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AMBIDENT REACTIVITY OF ARYLOXIDE IONS TOWARDS 1,3,5-TRINITROBENZENE, LOW-TEMPERATURE CHARACTERIZATION OF THE ELUSIVE OXYGEN-BONDED σ-COMPLEXES BY ^{1}H AND ^{13}C NMR SPECTROSCOPY

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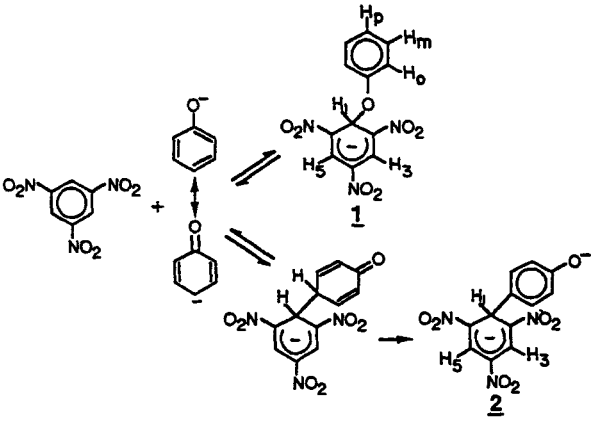
The ambident reactivity of phenoxide ion towards 1,3,5-trinitrobenzene (TNB) was re-examined by means of a novel reaction system (CD_3CN–glyme-d_{10}) which allows the investigation of species formed at low temperatures (−40 °C), contrasting with previous studies in dimethyl sulfoxide (DMSO) at ambient temperature. The new method coupled with 400 MHz NMR spectroscopy has allowed the definitive observation of both *O*- and *C*-bonded phenoxide σ-complex adducts for the first time, confirming the formation of the former through kinetic control and of the latter through thermodynamic control. The corresponding *O*-bonded σ-adduct in the TNB–mesitoxide system (where *C*-bonded σ-adduct formation is not possible but where there is competing nitro group displacement) has also been characterized by ^{1}H and ^{13}C NMR. Another *O*-bonded aryloxide adduct characterized is that from the reaction of TNB with 3,5-di-*tert*-butylphenoxide; in this system there is also competing NO_2 displacement. Stereoelectronic factors in the *O*-bonded σ-adducts and aryl ethers are discussed.

INTRODUCTION

The discovery[1] that phenoxide ion can act as a carbon nucleophile in σ-complex formation with 1,3,5-trinitrobenzene (TNB) has led to intensive explorations of the ambident reactivity of other nucleophilic species, including aniline[2] and indole,[3] towards electron-deficient aromatic and heteroaromatic compounds. Surprisingly, perhaps, in view of the large number of alkoxide adducts of TNB which have been characterized,[4] definitive evidence for the phenoxy oxygen-bonded adduct **1** has been lacking, possibly because of its fleeting nature, whereas the carbon-bonded adduct **2** has lent itself more readily to structure determination. While the supposition that in Scheme 1 the *O*-bonded adduct is kinetically favored and the *C*-bonded adduct is formed under thermodynamic control is plausible, it nevertheless requires experimental substantiation through observation of both adducts in a given system, and the conversion of one species into the other with time.

Previous work on the *O*-bonded phenoxide adduct was conducted in dimethyl sulfoxide (DMSO) as the reaction medium since equilibrium constants for σ-complex formation are known to be greatly enhanced in DMSO relative to hydroxylic media.[5] However, the presence of adventitious water in DMSO-d_6 in such NMR studies, coupled with the known thermodynamic stability of the TNB–hydroxide σ-complex, pose the



Scheme 1

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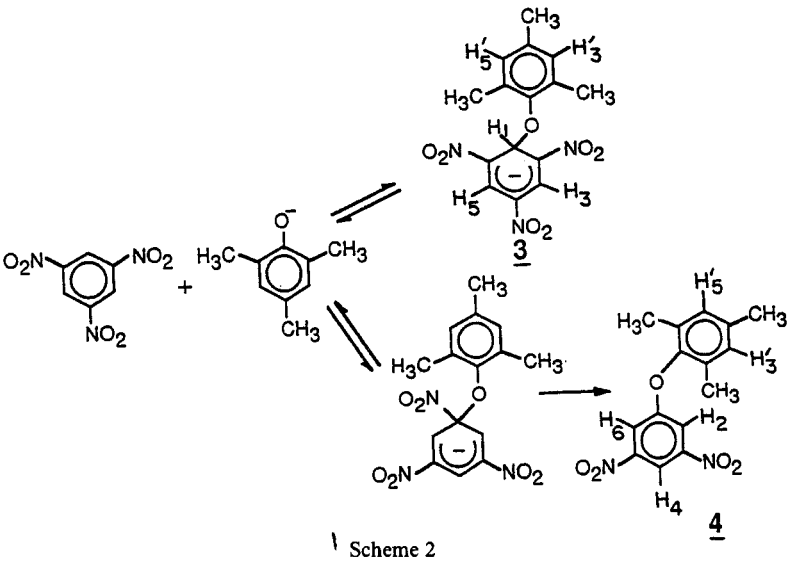


Scheme 2

problem that the competing TNB·OH^- adduct formation could mask the presence of the TNB·OPh^- adduct. In fact, the ^1H NMR spectral characteristics reported in studies by Shein and co-workers[6] for TNB·OPh^- at 60 MHz appear to be indistinguishable from those of the known TNB·OH^- adduct. Subsequent ^{13}C and ^{15}N NMR results by Machacek *et al.*[7] on the *O*-bonded TNB–phenoxide adduct need also be re-examined in this light as well as our own studies[8] on the TNB-2,4,6-trimethylphenoxide *O*-bonded adduct.

In a search for solvent systems alternative to the well studied DMSO system, we have found that acetonitrile–1,2-dimethoxyethane (CD_3CN–glyme-d_{10}, 1 : 1 v/v) provides the advantage of solubilizing many σ-complexes even at temperatures as low as $-50\,^{\circ}C$. This system could thus provide a better opportunity for unambiguous observation and identification of species that might be transient and perhaps not observable at *ca* 25 °C to which DMSO is limited. This work in the novel low-temperature solvent system has, indeed, provided definitive evidence for the formation of *O*-bonded aryloxide adducts. The structural elucidations reported in this study have been greatly aided through the availability of 400 MHz NMR instrumentation, contrasting with the 60 MHz[1,6,8] and 100 MHz[7] instrumentation available in the previous studies.

In a previous study[8] aimed at obtaining evidence for *O*-bonded phenoxide adducts, we examined the reaction of 2,4,6-trimethylphenoxide (mesitoxide) ion with TNB, on the expectation that carbon-adduct formation would be precluded and that *O*-adduct formation would remain as the only feasible process. The study showed, however, that a competing nitro group displacement occurred readily in conjunction with σ-complex formation and that the diaryl ether **4** was the only eventual product observed (Scheme 2). The structure of the σ-complex formed in this system was hence assigned as the expected *O*-bonded mesitoxide adduct (**3**). We have re-examined this system with our present low-temperature technique and we have now been able to identify the authentic adduct **3** and report its ^1H and ^{13}C NMR characteristics. Further confirmation of the structure of *O*-bonded aryloxide complexes has been derived from study of the interaction of TNB with 3,5-di-*tert*-butylphenoxide ion in which *C*-adduct formation is prevented by the bulky *tert*-butyl groups. The NMR parameters for the *O*-bonded σ-adducts and for the aryl ethers obtained following nucleophilic displacement have revealed some interesting facets which are discussed on the basis of stereoelectronic factors.

RESULTS

Reaction of TNB with equimolar PhOK in DMSO

A 400 MHz ^1H NMR study yields the following observations (δ relative to DMSO-d_5H in ppm, J in Hz). Addition of 1·0 equiv of PhOK in DMSO-d_6 to a DMSO-d_6 solution of TNB (final concentrations 0·1 M) produces a dark red solution. In Figure 1 is shown a spectrum of the reaction mixture acquired *ca* 3 min after mixing the reagents. Apparent in the spectrum are peaks representing three distinct σ-adducts. The sp^3-bound protons of the trinitrocyclohexadienate moiety, H_1, of these adducts are observed at δ 6·81 (30%), 6·19 (20%) and 5·51 (40%), while the corresponding ring protons, $H_{3,5}$, are found at δ 8·29, 8·34 and 8·31, respectively. The peaks at δ 8·31 (2H, s) and 5·51 (1H, s) can be at-

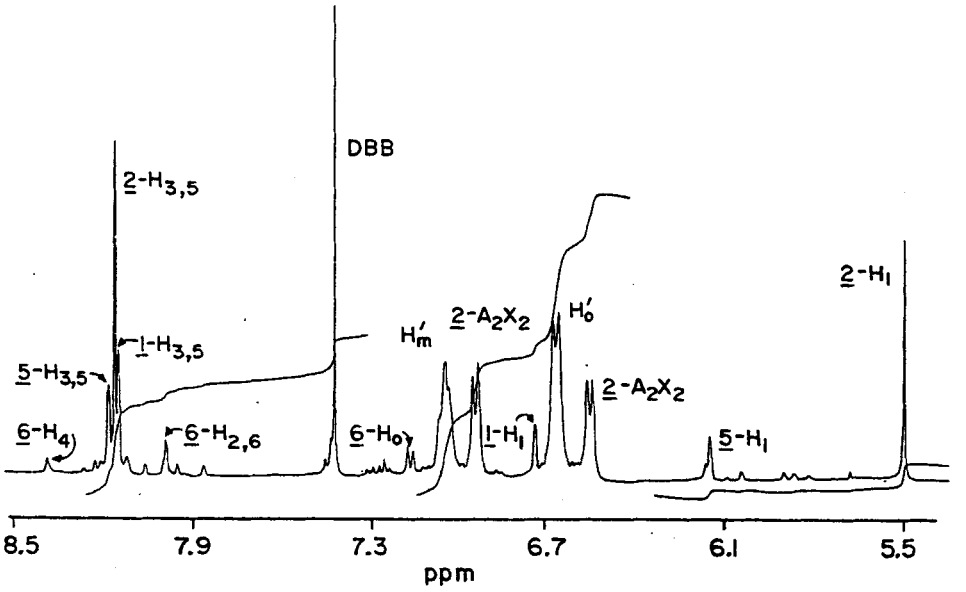


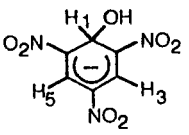
Figure 1. 400 MHz ^{1}H NMR spectrum in the 5·5–8·5 ppm region of TNB–PhOK (1:1) in DMSO-d_6, taken after 3 min reaction time at ambient temperature. Present in the spectrum are signals due to the *para*-carbon bonded adduct **2** and also TNB·OH$^-$ adduct **5**, the aryl either **6** and PhOH/PHO$^-$ ($H_{m'}$ and $H_{o'}$). Tentative assignment of peaks due to the *O*-bonded adduct **1** (**1**-$H_{3,5}$ and **1**-H_1) is also shown. DBB represents 1,4-dibromobenzene

tributed to the *para*-carbon-bonded TNB·PhO$^-$ adduct **2**. The requisite A_2X_2 splitting pattern of the attached phenoxy moiety is observed at δ 7·03 and 6·62 (J = 8·4). The resonances at δ 8·34 and 6·19 are due to the TNB·OH$^-$ adduct **5**, which is produced as a result of equilibration between PhO$^-$ and adventitious H_2O in the solvent. However, the OH resonance of **5** is not observed and its state of ionization is hence uncertain. Further evidence for this assignment was obtained through control experiments involving tetramethylammonium hydroxide (Me_4NOH) with TNB (see below). Assignment of the third adduct (δ 6·81, 8·29) is given subsequently.

Also present in Figure 1 are absorbances at δ 8·56 (1H, t, J = 1·9) and 8·13 (2H, d, J = 1·9). These signals correspond to the diaryl ether **6** resulting from NO_2 displacement. The *ortho*- and *para*-phenoxy protons of **6** are observed at δ 7·26 (2H, m) and 7·35 (1H, m); the *meta*-protons are obscured by the singlet for 1,4-dibromobenzene (DBB, δ 7·52), which served as an integration standard.

On further monitoring of the solution at ambient temperature, the absorbances at δ 8·29 and 6·81 decreased in intensity whereas those due to **2**, **5** and **6** increased. After 30 min the peaks at δ 8·29 and 6·81 were no longer visible and **2** made up 60% of the remaining signals. Also present was a singlet at δ 5·88 ppm, which can be assigned as H_1 of the *ortho*-carbon-bonded TNB·PhOH$^-$ adduct **7**.[1b] This species and **6** accounted for 10% of the reaction mixture. The remaining 30% consisted of resonances of **5** and phenoxy resonances at δ 7·13 (m) and 6·73 (m).

Subsequent monitoring of the reaction over a 5 h period revealed a gradual decline in the resonances due to **5** whereas the signals attributed to **2**, **6** and **7** increased in intensity. Eventually the only complexes in solution were the carbon-bonded species **2** and **7** along with the diaryl ether **6**. The complete structural assignment of **6** was obtained from a separately prepared sample (see Experimental).



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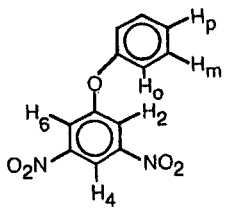

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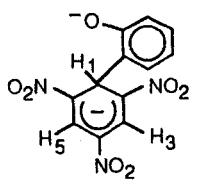

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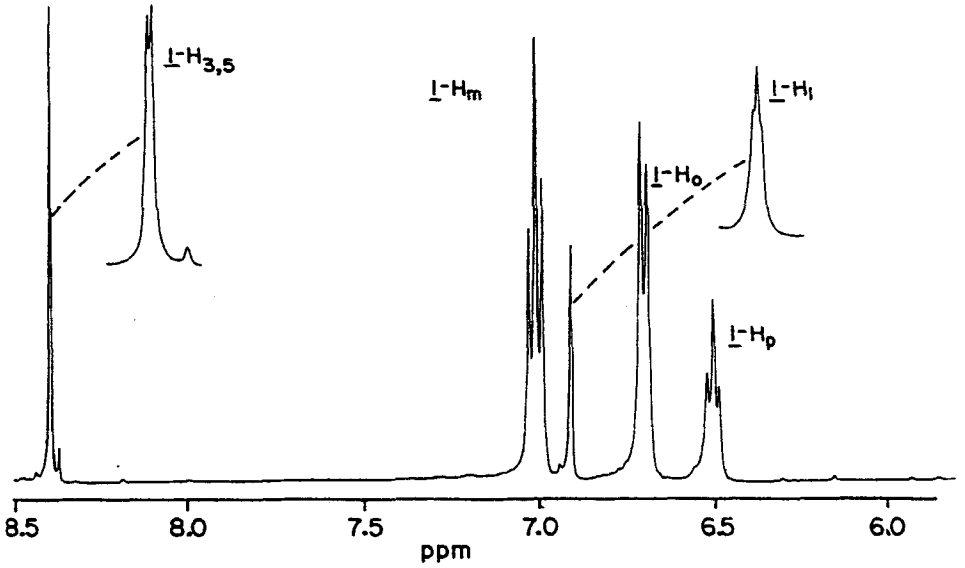


Figure 2a. 400 MHz ^{1}H NMR spectrum in the 6·0–8·5 ppm region of TNB–PhOK (1:1) in CD_3CN–glyme-d_{10} taken after 3 min reaction time at −40 °C. Apparent are signal due to the *O*-bonded TNB·OPh^- adduct **1**

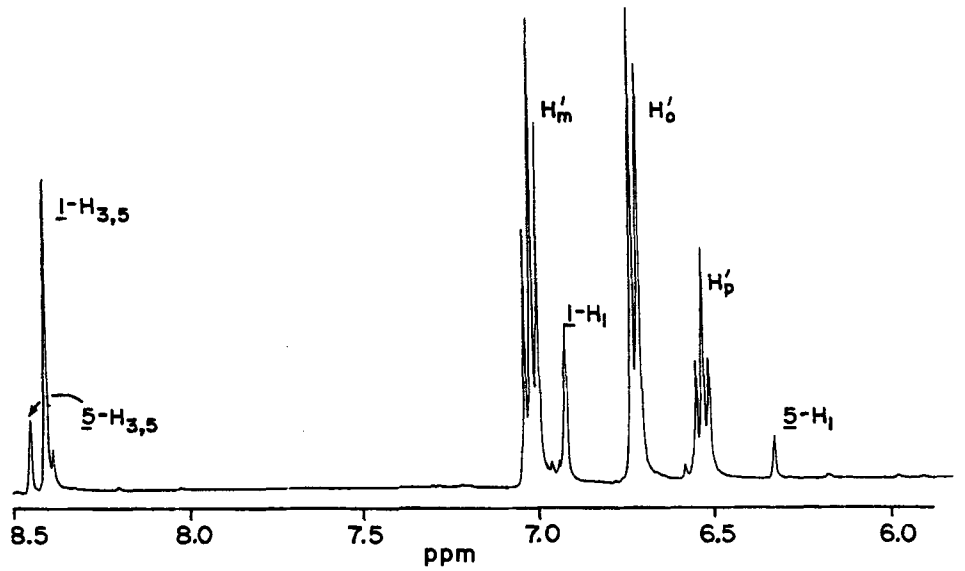


Figure 2b. 400 MHz ^{1}H NMR spectrum in the 6·0–8·5 ppm region of TNB–PhOK (1:1) in CD_3CN–glyme-d_{10} taken after 30 min reaction time at −30 °C. Apparent are signals due to the *O*-bonded TNB·OPh^- adduct **1** in addition to TNB·OH^- adduct **5** and phenoxy peaks ($H_{m'}$, $H_{o'}$ and $H_{p'}$)

In another experiment, 5 μl of trifluoroacetic acid (TFA) was added to the reaction mixture after an initial spectrum was acquired. On acidification the signals due to **5** at δ 8·34 and 6·19 and also those at δ 8·29 and 6·81 disappeared. Following acidification signals due to TNB (9·16, s) reappeared and **2**, **6** and **7** remained unchanged. Acid lability is characteristic of *O*-bonded adducts[9] so that the labile signals are attributable to *O*-adducts formed by TNB.

Since one of the two acid-labile complexes is shown to be **5**, it is reasonable to assign the peaks at δ 8·29 and 6·81 to the TNB·OPh^- adduct **1**. The transient nature of this species is consistent with previous reports indicating that the equilibrium constant for its formation should be small.[10] The present solvent system, however, did not allow assignment of the phenolic portion of the proposed adduct due to overlap with peaks due to free phenol [δ 7·13 (m) and 6·73 (m)] and hence the reaction was repeated in the novel CD_3CN–glyme-d_{10} (1 : 1 v/v) solvent medium, which has the advantage of observation of species at reduced temperatures.

Reaction of TNB with equimolar PhOK in MeCN–glyme

To a solution of TNB in CD_3CN–glyme-d_{10} (1 : 1 v/v), cooled to −40 °C, was added a similarly cooled solution of PhOK in CD_3CN–glyme-d_{10} (final concentrations *ca* 0.1 M). Figure 2(a) shows the initial spectrum of the reaction mixture taken at −40 °C. The resonances can be assigned to a single complex, the oxygen-bonded TNB·OPh^- adduct, **1** (Scheme 1). Peaks in the phenolic region are well resolved at this temperature and consequently the full assignment of **1** in this low-temperature solvent system can be made: δ 8·34 (2H, d, $J = 1·1$, $H_{3,5}$); 6·96 (2H, m, H_{meta}); 6·86 (1H, t, $J = 1·1$, H_1); 6·66 (2H, m, H_{ortho}); 6·46 (1H, m, H_{para}). The ^{13}C NMR parameters of **1** at −40 °C were also obtained.

On subsequent monitoring of the reaction, by gradually allowing the temperature to rise, it was found that the signals that represent **1** decreased in intensity whereas new resonances at δ 8·45 (s, $H_{3,5}$) and 6·31 (s, H_1) due to the hydroxide adduct **5** increased. In Figure 2(b) is shown a spectrum of the reaction mixture at −30 °C, in which peaks of both **1** and **5** are clearly shown. On allowing the solution to warm to 0 °C, resonances attributed to **1** were no longer visible and, in addition to signals for **5**, peaks ascribed to **2** were apparent. On further warming to ambient temperature, and at longer times (>5 h), the only species remaining in solution were found to be **2**, **6**, and a trace of **7**, as in the DMSO experiment.

Reaction of TNB with equimolar Me_4NOH

Reaction of TNB in 70 mol% DMSO-d_6–30 mol% H_2O/D_2O with equimolar Me_4NOH (25 wt% stock solution in H_2O, 11 μl for 1 equiv., made up with D_2O) at ambient temperature leads to the immediate formation of signals assignable to the TNB·OH^- adduct **5** at δ 8·34 (2H, d, $J = 1·0$) and 6·19 (1H, t, $J = 1·0$). Again, a resonance for the hydroxy proton was not observed. The ^{13}C NMR parameters of **5** were acquired to characterize this adduct fully.

Addition of equimolar Me_4NOH (25 wt% in H_2O) to a CD_3CN–glyme-d_{10} (95 mol%) solution of TNB and subsequent monitoring at room temperature showed peaks assignable to **5** and solvent. In this solvent system the signals due to **5** occur at δ 8·45 (2H, d, $J = 1·0$) and 6·31 (1H, t, $J = 1·0$). The small downfield shift of the parameters, compared with those in DMSO-d_6, may reflect differences in hydrogen-bonding properties, etc., of the two solvent systems.[11]

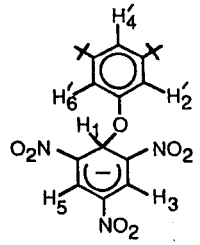
Reaction of TNB with 2,4,6-trimethylphenoxide ion

The interaction of TNB with 2,4,6-trimethylphenoxide ion ($MesO^-$) was re-examined in an effort to establish the structure of oxygen-bonded σ-complexes. In the mesitoxide system attachment via the *ortho* and *para* carbons of the phenoxide is precluded and σ-complex formation can only occur by *O*-attack.

Analogous to the TNB–PhO^- system, the complete structural assignment of the TNB·$OMes^-$ adduct **3** became possible in CD_3CN–glyme-d_{10} at −40 °C. As the temperature of the system was allowed to rise **3** was observed to break down in favor of **5**. The eventual stable product in the system is the diaryl ether **4**, resulting from competing NO_2 displacement (Scheme 2).[8] Experiments carried out in the DMSO-d_6 solvent system gave similar results overall, although the transient nature of **3** at room temperature and problems of peak overlap made assignments less definitive.

Reaction of TNB with 3,5-di-*tert*-butylphenoxide ion

To investigate further the characteristics of the TNB–aryloxide system, 3,5-di-*tert*-butylphenoxide ion ($DTBP^-$) was reacted with TNB. In this system *C*-adduct formation by the *ortho*- or *para*-carbons of the phenoxy moiety is blocked by the bulky *meta-tert*-



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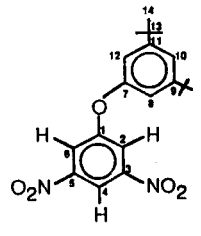

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butyl groups. Accordingly, *O*-attack to produce the TNB·DTBP$^-$ adduct **8** was observed and the adduct was characterized at $-40\,^{\circ}C$ in CD_3CN–glyme-d_{10}. As the temperature of the system was raised to ambient, the diaryl ether **9** became the final product observed.

Summary of observations

NMR parameters of the relevant species are summarized in Tables 1–3. In Table 1 are given the ^1H NMR parameters of the TNB σ-adducts. The parameters for the aryl *O*-adducts (**1**, **3** and **8**) are given for the systems monitored in MeCN–glyme where complete structural assignment was only possible at $-40\,^{\circ}C$. Table 2 contains the ^1H NMR signals obtained for the diaryl ethers. The ^{13}C NMR resonances of the species are listed in Table 3. The *ipso* position, C_7, of the attached aryl ring in the aryloxide σ-adducts was not fully resolved. For comparison with the diaryl ethers, the spectral parameters of 3,5-dinitroanisole (**10**) in DMSO-d_6 are also given.

Table 1. ^1H NMR spectral characteristics[a] of the σ-adducts of TNB in DMSO[b] and MeCN–glyme (1 : 1)[c]

Adduct	H_1	H_3, H_5	Other
1[c,d]	6·86, t, $J = 1·1$	8·34, d, $J = 1·1$	H_o 6·66, m; H_m 6·96, m; H_p 6·46, m
3[c,d]	6·89, t, $J = 1·1$	8·37, d, $J = 1·1$	$H_{3',5'}$ 6·54, s; *o*-Me 2·02, s; *p*-Me 2·05, s
8[c,d]	6·85, t, $J = 1·2$	8·32, d, $J = 1·2$	$H_{2',6'}$ 6·61, s; $H_{4'}$ 6·63, s; *t*-Bu 1·15, s
2[b,e]	5·51, s	8·31, s	A_2X_2 7·03, 6·62; $J = 8·4$
2[c,e]	5·44, s	8·34, s	A_2X_2 6·87, 6·48; $J = 8·6$
5[b,e]	6·19, t, $J = 1·1$	8·34, d, $J = 1·1$	
5[c,e]	6·31, t, $J = 1·0$	8·45, d, $J = 1·0$	
7[b]	5·88, s		

[a] Chemical shifts are given in ppm measured at 400 MHz; coupling constants are in Hz.
[b] DMSO-d_6 at ambient temperature.
[c] CD_3CN–glyme-d_{10} (1 : 1 v/v).
[d] Obtained at $-40\,^{\circ}C$.
[e] Hydroxyl proton not observed.

Table 2. ^1H NMR parameters[a] for the aryl ethers in DMSO[b] and MeCN–glyme (1 : 1)[c]

Ether	H_2, H_6	H_4	Other
6[b,d]	8·13, d, $J = 1·9$	8·56, t, $J = 1·9$	H_o 7·26, m; H_m 7·54, m; H_p 7·35, m
4[b]	7·87, d, $J = 1·9$	8·48, t, $J = 1·9$	$H_{3',5'}$ 7·06, s; *o*-Me 2·05, s; *p*-Me 2·30, s
4[c]	7·86, d, $J = 1·9$	8·53, t, $J = 1·9$	$H_{3',5'}$ 7·07, s; *o*-Me 2·07, s; *p*-Me 2·31, s
9[b,d]	8·09, d, $J = 1·9$	8·53, t, $J = 1·9$	$H_{2',6'}$ 7·07, d, $J = 1·5$; $H_{4'}$ 7·35, t, $J = 1·5$; *t*-Bu 1·29, s
10[b]	8·13, d, $J = 1·9$	8·41, t, $J = 1·9$	O*Me* 4·00, s

[a] Chemical shifts are given in ppm measured at 400 MHz; coupling constants are in Hz.
[b] DMSO-d_6 at ambient temperature.
[c] CD_3CN–glyme-d_{10} (1 : 1 v/v) at ambient temperature.
[d] Obtained from a prepared sample.

Table 3. ^{13}C NMR spectral characteristics[a] of the σ-adducts and aryl ethers in DMSO[b] and MeCN–glyme (1 : 1)[c]

Compound	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C_7	$C_{8,12}$	$C_{9,11}$	C_{10}	C_{13}	C_{14}
1[c,d]	67·9	135·1	125·8	122·6		115·0	129·0	117·3		
3[c,d]	67·8	135·1	125·8	122·6		125·0	129·8	125·0	20·8	17·3
8[c,d]	67·9	135·1	125·8	122·6		111·5	152·2	112·0	35·6	32·1
2[b,e]	40·3	136·1	125·9	120·3	132·0	129·2	114·9	156·6		
2[c]	42·6	137·4	126·2	120·9	128·5	131·5	116·9	163·5		
5[b]	59·2	134·8	124·5	120·5						
5[b,f]	59·0	134·7	124·5	120·5						
5[c,f]	61·4	135·4	126·0	121·2						
6[b,e]	158·4	117·9	149·0	112·5	154·3	120·0	130·7	125·8		
4[b]	158·3	115·0	149·2	111·6	147·1	129·9	130·1	135·7	20·3	15·6
4[c]	160·6	116·5	151·0	112·9	149·0	131·7	131·6	137·8	21·4	16·6
9[b,e]	158·7	117·3	148·9	112·1	153·7	114·3	153·3	119·2	34·8	31·0
10[g]	160·3	114·9	148·8	110·3	57·0					

[a] Chemical shifts are given in ppm measured at 100 MHz.
[b] DMSO-d_6 at ambient temperature.
[c] CD_3CN–glyme-d_{10} (1 : 1 v/v).
[d] Obtained at $-40\,^{\circ}C$.
[e] Obtained from a prepared sample.
[f] Obtained from control experiment using Me_4NOH.
[g] 3,5-Dinitroanisole in DMSO-d_6.

Inspection of Table 1 shows that the ^{1}H NMR spectral characteristics (H_1 and $H_{3,5}$) of the aryloxide *O*-adducts (**1**, **3**, **8**) are very similar but, importantly, H_1 is markedly shifted from that of the hydroxide analog, **5**.[4,12] In fact it now appears general that the proton attached to the sp^3-hybridized carbon, H_1, of TNB–aryloxide *O*-adducts is found 0·5–0·8 ppm downfield from the comparable proton of TNB–alkoxide or hydroxide adducts, in contrast to previous reports.[6,8] This new assignment, however, is in agreement with expectations based on the observed effect of a phenyl group on NMR parameters in other systems. For example, the chemical shift of the methylene protons of phenetole, $PhOCH_2CH_3$, are observed at δ 3·97 in DMSO-d_6, which is *ca* 0·6 ppm downfield from the corresponding protons of diethyl ether ($EtOCH_2CH_3$; δ 3·38 in DMSO-d_6).

Recalling briefly the evidence concerning TNB–aryloxide σ-complexes, Shein and co-workers[6] first reported that the reaction of TNB with phenoxide ion in DMSO produces the *O*-adduct **1** with ^{1}H NMR resonances at δ 8·35 (d, J = 2·0, 2H), 6·22 (t, J = 2.0, 1H) and 6·5–7·4 (m, 2H). However, Buncel and co-workers[1] only observed the *C*-bonded phenoxide adduct **2** in this system. Machacek *et al.*[7] then obtained ^{13}C and ^{15}N NMR data for the purported *O*-adduct formed in DMSO at ambient temperature, with the C_1 resonance found at δ 59·6 ppm. From the data in Table 3 it is seen that this value corresponds to the TNB·OH$^-$ adduct. For the simpler, in principle, system consisting of TNB reacting with mesitoxide ion, Buncel *et al.*[8] found for the supposed *O*-bonded mesitoxide adduct **3** a signal at δ 6·20 for the sp^3-bound proton, H_1, but it is now apparent that this species was also the TNB·OH$^-$ adduct.

In this work, using 400 MHz NMR spectroscopy and by means of the introduction of a new low-temperature solvent system, we have obtained definitive evidence for the structures of several TNB–aryloxide σ-adducts. Previously reported ^{1}H and ^{13}C NMR characteristics ascribed to *O*-bonded phenoxide adducts, in fact, correspond to the TNB·OH$^-$ adduct with phenol (mesitol) generated (or present in excess) in these systems generally obscuring the important δ 6·8 region where the sp^3-attached proton of the aryloxide σ-adducts appear.[6–8]

DISCUSSION

Reaction pathways; kinetic versus thermodynamic control

The 1,3,5-trinitrobenzene–phenoxide system

Based on the spectral observations in this study, it is clear that *O*-attack by PhO$^-$ at the unsubstituted position of TNB, to produce the TNB·OPh$^-$ adduct **1**, is the kinetically preferred interaction, as previously proposed.[1,6] This adduct is relatively unstable and is rapidly replaced by the hydroxide adduct **5**.[12] The latter species is generated through the facile reaction of TNB with OH$^-$, formed in small amounts by a thermodynamically unfavorable equilibrium between PhO$^-$ and H_2O present in the DMSO solvent system [pK_a(PhOH) = 18·0; pK_a(H_2O) = 32·0 in pure DMSO[13]]. Kinetically, this reaction is preferred over the irreversible processes (*C*-adduct and diaryl ether formation) between TNB and PhO$^-$.

The irreversible processes involve, respectively, σ-adduct formation through attack at the unsubstituted position of TNB by the *ortho*- and *para*-carbon centers of PhO$^-$, and nucleophilic nitrite displacement through *O*-attack at the carbon positions bearing NO_2 groups. *C*-Attack is envisioned to involve rate-determining formation of a quinoidal σ-complex which is rapidly rearomatized to form **2** (Scheme 1). The quinoidal complex is not detected, nor have related intermediates been observed in similar reactions.[9] Nucleophilic displacement of the NO_2 group to produce the diaryl ether **6** is rationalized in terms of an addition–elimination mechanism.[14] The proposed intermediate (Scheme 2) is not observed due to facile expulsion of the NO_2 group.[14]

From the product distribution found in the DMSO-d_6 study and the sequence of events in CD_3CN–glyme-d_{10}, it is apparent that *C*-attack via the *para*-carbon position, to produce **2**, is kinetically more favorable than formation of the *ortho*-carbon adduct **7** or the diaryl ether **6**. Apparently, formation of the quinoidal σ-complex (Scheme 1) is favored over the putative S_NAr intermediate (Scheme 2) leading to ether formation. This result may not have been intuitively expected since *C*-attack would require extensive structural reorganization because the aromaticity of the phenoxyl ring is disrupted. However, in the quinoidal complex leading to *C*-adduct formation (Scheme 1), the negative charge is stabilized by the *ortho*- and *para*-NO_2 groups, whereas in diaryl ether formation the negative charge in the proposed intermediate (Scheme 2) cannot be stabilized through resonance since the NO_2 groups are *meta* to the position of attack.

Insight into the kinetic preference for *para*-carbon attack over *ortho*-carbon attack can be obtained from consideration of the ^{13}C NMR resonances of the phenoxy ring carbon positions displayed in Table 4. The C_4 resonance (*para* position) of PhOK occurs at δ 106·4, whereas the resonance for the *ortho*-carbons ($C_{2,6}$) is observed at 119·1 ppm in DMSO-d_6. This apparent shielding of the *para* position (higher electron density) relative to the *ortho* position may account for the kinetic preference for *para* attack, although a steric factor may also contribute. In this regard, it is interesting to note that *C*-attack by PhO$^-$ at the 'super-electrophilic' centers of 2-*N*-(2′,4′dinitrophenyl)- and

Table 4. Comparison of ^{13}C NMR parameters of the phenoxy and mesitoxy ring positions of the σ-adducts, aryl ethers and parent phenols[a,b]

Compound	C_1	$C_{2,6}$	$C_{3,5}$	C_4
PhOK	172·4	119·1	128·8	106·4
PhOH	157·5	115·4	129·5	118·9
PhOMe	159·2	113·8	129·4	120·4
1		115·0	129·0	117·3
6	154·3	120·0	130·7	125·8
MesOK	167·1	122·7	127·8	111·5
MesOH	151·1	124·0	128·6	127·0
MesOMe[c]	154·4	129·5	129·0	132·1
3		125·0	129·8	125·0
4	147·1	129·7	130·1	135·7

[a] Chemical shifts are given in ppm measured at 100 MHz.
[b] Parameters are measured in DMSO-d_6, except for **1** and **3**, which were obtained in MeCN–glyme at −40 °C.
[c] Taken from Ref. 18, measured in DMSO-d_6.

2-*N*-(4′-nitrophenyl)-4,6-dinitrobenzotriazole 1-oxides[9c] was less selective and produced the *C*-adducts in a statistical ratio (2 : 1 favoring *ortho* attack).

The 1,3,5-trinitrobenzene–mesitoxide system

Analogous to the TNB–PhO^- system, attack by $MesO^-$ at the unsubstituted position of TNB to form the σ-adduct **3** was the initial process observed in MeCN–glyme at −40 °C, which was followed by formation of **5** and MesOH as the temperature was slowly raised. As the reaction was allowed to proceed at room temperature, **5** and MesOH were observed to slowly give way to the aryl ether **4**. Although in this system formation of a σ-adduct through *C*-attack is precluded, the competing NO_2 displacement results in the *O*-adduct being a metastable species.

*The 1,3,5-trinitrobenzene–3,5-di-*tert*-butylphenoxide system*

As predicted, the presence of the *meta-tert*-butyl groups effectively blocked *C*-attack by the *para*- and *ortho*-aryloxy sites. The reactivity pattern observed for this system mimicked the TNB–$MesO^-$ system. Thus, production of the *O*-bonded aryloxide σ-adduct **8** is followed by formation of the diaryl ether **9**. The hydroxide adduct **5** is also formed as a side-product in this system.

Stereoelectronic factors in the aryloxide σ-complexes and the aryl ethers

It has been well documented that in the absence of steric hindrance, substituents with lone pairs attached to aromatic rings, such as methoxy, prefer planar conformations over *gauche* or perpendicular.[15] In the planar conformation, conjugation of the p-type lone-pair or-bital of the heteroatom with the aromatic system is maximized. When this type of resonance is operative the *ortho* and *para* positions of the aromatic ring are shielded relative to the meta position.

Using ^{13}C NMR chemical shift data, Dhami and Stothers[16] found that in substituted anisole derivatives the *ortho*- and *para*-carbon shieldings reflect the degree of orbital overlap and how this is influenced by steric interactions. Using this approach, Buchanan *et al.*[17] evaluated conformational preferences in aryl ethers and found that the *para*-carbon shifts could be used to predict the average twist angle of the phenyl rings from a reference plane. More recently, Fujita *et al.*[18] measured the effect of *O*-methylation on ^{13}C NMR signals of *ortho*-disubstituted phenols in DMSO-d_6 and found that, in general, the *ortho*-carbons are shifted 5·2 ppm and the *para*-carbon 4·6 ppm downfield from the corresponding resonances of the parent phenol. This result was interpreted as consistent with steric inhibition of resonance between the methoxy group and the aromatic ring when the methoxy group is perpendicular to the π-system. Thus the ^{13}C NMR chemical shifts of the *ortho* and *para* positions of an attached aryloxy moiety can be used as an indicator of conjugative stabilization.[17,18]

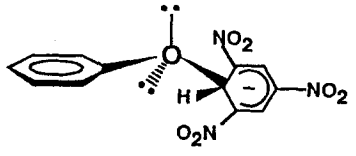
In order to explore such interactions in the present systems, we compared the ^{13}C NMR shift parameters of the phenoxy and mesitoxy moiety in the aryloxide σ-adducts (**1** and **3**) and in the diaryl ethers (**4** and **6**) to the corresponding positions of the parent phenol and mesitol (Table 4). The data were recorded in DMSO-d_6, except for the σ-adducts, which were obtained in CD_3CN–glyme-d_{10} at −40 °C. As discussed above, the relative positions of the *ortho*- and *para*- carbons serve as a measure of conjugative stabilization and can be used to predict the conformational preferences of the σ-adducts and the diaryl ethers. The arguments and trends for the phenoxy derivatives also apply to the di-*tert*-butyl derivatives **8** and **9**, which do not possess *ortho* substituents.

Phenoxy derivatives 1 and 6

Considering phenol as the standard, inspection of Table 4 shows that the chemical shifts of the *ortho* (115·4) and *para* (118·9) positions of PhOH are shielded relative to the *meta* position (129·5), consistent with a conformation where the hydroxy group is in the plane of the aromatic ring allowing overlap between the lone pair on the oxygen and the benzenoid π-system. On *O*-methylation to produce anisole, the *ortho*-carbons (113·8) are shifted 1·6 ppm upfield and the *para*-carbon (120·4) 1·5 ppm downfield from PhOH, whereas the *meta* carbons remain in virtually the same position. These observations are once again in agreement with a conformation for PhOMe where the methyl group is approximately in the plane of the aromatic

ring. While this maximizes steric interactions with the *ortho*-hydrogens, it allows for the aforementioned conjugative interaction to occur.

For the σ-adduct **1**, the *ortho*- (115·0) and *para*-carbon (117·3) resonances occur slightly upfield from those of PhOH. This indicates that the p-orbital overlap in this structure dominates over steric influences, analogous to that found for PhOMe. The conformation of **1** which fits this description is shown by **1a**. In this conformer the sp^3-bound proton of the TNB^- moiety is almost in the plane of the phenoxy ring whereas the *ortho*-NO_2 groups are perpendicular; this conformation allows for maximum overlap in the phenoxy moiety and possesses only moderate steric interactions.



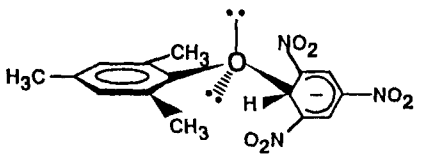
1a

In the diaryl ether **6** the *ortho*- and *para*-carbon resonances of the phenoxy moiety are shifted 4·6 and 6·9 ppm downfield from those of PhOH, consistent with reduced conjugative overlap. For diphenyl ether itself, a variety of experimental and theoretical approaches suggest that the molecule adopts a helical conformation in which the twist angle lies in the vicinity of 25–50°.[19] However, evidence has been adduced showing that the electron-withdrawing NO_2 group is able to effect a conformational preference in diaryl ethers by enhancing through-conjugation.[17,20] Comparison of the chemical shifts in the 3,5-dinitrophenyl ring of **6** with the corresponding ring of 3,5-dinitroanisole (**10**) reveals only slight differences (Table 3). In 3,5-dinitroanisole it is reasonable to presume that the methoxy group is coplanar with the π-system (no *ortho* substituents) and the upfield resonances of the *ortho* (114·9) and *para* (110·3) positions are consistent with this deduction. It may therefore be concluded that in **6** the conjugative overlap is with the 3,5-dinitrophenyl ring and not with the attached phenoxy group, in accord with the greater electron-withdrawing capability of the 3,5-dinitrophenyl ring. The NO_2 groups are not envisioned to exert an unfavorable steric influence in such a conformation.

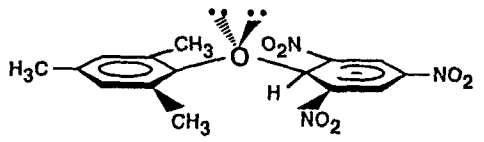
Mesitoxy derivatives 3 and 4

For the parent mesitol (MesOH) in DMSO-d_6 the *ortho*- and *para*- carbon resonances are observed at δ 124·0 and 127·0 ppm (Table 4). On *O*-methylation, these sites are shifted downfield by 5·5 and 5·1 ppm, respectively, which indicates that the methoxy group in MesOMe deviates from planarity. For 2,6-dimethylanisole, Buchanan *et al.*[17] predicted on the basis of ^{13}C NMR data that the angle of deviation is 44°, whereas evidence obtained from photoelectron spectroscopy[21] leads to the conclusion that the OMe group in 2,6-dimethylanisole assumes a perpendicular arrangement with respect to the benzene ring. Hence the preferred conformer of MesOMe appears to be one with perpendicular OMe, in which steric interactions between the OMe group and the aromatic *ortho*-methyls are minimized, and overlap between the oxygen p-orbital and the aromatic ring is correspondingly greatly diminished.

In the aryloxide σ-adduct **3**, the *ortho*- and *para*-carbon resonances occur at δ 125·0 ppm, differing only slightly (1 and 2 ppm, respectively) from those of MesOH, which points to a planar geometry for **3** with maximum p–π overlap. Inspection of molecular models (CPK and Darling) suggests that a planar configuration of **3** (i.e. **3a**) does not possess appreciable additional steric hindrance over planar MesOMe. In **3a** the sp^3-bound proton of the TNB^- group is almost in the plane of the mesitoxy moiety, whereas the NO_2 groups are perpendicular. However, in contrast to MesOMe, which has been shown to adopt a perpendicular conformation to alleviate steric interactions, a perpendicular conformation for **3** (i.e. **3b**) exhibits highly unfavorable steric interactions. Also, if in **3b** the TNB^- moiety is rotated, there will be unfavorable interactions between one of the nitro groups and the aromatic ring. Since a perpendicular geometry (**3b**) does not relieve steric hindrance in the σ-adduct, a planar configuration is adopted which can benefit from orbital overlap.



3a



3b

In the diaryl ether **4**, the *ortho*- and *para*-carbon resonances occur 5·7 and 8·7 ppm, respectively, downfield relative to MesOH (Table 4). Analogous to the situation for **6**, the preferred conformer places the mesitoxy moiety in the plane of the 3,5-dinitrophenyl ring, resulting in orbital overlap with the latter moiety.

The least sterically hindered rotamer directs the *ortho*-hydrogens of the 3,5-dinitrophenyl ring into the mesitoxy π-system and away from the *ortho*-methyls. This rotamer, previously called the 'H-inside' conformer,[8] was also proposed as the preferred conformation of **4** in our ^{1}H NMR studies of this system.

CONCLUSIONS

The results of these studies on the course of the reactions of 1,3,5-trinitrobenzene (TNB) with an ambident nucleophile, phenoxide ion, and with mesitoxide ($MesO^-$) and 3,5-di-*tert*-butylphenoxide ($DTBP^-$), permit us to draw the following conclusions.

The *O*-bonded $TNB \cdot OAr^-$ σ-adducts **1**, **3** and **8** are kinetically favored and are observed first in the NMR spectra at $-30\,^{\circ}C$ in MeCN–glyme as the solvent system. Results in DMSO are similar but less definitive.

From the ^{1}H NMR spectral characteristics, the sensitive H_1 sp^3-bound proton of the $TNB \cdot OAr^-$ σ-adducts is markedly different from those of alkoxide and hydroxide analogs. This proton appears 0·5–0·8 ppm downfield from the comparable proton of alkoxide or hydroxide adducts.

As the temperature of the reaction system is increased, the $TNB \cdot OAr^-$ σ-adducts are observed to give way to the $TNB \cdot OH^-$ adduct **5** as a result of reaction of OH^- from adventitious H_2O in the MeCN–glyme or DMSO media.

The final products in these systems are the diaryl ethers **4**, **6** and **9** and the *C*-bonded adducts **2** and **7**. In the PhO^- system, *C*-attack is favored over NO_2 displacement. The irreversible formation of these species renders them the ultimate products of thermodynamic control.

From the ^{13}C NMR parameters it was concluded that the σ-adducts **1**, **3** and **8** adopt a planar configuration in which conjugation of the p-type lone-pair orbital of the oxygen with the aromatic π-electron system is maximized. In the diaryl ethers **4**, **6** and **9**, the orbital overlap occurs preferentially with the 3,5-dinitrophenyl moiety.

EXPERIMENTAL

Materials and methods. 1,3,5-Trinitrobenzene (TNB) was prepared by nitrating 1,3-dinitrobenzene[22] and recrystallized from ethanol, m.p. 121 °C. CD_3CN, DMSO-d_6 and glyme-d_{10} (Merck) were dried by treatment with 3 Å molecular sieves. 18-Crown-6 (Aldrich) was recrystallized from acetonitrile, then dried under vacuum [<1 Torr (133·3 pa)] before use. Trifluoroacetic acid (TFA) and tetramethylammonium hydroxide (Me_4NOH, 25 wt% solution in water) (Aldrich) were used without further purification. 1,4-Dibromobenzene (Eastman) was recrystallized from ethanol and dried *in vacuo* (<1 Torr), m.p. 89 °C. Potassium ethoxide (EtOK) solutions were prepared from freshly cut potassium metal and dry EtOH (distilled from magnesium turnings[23]) under nitrogen and standardized with potassium hydrogen phthalate. Phenol (BDH) was distilled under vacuum and stored and handled in an argon-filled dry-box. 1,3,5-Trimethylphenol (mesitol, MesOH) and 3,5-di-*tert*-butylphenol (DTBP) (Aldrich) were purified by recrystallization from light petroleum.

Following the method described by Kornblum and Laurie[24] for the preparation of phenoxide ion, potassium 3,5-di-*tert*-butylphenoxide ($DTBP^-$) was prepared from the phenol and EtOK–EtOH as a colorless powder. Its ^{1}H NMR spectrum in DMSO-d_6 showed the following resonances: δ 5·90 (1H, t, J = 1·7), 5·86 (2H, d, J = 1·7) and 1·16 (18H, s). PhOK and MesOK were prepared in a similar fashion.

The NMR experiments were carried out on a Bruker AM-400 spectrometer (^{1}H, 400 MHz, ^{13}C, 100 MHz) in CD_3CN–glyme-d_{10} (1 : 1 v/v) and in DMSO-d_6. In the mixed solvent system, CD_2HCN served as reference (^{1}H, 1·93) and lock signal, while spectra recorded in DMSO were referenced to the DMSO-d_5H peak (2·50). Chemical shifts are given in parts per million (ppm), coupling constants in Hz. For ^{13}C NMR experiments, spectra were acquired using the *J*-modulated (JMOD) pulse sequence.[25] The spectra were recorded with the CH and CH_3 signals displayed in the positive direction and quaternary carbon and CH_2 signals in the negative direction. Wilmad PP-507 NMR tubes (5 mm) were used in all experiments. All stock solutions and the NMR tubes were capped with rubber septa and swept out with nitrogen prior to injection of the reactants.

A representative experiment in DMSO. A TNB stock solution (0·513 M) was prepared by dissolving 54·7 mg of the substrate in 500 µl of DMSO-d_6. An initial sample was prepared by injecting the substrate solution (100 µl) into an NMR tube containing solvent (285 µl) and DBB (5 µl of a 1 M stock solution). DBB functioned as the internal integration standard. Injection of the relevant quantity of PhOK (110 µl for 1 equiv.) initiated the reaction. Spectra were recorded at various intervals as the reaction proceeded.

In a separate experiment, 1 equiv. of PhOK was added to the NMR tube containing the TNB solution. After acquisition of an initial spectrum (*ca* 3 min after mixing), TFA (5 µl) was added and the spectrum again recorded.

The reaction of TNB with MesOK and with DTBPK in DMSO-d_6 were carried out in an analogous fashion.

Low-temperature NMR experiments in MeCN–glyme (1 : 1). Typically, 1 equiv. of PhOK was dissolved in a 1 : 1 (v/v) mixture of CD_3CN and glyme-d_{10}. This solution (300 µl) was injected into an NMR tube and the

solution frozen by immersion in liquid nitrogen. To the frozen solution was added 1 equiv. of TNB (200 μl; final concentrations 0·1 M). The resulting mixture was placed in a dry-ice–acetone bath maintained at −50 °C. The contents of the tube were slowly allowed to mix and the tube was again immersed in liquid nitrogen. The sample was transferred to the spectrometer probe (−40 °C) and spectra were recorded at various intervals, a standard sequence being 3, 5, 7, and 9 min and then as warranted by the observed changes. At the same time the temperature of the probe would gradually be raised.

In separate experiments the ^{1}H NMR spectral characteristics of the *O*-bonded aryloxide σ-adducts were quickly obtained at −40 °C, and then the ^{13}C NMR parameters were obtained at this temperature. The ^{13}C NMR parameters of the *para*-carbon-bonded adduct **2**, the hydroxide adduct **5** and the diaryl ethers **4**, **6** and **9** were obtained at room temperature.

For the reaction of TNB with DTBPK in CD_3CN–glyme-d_{10} (1 : 1 v/v), the stock solution of nucleophile contained 18-crown-6 (final concentration 0·1 M).

3,5-Dinitrophenyl phenyl ether (6). TNB (1·02 g) was dissolved in 10 ml of dry DMSO (distilled over CaH_2). To this stirred solution was added 15 ml of a DMSO solution of PhOK (1 equiv.) and the resulting dark-red solution was stirred for 24 h. The mixture was then acidified (1 ml of TFA) and DMSO removed under vacuum. The resulting red slurry was extracted with light petroleum and the extracts were combined and concentrated to give 0·095 g (7·6%) of crude **6**. Recrystallization from ethanol afforded the pure diaryl ether, m.p. 118 °C. ^{1}H NMR (DMSO-d_6), δ 8·56 (H_4, t, J = 1·9), 8·13 ($H_{2,6}$, d, J = 1·9), 7·54 (H_{meta}, m), 7·35 (H_{para}, m), 7·26 (H_{ortho}, m). Analysis: calculated for $C_{12}H_8O_5N_2$, C 55·39, H 3·10, N 10·77; found, C 53·65, H 3·20, N 10·32%.

3,5-Dinitrophenyl 3,5-di-tert-butylphenyl ether (9). In a similar fashion to the preparation of **6**, the diaryl ether **9** was obtained in 80% yield, m.p. 137 °C (from ethanol). ^{1}H NMR (DMSO-d_6), δ 8·53 (H_4, t, J = 1·9), 8·09 ($H_{2,6}$, d, J = 1·9), 7·35 ($H_{4'}$, t, J = 1·5), 7·07 ($H_{2',6'}$, d, J = 1·5), 1·29 (*t*-Bu, s). Analysis: calculated for $C_{20}H_{24}O_5N_2$, C 64·50, H 6·50, N 7·52; found, C 64·14, H 6·31, N 7·41%.

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