \times 10^{-4}$	$1.87 \times 10^4$
0.0110	$5.45 \times 10^{-5}$	$7.91 \times 10^{-8}$	$14.7 \times 10^{-4}$	$1.86 \times 10^4$
0.0066	$5.45 \times 10^{-5}$	$4.79 \times 10^{-8}$	$9.0 \times 10^{-4}$	$1.88 \times 10^4$

<sup>A</sup> Concentration is  $3.3 \times 10^{-5}$  mol dm<sup>-3</sup>.

<sup>B</sup> Equilibrium methoxide concentrations in bromophenol buffers.

<sup>C</sup> Calculated using  $pK_a$  values determined in this work.

<sup>D</sup>  $k_{\text{obs}}/[3]$ .

**Table 5** Summary of kinetic and acidity data in methanol.

Carbanion	pK <sub>a</sub> <sup>A</sup>	k <sub>5</sub> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	
		4a	4b
4-Me	20.23	2.95 × 10 <sup>4</sup>	8.30 × 10 <sup>4</sup>
4-Br	18.62	10.00 × 10 <sup>3</sup>	3.27 × 10 <sup>4</sup>
3-CF <sub>3</sub>	17.80	6.10 × 10 <sup>3</sup>	1.87 × 10 <sup>4</sup>
H <sup>B</sup>	19.50	1.5 × 10 <sup>4</sup>	–
4-CF <sub>3</sub> <sup>B</sup>	17.50	4.5 × 10 <sup>3</sup>	1.5 × 10 <sup>4</sup>
4-CN <sup>B</sup>	16.00	1.5 × 10 <sup>3</sup>	–

<sup>A</sup> Values for corresponding acids.

<sup>B</sup> From Asghar and Crampton (2007b).

showed good first-order kinetics with values of rate constants,  $k_{\text{obs}}$ , given in Table 3. The amplitudes of the absorbance change did not depend on the carbanion concentration indicating that reactions went to completion. There is no spectroscopic evidence to build up in the concentration of the  $\sigma$ -adduct intermediates, **5**, and application of the steady-state principle leads to Eq. (7). The results in Table 3 show that values of  $k_{\text{obs}}$  give a linear dependence on the equilibrium concentrations of the carbanion present but are not directly dependent on the equilibrium methoxide concentrations. These dependences correspond to the condition  $k_{\text{el}}[\text{MeO}^-] \geq k_{-5}$ , so that Eq. (7) reduces to Eq. (8).

$$k_{\text{obs}} = k_5[\mathbf{3}] \cdot \frac{k_{\text{el}}[\text{MeO}^-]}{k_{\text{el}}[\text{MeO}^-] + k_{-5}} \quad (7)$$

$$k_{\text{obs}} = k_5[\mathbf{3}] \quad (8)$$

This indicates that nucleophilic attack by carbanions on the nitrobenzofurazans is rate limiting so that the slopes of plots of  $k_{\text{obs}}$  versus (Bug and Mayr, 2003) give values of  $k_5$ . I note that if elimination were rate determining values of  $k_{\text{obs}}$  would be expected to show dependences on both carbanion and methoxide concentrations, which is not the case. Additionally 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.

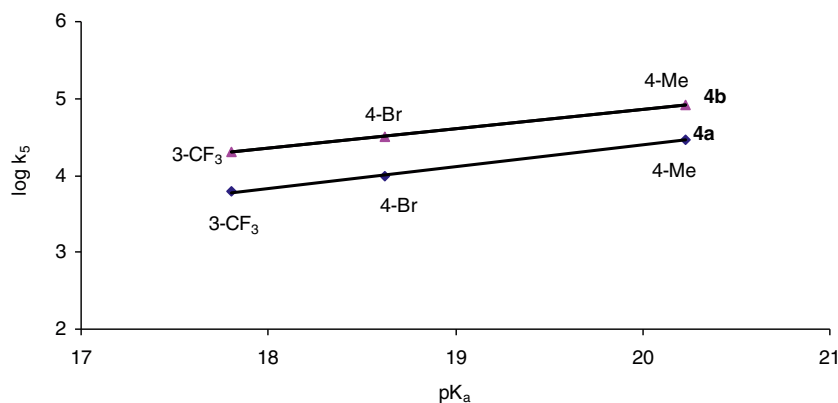
7-Chloro-4-nitrobenzofurazan, **4b**, shows an absorption maximum at 337 nm,  $\epsilon = 7.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Measure-

ments at the absorption maxima of the products showed good first-order kinetics with values of rate constants,  $k_{\text{obs}}$ , given in Table 4. Summary of kinetics data are shown in Table 5.

#### 4. Conclusions

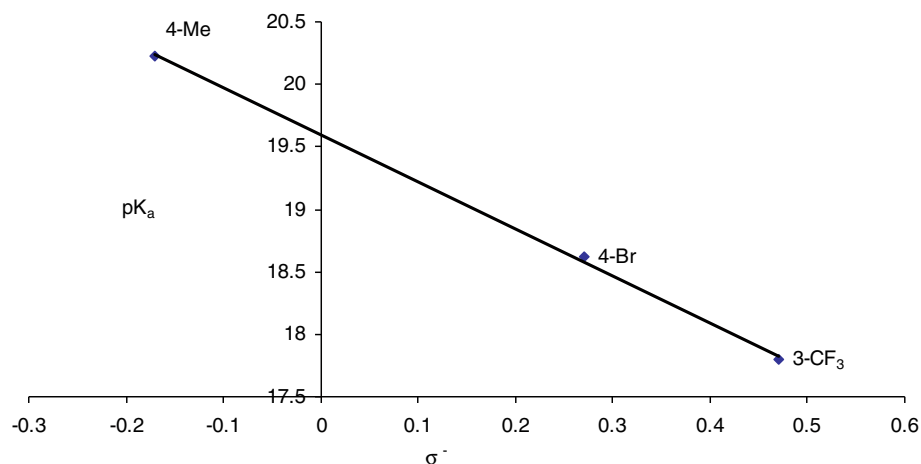
From both the NMR spectra and the kinetic studies for reaction of nitrobenzofurazans with **3** the following conclusions were inferred:

1. The reaction proceeds via the initial formation of sigma adduct intermediates **5a–c** and is followed by the rapid elimination of trifluoromethyl sulfinic acid from the adducts to give the corresponding alkenes **6a–c**.
2. The kinetic data in Table 5 allows the determination of rate constants for nucleophilic attack of the carbanion **3** with **4** and are in accord with reaction at position 5. The usual behaviour of 4-nitrobenzofurazan and its derivatives in reactions with nucleophiles is that 5-adducts are kinetically favored while the isomeric 7-adducts are thermodynamically more stable (Atherton et al., 1995; Asghar and Crampton, 2007a; Terrier et al., 1980; DiNunno et al., 1975; Crampton et al., 2002, 1999).
3. The threefold faster reaction of carbanion **3** with **4b** than with **4a** is consistent with the electronic effect of the 7-chloro substituent exerted at the 5-position (Asghar and Crampton, 2007a; Crampton et al., 2002; DiNunno et al., 1975; Makosza et al., 2004).
4. Although the negative charge is likely to be localized at the carbon center (Terrier et al., 1990) in both carbanions **3** and 4-cyanobenzylcyanide, the value of  $k_5$  for the reaction of 4-cyanobenzylcyanide with **4a** is 10<sup>4</sup> times higher than the value for **3a**. This lower reactivity of **3a** may be attributed to steric factors.
5. Brønsted plots shown in Fig. 1 of log  $k_5$  versus pK<sub>a</sub> values of the benzyltriflones provide further evidence for the high steric requirement of the benzyltriflone anions. Thus the slopes  $\beta$ , of the plots have the values of 0.28 and 0.26 for the 4-nitrobenzofurazan and 7-chloro-4-nitrobenzofurazan, respectively. The lower reactivity of the benzyltriflone carbanions may result from their large bulk which will sterically inhibit their approach to the reaction center.
6. Comparison of the values in Table 5 of rate constant  $k_5$  with corresponding values of previously reported (Asghar and Crampton, 2007b) carbanion derivatives it was



**Figure 1** Brønsted plots of log  $k_5$  versus pK<sub>a</sub> values of the benzyltriflones have slopes,  $\beta$ , of 0.28 and 0.26 for **4a** and **4b**, respectively.





**Figure 2** A plot values of  $pK_a$  versus  $\sigma^-$  give a good straight line with slope  $-3.8$ .

concluded that the 4-methyl benzyl triflone **3a** is the most reactive carbanion while the 4-cyano benzyltriflone is the less reactive one.

- The measurements do not allow the determination of rate constant for the elimination of  $HSO_2CF_3$  from the  $\sigma$ -adduct formed but the failure to observe the  $\sigma$ -adduct precursors suggests that elimination is a relatively facile process.
- As shown in Fig. 2, plot of  $pK_a$  of the benzyl triflones *versus* sigma minus values (Barlin and Perrin, 1966), rather than sigma values are needed because the negative charge on the carbanion can be delocalized onto the ring substituents. The plot gives a good straight line with slope  $-3.8$ , which is in the correct range for a molecule where a negative charge develops adjacent to the aromatic ring.

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