Aromatic radical anions as possible intermediates in the nucleophilic aromatic substitution (S_NAr): an EPR study

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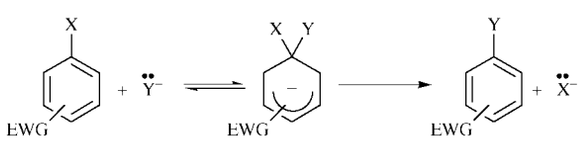
The reactions among halonitrobenzenes or polynitrobenzenes and alkoxides, thiolates or tertiary amines have provided the evidence that in a S_NAr reaction type a single electron transfer from the nucleophile to the aromatic substrate, to generate two radical species within the solvent cage, can take place to some extent. The detection of radical intermediates by EPR spectroscopy, in several S_NAr reactions, is reported.

Introduction

It is commonly accepted [2] that nucleophilic aromatic substitution reactions involving activated substrates and good leaving groups proceed by a two-step mechanism: the first step is the covalent addition of a nucleophile to a substituted or unsubstituted ring carbon atom of the aromatic substrate, leading to an anionic σ-complex known as the Meisenheimer complex; the second step is the departure of the leaving group to form the substituted product, Scheme 1.



EWG = Electron-withdrawing group

Scheme 1

However, the polar mechanism of several organic reactions, including S_N2 and S_NAr, has been reconsidered [3] several times and a composite multi-step mechanism within the solvent cage, with an initial single electron transfer (SET) between the reactants, has been suggested.[3] In principle, the mechanism could move from polar to SET, depending on many factors, such as the nature of the two reactants (the redox potentials) and the polarity of the solvent.

In 1970 Bunnett [4] showed that the SET pathway could be involved also in some cases of nucleophilic aromatic substitution: in fact, the corresponding radical anion once formed, for instance by promoting this process with light, could lead to the substituted product *via* an $S_{RN}1$ mechanism, as shown in Scheme 2.

$$RX + e^- \longrightarrow RX^{\bullet -}$$
$$RX^{\bullet -} \rightleftharpoons R^\bullet + X^-$$
$$R^\bullet + Nu^- \rightleftharpoons RNu^{\bullet -}$$
$$RX + RNu^{\bullet -} \rightleftharpoons RX^{\bullet -} + RNu$$

Scheme 2

Since then many other examples have been reported [5] in which the initial step of this process involves the stimulated formation of the aromatic radical anion. For example, the first step in the S_NAr process among several nitroarenes, their halo and nitrile derivatives, and both the hydroxide ion [6,7] and tertiary amines [8] has been argued to be the formation of a π electron donor–acceptor complex followed by transfer of an electron to yield a radical pair.[6–10] Thus, the occurrence of the radical-coupling within the solvent cage should lead to the corresponding Meisenheimer complex,[7,8] whilst, if the radical pair escapes from the solvent cage, the free radical species could become detectable.[6,8] These arguments led us to investigate, by EPR spectroscopy, the S_NAr reaction of many polynitrobenzenes and their halo derivatives with a large variety of nucleophiles such as alkoxides, thiolates and tertiary amines. The spectroscopic results, as well as the identification among the reaction products of species whose formation can be accounted for only by the occurrence of radical processes, support the hypothesis that a SET mechanism could make a contribution to the whole process, depending on the substrate/nucleophile pair.

Table 1 Hyperfine coupling constants of the detected aminoxyls [a]

Tertiary amines	Radical [b]	hfc/G
$N(Me)_2CH_2CH_2OH$ $N(Me)_2CH_2CH_2CH_2OH$		$a_{6H} = 12.50$ $a_N = 15.25$
NEt_3 $N(Et)_2CH_2CH_2OH$		$a_{4H} = 9.75$ $a_N = 14.50$
NPr_3		$a_{4H} = 9.85$ $a_N = 14.60$
$NEt(Pr^i)_2$		$a_H = 4.55$ $a_{2H} = 10.45$ $a_N = 14.95$
$NEt(Pr^i)_2$		$a_{2H} = 4.25$ $a_N = 14.55$

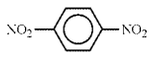
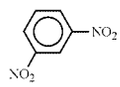
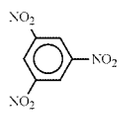
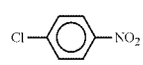
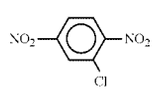
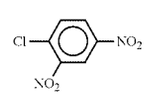
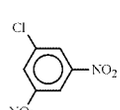
[a] Typically at 0 °C or room temperature. [b] The *g*-values (2.0054 ± 0.0002) have been evaluated by comparison with the *g*-factor of the diphenylpicrylhydrazyl (DPPH) (2.0037).

Results and discussion

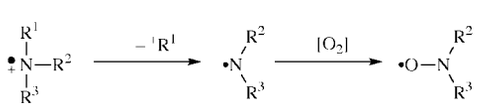
EPR studies

It has been previously reported [8] that the reaction between nitroaromatic derivatives and tertiary amines, conducted directly in the cavity of the EPR spectrometer, leads to the detection of dialkyl aminoxyls, Table 1, together with the appropriate aromatic radical anions. The formation of the former species could be explained by invoking a dealkylating process that the intermediate tertiary aminium radical cations can undergo, followed by oxidation of the resultant aminyl radical, Scheme 3. This finding [8] could support the involvement

Table 2 Substrates analysed by EPR spectroscopy[a]

	Substrate	Alkoxide	Thiolate	Tertiary amine
1		**a**) Bu^tO^-	**b**) Bu^tS^-	**c**) NEt_3
2		**a**) Bu^tO^-	**d**) CH_3S^- **e**) Pr^iS^- **b**) Bu^tS^-	**c**) NEt_3 **f**) NPr_3 **g**) $N(Me)_2CH_2CH_2OH$ **h**) $N(Et)_2CH_2CH_2OH$ **i**) $N(Me)_2CH_2CH_2CH_2OH$
3		**a**) Bu^tO^-	**b**) Bu^tS^-	**c**) NEt_3 **f**) NPr_3 **g**) $N(Me)_2CH_2CH_2OH$ **h**) $N(Et)_2CH_2CH_2OH$ **i**) $N(Me)_2CH_2CH_2CH_2OH$
4		**a**) Bu^tO^-	**d**) CH_3S^- **e**) Pr^iS^- **b**) Bu^tS^-	**c**) NEt_3 **h**) $N(Me)_2CH_2CH_2OH$
5		**l**) CH_3O^- **m**) EtO^- **a**) Bu^tO^-	**d**) CH_3S^- **n**) EtS^- **o**) PrS^- **e**) Pr^iS^- **b**) Bu^tS^-	**c**) NEt_3 **f**) NPr_3 **g**) $N(Me)_2CH_2CH_2OH$ **h**) $N(Et)_2CH_2CH_2OH$ **i**) $N(Me)_2CH_2CH_2CH_2OH$ **p**) $NEt(Pr^i)_2$
6		**l**) CH_3O^- **m**) EtO^- **a**) Bu^tO^-	**b**) Bu^tS^-	**c**) NEt_3 **f**) NPr_3 **g**) $N(Me)_2CH_2CH_2OH$ **h**) $N(Et)_2CH_2CH_2OH$ **i**) $N(Me)_2CH_2CH_2CH_2OH$
7		**l**) CH_3O^-	**b**) Bu^tS^-	**c**) NEt_3 **f**) NPr_3 **g**) $N(Me)_2CH_2CH_2OH$ **h**) $N(Et)_2CH_2CH_2OH$ **i**) $N(Me)_2CH_2CH_2CH_2OH$

[a] Solutions in CH_3CN, THF or CH_3CN–THF mixture (70:30). The molar ratio between the substrates and the nucleophiles is 1:1.



Scheme 3

of a SET mechanism for such a type of reaction; but, to strengthen this hypothesis it was necessary to verify whether with different nucleophiles the intermediate radical anions were still detectable. Experiments on nitroaromatic substrates with well known nucleophiles such as alkoxides and thiolates were then conducted, Table 2.

The reactants, in CH_3CN, THF, or CH_3CN–THF (70:30) solution, were mixed directly in the EPR sample tubes and the samples analysed at low temperature: all the substrates investigated enabled the detection of the corresponding aromatic radical anions, Table 3. The hyperfine coupling (hfc) of the radical anions reported in Table 3 show the typical values of ion-pairs[11] (see for example radical **2a** in which the hyperfine coupling for Na^+ is observed): that accounts for the unsymmetrical distribution of the spin density.[11–13] For radical **1a**, however, we observed a symmetric spin distribution:[14] we may argue that it is not possible to rule out contact ion-pairing for the *p*-dinitrobenzene radical anion[12] as a result of the fast counter-ion exchange between the two *p*-nitro groups which averages completely the hyperfine splitting (hfs) pattern.[12,13]

As reported in the literature,[12] the hfs pattern can change depending on the nature of the counter-ion. In particular, we observe smaller coupling constants for the ion-pairs where the tertiary aminium radical cations are involved.[12]

Although we did not have the unequivocal proof needed to draw a definitive mechanism for this class of reactions, the

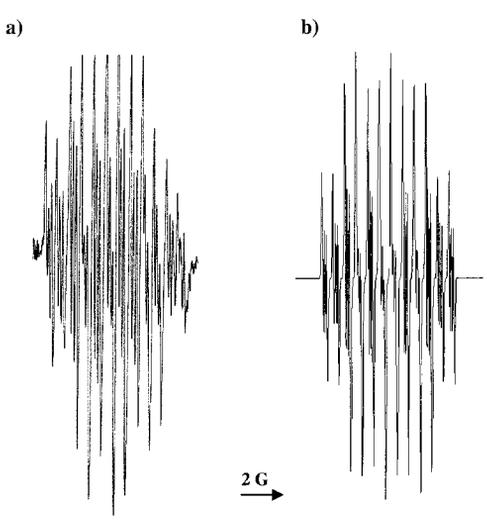
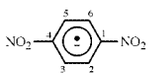
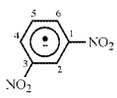
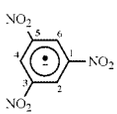
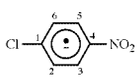
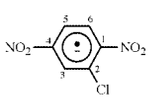
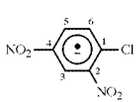
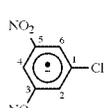


Fig. 1 (a) EPR spectrum, at −50 °C, of **7a** in CH_3CN solution; (b) computer simulated spectrum.

detection of radical anion intermediates, Fig. 1, for a large number of substrates with different nucleophiles, was of course supporting the hypothesis for the involvement of a SET process.

In a few cases the EPR experiments showed also the incoming formation of other radical species: for some substrates, when the reaction mixture was kept at *ca.* −50 °C for 6–7 hours, it was possible to detect the radical anions corresponding to the product of the previously occurred S_NAr reactions. For instance, when the 2-chloro-1,4-dinitrobenzene (**5**) and the

Table 3 Hyperfine coupling constants of the detected radical anions[a]

Radical anion[b]	hfc/G
1a 	$a_N(1) = a_N(4) = 1.80$ $a_H(2) = a_H(6) = 1.11$ $a_H(3) = a_H(5) = 1.11$
2a[c] 	$a_N(1) = 9.38$ $a_N(3) = 0.26$ $a_H(2) = 3.25$ $a_H(4) = 4.45$ $a_H(5) = 1.10$ $a_H(6) = 4.15$ $a_{Na} = 0.22$
3a 	$a_N(1) = 3.54$ $a_N(3) = a_N(5) = 0.71$ $a_H(2) = 4.25$ $a_H(4) = 3.08$ $a_H(6) = 1.96$
4a 	$a_N(4) = 10.18$ $a_H(2) = a_H(6) = 3.38$ $a_H(3) = a_H(5) = 1.13$
5a 	$a_N(1) = 0.16$ $a_N(4) = 1.87$ $a_H(3) = 1.27$ $a_H(5) = 1.31$ $a_H(6) = 0.60$
6a 	$a_N(2) = 0.13$ $a_N(4) = 1.76$ $a_H(3) = 1.26$ $a_H(5) = 1.40$ $a_H(6) = 0.54$ $a_{Cl} = 0.03_6$
7a 	$a_N(3) = 2.05$ $a_N(5) = 0.12_5$ $a_H(2) = 1.32_5$ $a_H(4) = 1.35$ $a_H(6) = 0.65$

[a] Typically at −50 °C. [b] The *g*-values (2.0045 ± 0.0002) have been evaluated by comparison with the *g*-factor of the DPPH (2.0037). [c] The coupling with the counter-ion has been observed only for the reactions with sodium thiolates.

sodium propane-2-thiolate mixture was investigated, in addition to the radical anion **5a**, Fig. 2a, the 2-chloro-1-(isopropylsulfanyl)-4-nitrobenzene radical anion, **5b**, [$a_N = 9.78$ G, $a_{2H} = 3.25$ G, $a_H = 1.18$ G, $a_{Cl} = 0.28$ G, $g = 2.0045$] was detected after *ca*. 7 hours, Fig. 2b.

Identical behaviour was observed in the reactions of **5** with both EtS^- and PrS^-: it was possible to detect the 2-chloro-1-(ethylsulfanyl)-4-nitrobenzene and the 2-chloro-1-(propylsulfanyl)-4-nitrobenzene radical anions respectively, with hyperfine coupling constants like those found for **5b**.

Note, that these spectroscopic results show that in these processes a nitro group instead of the chlorine atom acts as the leaving group, reflecting the *para*-orienting attitude of the nitro-ring substituents.

Product studies

To support these spectroscopic results, and then the hypothesised involvement of a SET pathway, we conducted product analysis for some representative reactions. Along with the products of the substitution reaction, compounds exclusively due to the occurrence of free radical processes were identified.

i) S_NAr reaction between 1-chloro-2,4-dinitrobenzene and sodium pent-4-enoxide. When the reaction between 1-chloro-2,4-dinitrobenzene and sodium pent-4-enoxide[3d] was performed in THF, products which indicated the presence of a pent-4-enoxyl radical intermediate were found.

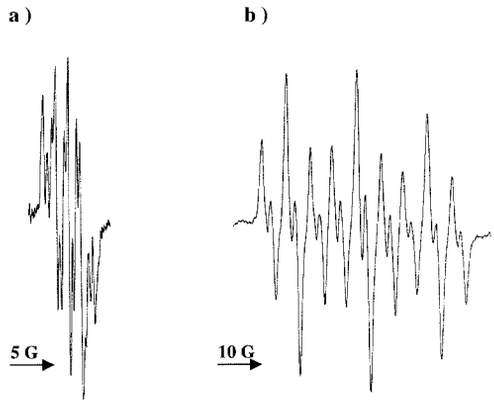
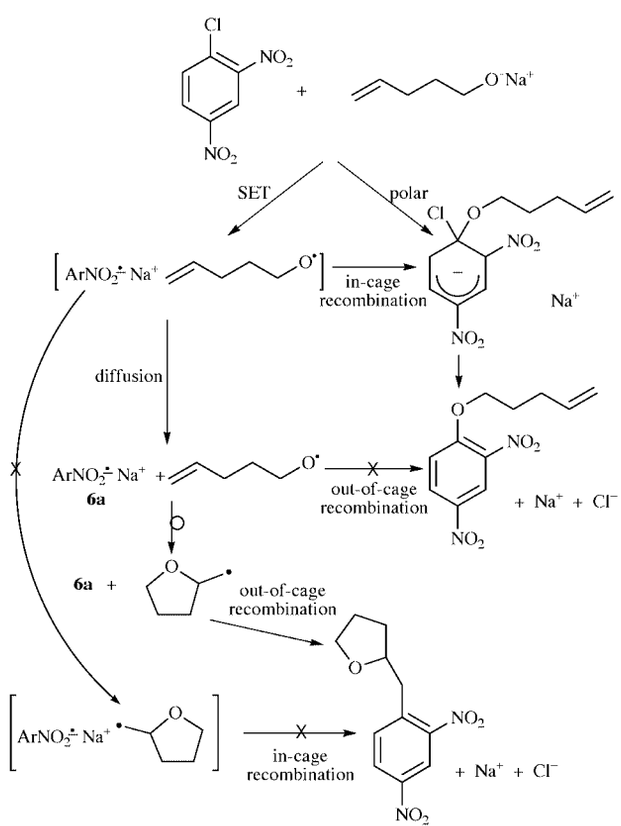


Fig. 2 (a) EPR spectrum, at −50 °C, of **5a** in CH_3CN solution; (b) EPR spectrum, at −50 °C, of **5b** in CH_3CN solution.

The use of sodium pent-4-enoxide represents an unequivocal probe[3d] to establish if the formation of radicals is involved in such a type of reaction. In fact, if free pent-4-enoxyl radicals are formed during the reaction course, they may rapidly cyclise to tetrahydrofurfuryl radicals before decaying[15,16] and then products containing the tetrahydrofurfuryl framework may be obtained in a reaction proceeding with radical character (see Scheme 4).



Scheme 4

From the crude reaction mixture, we recovered unreacted starting material along with the 1-(pent-4-enyloxy)-2,4-dinitrobenzene (*ca.* 21% yield), *i.e.* the product of the nucleophilic substitution, the pent-4-en-1-ol (*ca.* 30%) and the 2-methyltetrahydrofuran (GC-MS detectable quantity), *i.e.* the product of the cyclization reaction of the intermediate pent-4-enoxyl radical. No evidence for the formation of the product arising from the trapping of the cyclised pent-4-enoxyl radical by the nitroarene radical anion was found.

Actually, the recombination of both the pent-4-enoxyl and the tetrahydrofurfuryl radicals with the nitroarene radical anion leading to the corresponding substituted products can be reasonably assumed to arise from the in-cage and the out-of-cage reaction respectively (Scheme 4). In fact, since the in-cage recombination must be complete before the radicals can escape their cage (with a diffusion coefficient of *ca.* 10^9 s^{-1}),[17] the cyclization of the alkenoxyl radical, even though fast (k_c of *ca.* 10^8 s^{-1}),[15] can be assumed not to compete with the in-cage coupling reaction which leads to the 1-(pent-4-enyloxy)-2,4-dinitrobenzene. Thus, only the cage-escaped pent-4-enoxyl radical can lead to the tetrahydrofurfuryl radical: this process is also expected to be faster than the out-of-cage recombination of the alkenoxyl radical with the nitroarene radical anion. The tetrahydrofurfuryl radical could eventually recombine with **6a** leading to the cyclised substituted product, but in fact we did not recover any nitroarylmethyltetrahydrofuran. This finding could be explained by admitting that the out-of-cage recombination of the tetrahydrofurfuryl radical with **6a** is slower than the hydrogen abstraction reaction of the alkyl intermediate. It should be noted, however, that, according to the low quantity of 2-methyltetrahydrofuran recovered, the SET route represents a minor pathway in this reaction, as could be predicted since the single electron oxidation of an alkoxide is expected to be a difficult process.

ii) S_NAr reaction between 1-chloro-2,4-dinitrobenzene and sodium 2-methylpropane-2-thiolate. When the reaction between 1-chloro-2,4-dinitrobenzene and sodium 2-methylpropane-2-thiolate was performed in CH_3CN, the 1-(*tert*-butylsulfanyl)-2,4-dinitrobenzene was identified as the main reaction product, but the GC-MS analysis of the crude reaction mixture also revealed the presence of a significant quantity of di(*tert*-butyl) disulfide, *i.e.* the product of the $Bu^tS^{\bullet}$ radical coupling.

iii) S_NAr reaction between 1-chloro-2,4-dinitrobenzene and triethylamine. Only a few examples of S_NAr reactions of aromatic compounds by tertiary amines have been reported,[18] probably because of the low reactivity of tertiary amines due to steric hindrance. When we performed the reaction of 1-chloro-2,4-dinitrobenzene with triethylamine in CH_3CN, we obtained the *N*,*N*-diethyl-2,4-dinitroaniline, *i.e.* the substituted product, in *ca.* 5% yield (it is worth noting that we conducted this reaction in very mild conditions compared to those reported in the literature[18] for which an overall yield of only *ca.* 11% is reported). The difficulty of the formation of the Meisenheimer adduct, and its slow dealkylation, can be considered to be responsible for the low yield of the S_NAr reaction. On the other hand, the slow recombination of the radical pair in the solvent cage allowed, in principle, the two radicals to escape the cage itself and EPR evidence of both radical anions and aminoxyls could thus be obtained.[8]

Mechanistic interpretation

The obtained results seem consistent with a possible contribution of a SET process to the first step in any reaction between a nucleophile and a polynitrobenzene. The radical pair can in fact combine within the solvent cage and lead to the corresponding Meisenheimer complex, or, escaping from the solvent cage, form two free radical species, which could be detectable by EPR. The fate of these free radical species depends upon several factors and the most common route of decay is the occurrence of typical free radical processes (coupling, H-abstraction, cyclization, β-scission, *etc.*) as confirmed by the formation of side-products such as disulfides or cyclic derivatives. The recombination of the two radicals can eventually occur also through an out-of-cage reaction, though this pathway is quite unlikely.

Furthermore, the EPR detection of **5a** and **5b** in the reaction of **5** with *i*-PrS^- suggests that a concurrent radical pathway can contribute to the formation of the substituted product presumably through a $S_{RN}1$ mechanism.[19–21]

For S_NAr processes where the thioanions are involved, this is also supported by the comparison of the yields obtained for the processes between 1-chloro-2,4-dinitrobenzene and sodium 2-methylpropane-2-thiolate performed in the absence (72.1%) and in the presence (46.4%) of an inhibitor of radicals such as benzoquinone.

Conclusions

Our experimental results support the hypothesis that a SET process, leading to a radical pair within the solvent cage, could be involved as a concomitant first step in the mechanism of the S_NAr reaction of different polynitrobenzenes. The radical species if stabilised for instance by extensive delocalization, as for the presence of nitro substituents,[3a] can escape from the solvent cage and become detectable by EPR. The SET process should also be favoured when the substrate is easily reduced, *i.e.* when it is characterised by a small negative reduction potential[3d] as for nitroaromatic compounds. At the present time, we believe that the S_NAr product can be formed mainly through the classical pathway, *i.e.* the formation of the Meisenheimer complex, *via* the combination of the two radical species in the solvent cage. In particular, when alkoxides are involved, since the single electron oxidation of these nucleophiles is disfavoured on account of the electronegativity of oxygen, we expect the polar pathway to be prevailing. On the other hand, the ability of thioanions to act as one-electron donors and their efficiency as nucleophiles in aromatic $S_{RN}1$ reactions[4,9,19,20] (see Scheme 2), suggests that the concurrent SET pathway in these processes occurs to a major extent. This is also supported by the decrease of the yield of the S_NAr reaction between 1-chloro-2,4-dinitrobenzene and sodium 2-methylpropane-2-thiolate in the presence of benzoquinone.

Experimental

Materials

The tertiary amines were commercial products, all distilled before use. CH_3SNa, EtSNa, PrSNa, *i*-PrSNa, *t*-BuSNa, CH_3ONa, EtONa and *t*-BuOK were Fluka or Aldrich products, used as received. Sodium pent-4-enoxide was prepared as follows: 0.5 g of pent-4-en-1-ol were added dropwise to a stirred solution of anhydrous THF and Na wires; the reaction mixture was gently refluxed under nitrogen atmosphere for *ca.* 45 minutes, then the THF solution of the alkoxide was transferred in a flask by means of a long double-tipped deflecting needle and used without further purification. THF was distilled from sodium–benzophenone just prior to use and stored under nitrogen. CH_3CN was dried over molecular sieves and distilled under nitrogen before use. The 1,4-dinitrobenzene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, 1-chloro-4-nitrobenzene and 1-chloro-2,4-dinitrobenzene were commercially available and were recrystallised twice from ethanol before use. The 2-chloro-1,4-dinitrobenzene was synthesised according to the literature method.[22] The 1-chloro-3,5-dinitrobenzene was prepared from the corresponding 3,5-ditroaniline by diazotisation and following Sandmeyer reaction.[23]

EPR experiments

EPR spectra were recorded with a Varian E-104 spectrometer, equipped with a variable temperature apparatus, at −50/−70 °C, except for the spectra of the aminoxyls which were recorded at 0 °C or room temperature. All the experimental spectra were simulated by means of a computer program, to confirm the assignment of the hfc.

The EPR samples were prepared in "H-shaped" quartz tubes: this particular shape allowed to keep the two reactants separate and to mix them just prior to introduce the sample-tube in the spectrometer cavity. A solution (typically 10^{-2} M) of a nitroaromatic substrate in THF, CH_3CN or CH_3CN–THF mixture, was introduced in one of the two branches of the EPR tube and analogously the nucleophile, dissolved in the minimum amount of the solvent, was introduced in the other (1:1 molar ratio between the reagents). The solution was degassed by means of the freeze–pump–thaw technique and the tube sealed off. The two reagents were then mixed and the mixture immediately analysed at the EPR spectrometer.

Product analysis

General procedure. The S_NAr reactions were carried out as follows: a CH_3CN or THF solution (*ca.* 0.20 M) of the reagents (1:1 molar ratio, except for the reaction with the tertiary amine, where an excess of the nucleophile, 1:2, was employed) was stirred under nitrogen and refluxed for a variable period, depending on the reactivity of the nucleophile. The reaction mixture was then quenched with H_2O and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The products were characterised by ^{1}H-NMR and ^{13}C-NMR (Varian Gemini 200 MHz Spectrometer), and by GC-MS (Carlo Erba QMD 1000 GC-MS Spectrometer equipped with a methyl silicon plus 5% phenyl silicon capillary column). All compounds were identified by comparison of their retention times with those of authentic samples and by their mass spectra.

Reaction of 1-chloro-2,4-dinitrobenzene with sodium pent-4-enoxide. The THF solution of sodium pent-4-enoxide (*ca.* 5.8 mmol), prepared as described previously (see material), was added to a stirred THF solution of 1-chloro-2,4-dinitrobenzene (1.17 g, 5.8 mmol) by means of a long double tipped deflecting needle. The reaction mixture was refluxed under nitrogen atmosphere for 3 hours and then quenched with H_2O. The organic layer was extracted with Et_2O, dried over Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (diethyl ether–light petroleum = 2:1). After purification, 0.31 g of 1-(pent-4-enoxy)-2,4-dinitrobenzene (21.2%) were obtained: ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 2.02 (m, 2H, CH_2), 2.31 (q, 2H, CH_2), 4.27 (t, 2H, CH_2), 5.08 (m, 2H, CH_2=), 6.82 (m, 1H, CH=), 7.26 (d, H^6, Ar), 8.43 (m, H^5, Ar), 8.72 (d, H^3, Ar); ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ 29.5 (CH_2), 30.7 (CH_2), 70.4 (CH_2), 114.4 (CH, Ar), 115.3 (CH_2=), 122.8 (CH, Ar), 129.5 (CH, Ar), 138.0 (CH=), 139.1 (quat, Ar), 142.5 (quat, Ar), 154.4 (quat, Ar). Anal. Cald. for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.32; H, 4.75; N, 11.16%.

Reaction of 1-chloro-2,4-dinitrobenzene with sodium 2-methylpropane-2-thiolate. 1-Chloro-2,4-dinitrobenzene (0.80 g, 3.9 mmol) was dissolved in 20 mL of CH_3CN and stirred under nitrogen. 0.45 g of Sodium 2-methylpropane-2-thiolate (4 mmol) were then added and, after an additional hour of stirring at room temperature, the reaction was quenched with H_2O. The reaction mixture was washed with Et_2O, the organic phase was dried over Na_2SO_4 and the solvent removed. The solid residue was then crystallised from methanol (2 × 7 mL) to yield yellow crystals of 1-(*tert*-butylsulfanyl)-2,4-dinitrobenzene (0.72 g, 72.1%; mp 104–107 °C): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.48 (s, 9H, CMe_3), 7.91 (d, H^6, Ar), 8.34 (m, H^5, Ar), 8.67 (d, H^3, Ar); ^{13}C-NMR ($CDCl_3$, 50.3 MHz) δ 31.6 (CMe_3), 50.2 (quat, CMe_3), 120.3 (CH, Ar), 125.8 (CH, Ar), 135.6 (CH, Ar), 140.4 (quat, Ar), 146.2 (quat, Ar), 152.1 (quat, Ar). Anal. Calcd. for $C_{10}H_{12}N_2O_4S$: C, 46.87; H, 4.72; N, 10.93; S, 12.51. Found: C, 46.92; H, 4.68; N, 10.85; S, 12.54%.

When the reaction, in the same experimental conditions, was repeated in the presence of a small amount of benzoquinone (0.20 g, 1.8 mmol), an overall yield of 46.4% of the S_NAr product was obtained.

Reaction of 1-chloro-2,4-dinitrobenzene with triethylamine. A mixture of 1-chloro-2,4-dinitrobenzene (2.00 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in 50 mL of CH_3CN was refluxed under nitrogen for 6 hours. After the addition of 20 mL of H_2O, the reaction mixture was extracted with diethyl ether and the extract dried over Na_2SO_4. The solvent was removed and the crude product was purified by silica gel column chromatography using light petroleum–diethyl ether (2:1) as the eluent. 0.13 g of *N*,*N*-Diethyl-2,4-dinitroaniline (5.4%) were obtained: mp 80 °C (*lit.*[24] 79–80 °C), ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.23 (t, 6H, $2CH_3$), 3.37 (q, 4H, $2CH_2$), 7.06 (d, H^6, Ar), 8.19 (m, H^5, Ar), 8.63 (d, H^3, Ar).[25]

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