An Electron Spin Resonance Study of Side Reactions in the Equilibria of Formation of Triple Ions

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Reduction of aromatic compounds A (A = nitrobenzene,1,2-dinitrobenzene, 1,3-dinitrobenzene, 1,4-dinitrobenzene, 3-nitropyridine, 3,5-dinitropyridine, 4-nitrobenzophenone, 4,4'-dinitrobenzophenone, benzonitrile, 1,2-dicyanobenzene, 1,3-dicyanobenzene, 1,4-dicyanobenzene, and 4,4'-dicyanobenzophenone) by alkali metals in ethereal solvents containing sodium tetraphenylborate, yields ion pairs $A^{-\cdot}Na^+$, which are in equilibrium with the corresponding triple ions $Na^+A^{-\cdot}Na^+$. In a few cases side reactions in the formation equilibria of triple ions are observed by e.s.r. spectroscopy. The decomposition of sodium tetraphenylborate is ascertained and the formation of biphenyl and *p*-benzosemiquinone is explained as dependent on the number and the position of the substituents in the radical anion $A^{-\cdot}$.

THE triple ions $M^+A^{-\cdot}M^+$, where A is an aromatic substrate and M an alkali metal, have attracted much attention in recent years.[1] These species are observed when a salt of the same alkali cation is added to the solution of the ion pair $A^{-\cdot}M^+$, and their formation follows a two-step process, *i.e.* reaction (1). During our

$$A \xrightarrow{M} A^{-\cdot}M^+ \underset{}{\overset{M^+BPh_4^-}{\rightleftharpoons}} M^+A^{-\cdot}M^+ \qquad (1)$$

investigations on ion pairs [2-5] and triple ions [6] we found that ethereal solutions of ion pairs, with added sodium tetraphenylborate ($NaBPh_4$), exhibited e.s.r. spectra of different paramagnetic species. Figures 1 and 2 show the e.s.r. spectra obtained from the solutions of 3,5-dinitropyridine- and *m*-dinitrobenzene-sodium in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) containing $NaBPh_4$.

The presence of two different paramagnetic species is easily recognized. One hyperfine pattern is promptly assigned to the triple ion † of the starting organic substrate.[6] The other has been identified as that of the triple ion of *p*-benzosemiquinone ($Na^+BSQ^{-\cdot}Na^+$), as it consists of a quintet (1 : 4 : 6 : 4 : 1) due to four equivalent protons (a^H 2.44 G, g 2.005 2). Both the magnitude of a^H and the relative amplitudes of the hyperfine components do not change significantly with temperature, as previously observed by Gough and Hindle.[7] In Figures 1 and 2 the points represent experimental data and the solid lines the spectra calculated by the least-squares lineshape fitting procedure, described in the experimental section.

Starting from the three isomers of dicyanobenzene (DCB) the e.s.r. spectrum of $Na^+BSQ^{-\cdot}Na^+$ was not observed. Indeed, reduction of dicyanobenzenes in ethereal solvents containing 0.4M-$NaBPh_4$ yields first $Na^+DCB^{-\cdot}Na^+$, whose e.s.r. spectrum can be observed over many hours. However, after about a day, the solutions exhibit only the well resolved spectrum of the triple ion of biphenyl ($Na^+BP^{-\cdot}Na$), shown in Figure 3. The degradation of various radical anions (or ion aggregates) to biphenyl derivatives has been encountered before in e.s.r. investigations. For example $BP^{-\cdot}$ was detected after reduction of pivalophenone [$(CH_3)_3$–C–CO–Ph] on a potassium mirror in DME.[8] Moreover, the radical anion of 4,4'-dinitrobiphenyl was observed after reduction of 4,4'-dinitrobenzophenone by potassium t-butoxide in dimethyl sulphoxide.[9] There is no doubt that in these cases the biphenyl radicals come from the decomposition of the starting organic substrates.

Conversely the presence of biphenyl in solutions of $Na^+DCB^{-\cdot}$ containing $NaBPh_4$ may by due either to an impurity in $NaBPh_4$ or to the decomposition of the salt itself. Even if traces of BP have been found both by t.l.c. and g.l.c. in the commercial salts (see Experimental section), no e.s.r. signals were detected from the samples obtained by the contact of 0.4M-$NaBPh_4$ solutions in DME or THF with a sodium mirror in high vacuum. Consequently it appears that BSQ and BP result from the decomposition of $NaBPh_4$ ' catalysed ' by ion pairs. As reported by Sato and his co-workers [10a,b] for the binary systems of tetraphenylborate salt and organic acids, it is likely that triphenylboron is produced first by reaction (2) and then decomposes into phenyl and

$$BPh_4^- + H^+ \longrightarrow BPh_3 + Ph \qquad (2)$$

$$2BPh_3 \longrightarrow Ph^{\cdot} + {}^{\cdot}B_2Ph_5 \qquad (3)$$

pentaphenyldiboron radicals [reaction (3)]. The pentaphenyldiboron radical has been observed by e.s.r. spectroscopy [10a] and it was found to be stable only in ethanol.[10a]

Formally the phenyl radicals can dimerize, yielding BP on starting from DCBs, or they can be oxidized to BSQ by nitro-derivatives. Indeed, dimerization of the highly reactive phenyl radical seems improbable, as it would be expected to abstract hydrogen very rapidly from an ethereal solvent. Recent electrochemical studies [11] suggest that free phenyl radicals are not

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† Throughout this paper we use the term ' triple ion ' to indicate a chemical equilibrium between the ion pair and the triple ion, according to equation (1). In this view, the e.s.r. spectrum of the triple ion is properly an averaged spectrum, *i.e.*, the sum of the individual spectra of the ion pair and the triple ion, weighted by their equilibrium population.[6]

intermediates in the oxidation of BPh_4^-, and biphenyl is formed[12] by intramolecular coupling of two phenyl groups in neutral $\cdot BPh_4$. A similar reaction is expected[11] in the potassium metal reduction of tetraphenylmethane in ethereal solvents, where biphenyl radical anion is detected.[13] Formation of BSQ and BP appears to be dependent both on the solvent and the structure of the radical anion. As shown in the Table and Figures 1 and 2, the formation of BSQ occurs more favourably in THF, whereas in DME it occurs to a lesser extent, or not at all. As for the structure of the radical anions, the number and the relative position of the substituents appear to be a decisive factor in the occurrence of the reaction. As shown in the Table, only radical anions with two substituents on the same aromatic ring promote the formation of BSQ and BP. An exception is found in the case of the dinitro-derivatives, as 1,2-dinitrobenzene does not promote the formation of BSQ. However, the e.s.r. spectrum of the triple ion of 1,2-dinitrobenzene (g 2.004 2) changes within few hours to a new one (g 2.006 7) shown in Figure 4. The hyperfine pattern of the unknown species is consistent with only one large nitrogen hyper-

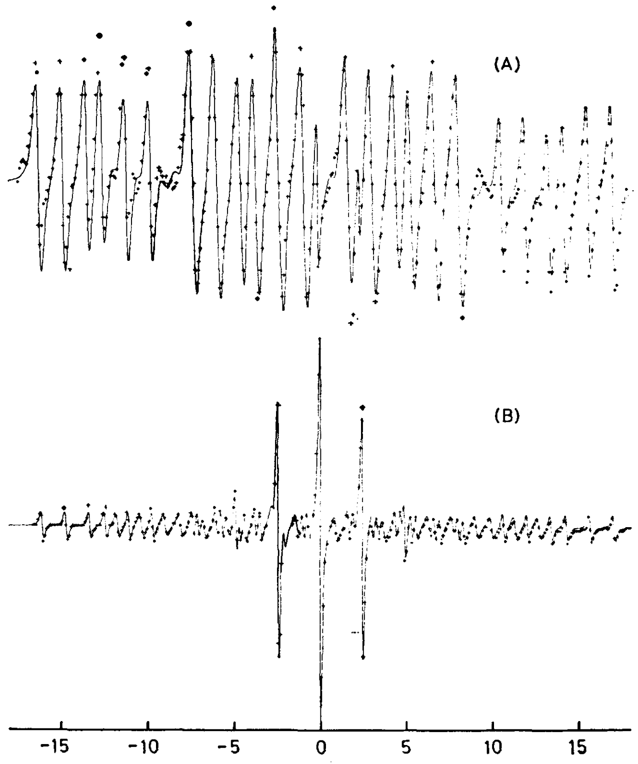

FIGURE 1 E.s.r. spectra of 3,5-dinitropyridine$^{-\cdot}$Na$^+$ in ethereal solvents containing 0.4M-NaBPh$_4$ at 20 °C. Solid lines: simulated spectra; points: experimental spectra. (A) In DME: first hyperfine pattern, $a_{H(NO_2)}$ 8.949 ± 0.004, $a_{N(-N=)}$ 1.386 ± 0.004, $a_H^{triplet}$ 4.353 ± 0.003, $a_H^{doublet}$ 3.635 ± 0.006, W_0 0.353 ± 0.010, B_N 0.010 ± 0.004, W_{exch} 0.487 ± 0.031 G; second hyperfine pattern, $a_H^{quintet}$ 2.419 ± 0.013, W_0 0.183 ± 0.025 G; [BSQ$^{-\cdot}$]/[A$^{-\cdot}$] 0.008 ± 0.002; the second hyperfine pattern is at lower fields with respect to the first one (ΔH 0.482 ± 0.010 G). (B) In THF: first hyperfine pattern, $a_{N(No_2)}$ 8.995 ± 0.003, $a_{N(-N=)}$ 1.368 ± 0.003, $a_H{}^{triplet}$ 4.340 ± 0.002, $a_N^{doublet}$ 3.630 ± 0.005, W_0 0.155 ± 0.008, B_N 0.002 ± 0.001, C_N 0.008 ± 0.002, W_{exch} 0.093 ± 0.005 G; second hyperfine pattern, $a_H^{quintet}$ 2.439 ± 0.002, $W_0 = 0.132 \pm 0.002$ G; [BSQ$^{-\cdot}$]/[A$^{-\cdot}$] 0.348 ± 0.017; the second hyperfine pattern is at lower fields with respect to the first one (ΔH 0.450 ± 0.011 G)

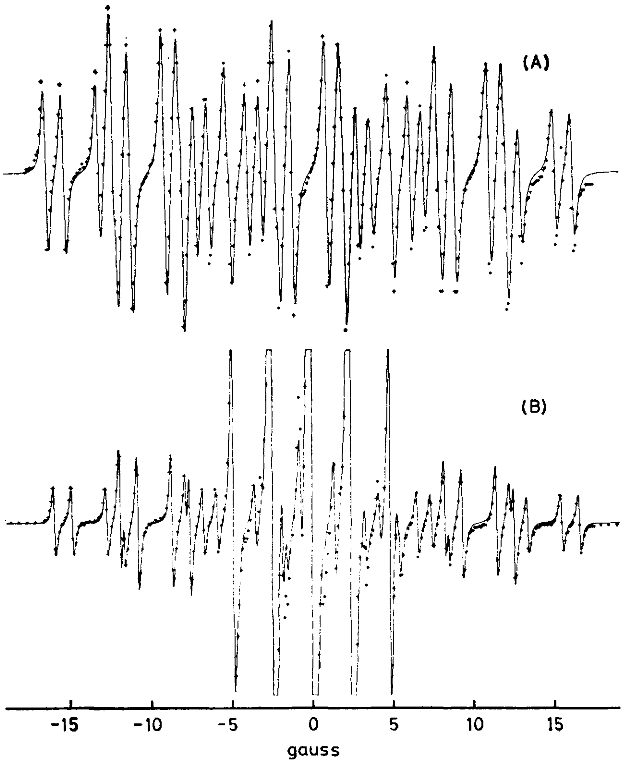

FIGURE 2 E.s.r. spectra of m-dinitrobenzene $^{-\cdot}$Na$^+$ in ethereal solvents containing 0.4M-NaBPh$_4$ at 20 °C. Solid lines: simulated spectra; points: experimental spectra. (A) In DME: $a_{N(NO_2)}$ 10.021 ± 0.004, $a_H^{triplet}$ 4.060 ± 0.004, $a_H^{doublet}$ 3.215 ± 0.005, $a_H^{doublet}$ 1.083 ± 0.005, W_0 0.263 ± 0.010, B_N 0.019 ± 0.004, C_N 0.012 ± 0.007, W_{exch} 0.025 ± 0.006 G; only one hyperfine pattern is displayed. (B) In THF: first hyperfine pattern: $a_{N(NO_2)}$ 10.053 ± 0.003, $a_H^{triplet}$ 4.047 ± 0.004, $a_H^{doublet}$ 3.214 ± 0.005, $a_H^{doublet}$ 1.096 ± 0.005, W_0 0.188 ± 0.006, B_N 0.009 ± 0.004 G, second hyperfine pattern, $a_H^{quintet}$ 2.427 ± 0.003, W_0 0.184 ± 0.007 G; [BSQ$^{-\cdot}$]/[A$^{-\cdot}$] 2.045 ± 0.123; the second hyperfine pattern is at lower fields with respect to the first one (ΔH 0.356 ± 0.004 G)

Paramagnetic species observed in the system
(A$^{-\cdot}$Na$^+$–THF or DME–NaBPh$_4$–)

A	DME	THF
Nitrobenzene	$A^{-\cdot}$	$A^{-\cdot}$
1,2-Dinitrobenzene	$A^{-\cdot}$ [a]	$A^{-\cdot}$ [a]
1,3-Dinitrobenzene	$A^{-\cdot}$	$A^{-\cdot}$ + $BSQ^{-\cdot}$ [b]
1,4-Dinitrobenzene	$A^{-\cdot}$	$A^{-\cdot}$ + $BSQ^{-\cdot}$
3-Nitropyridine	$A^{-\cdot}$	$A^{-\cdot}$
3,5-Dinitropyridine	$A^{-\cdot}$ + $BSQ^{-\cdot}$ [c]	$A^{-\cdot}$ + $BSQ^{-\cdot}$ [c]
4-Nitrobenzophenone	$A^{-\cdot}$	$A^{-\cdot}$
4,4′-Dinitrobenzophenone	$A^{-\cdot}$	$A^{-\cdot}$
Benzonitrile	$A^{-\cdot}$	$A^{-\cdot}$
1,2-Dicyanobenzene	$A^{-\cdot}$ + $BP^{-\cdot}$ [d]	$A^{-\cdot}$
1,3-Dicyanobenzene	$A^{-\cdot}$ + $BP^{-\cdot}$	$A^{-\cdot}$
1,4-Dicyanobenzene	$A^{-\cdot}$ + $BP^{-\cdot}$	$A^{-\cdot}$
4,4′-Dicyanobenzophenone	$A^{-\cdot}$	$A^{-\cdot}$

[a] In a few hours $A^{-\cdot}$ reacts to the more stable radical anion, whose spectrum is shown in Figure 4. [b] The ratio [BSQ$^{-\cdot}$]/[A$^{-\cdot}$] is 2.0 ± 0.1. [c] The ratio [BSQ$^{-\cdot}$]/[A$^{-\cdot}$] is 0.35 ± 0.02 in THF and 0.008 ± 0.002 in DME solutions respectively, as shown in Figure 2. [d] After about one day BP$^{\cdot}$ is the only radical present in solution.

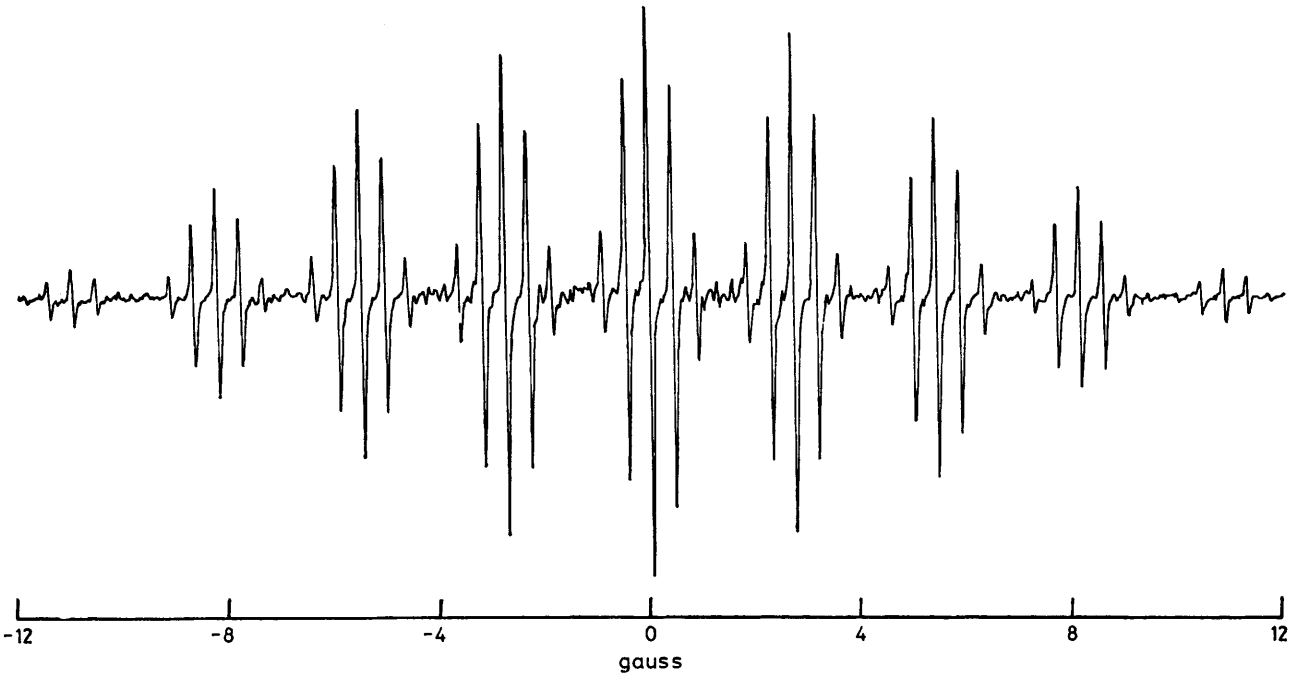

FIGURE 3 Experimental e.s.r. spectrum displayed by DME solutions of the dicyanobenzene radical anions containing 0.4M-NaBPh$_4$, a day after the reduction of the organic substrates on a sodium mirror. The spectrum was simulated with the following parameters: $a_{\mathrm{H}}^{\mathrm{triplet}}$ 5.333 $\pm$ 0.002, $a_{\mathrm{H}}^{\mathrm{quintet}}$ 2.653 $\pm$ 0.002, $a_{\mathrm{H}}^{\mathrm{quintet}}$ 0.430 $\pm$ 0.001, W_0 0.103 $\pm$ 0.002 G

fine splitting coupling constant (a^{N} 8.08 G), a triplet due to two equivalent protons (a^{H} 4.25 G), and two proton doublets of 1.29 and 0.88 G, respectively. The same spectrum is observed when the ion pair of 1-nitro-2-nitrosobenzene and sodium is allowed to react with NaBPh$_4$. The observed spectrum is consistent with the hyperfine pattern of a nitro- (or nitroso-) benzene radical anion substituted in the *ortho*-position by an electron-withdrawing group.

On the basis of these results we can tentatively conclude that phenyl acts as a substituent. Indeed the reaction of an authentic sample of 2-nitrobiphenyl with

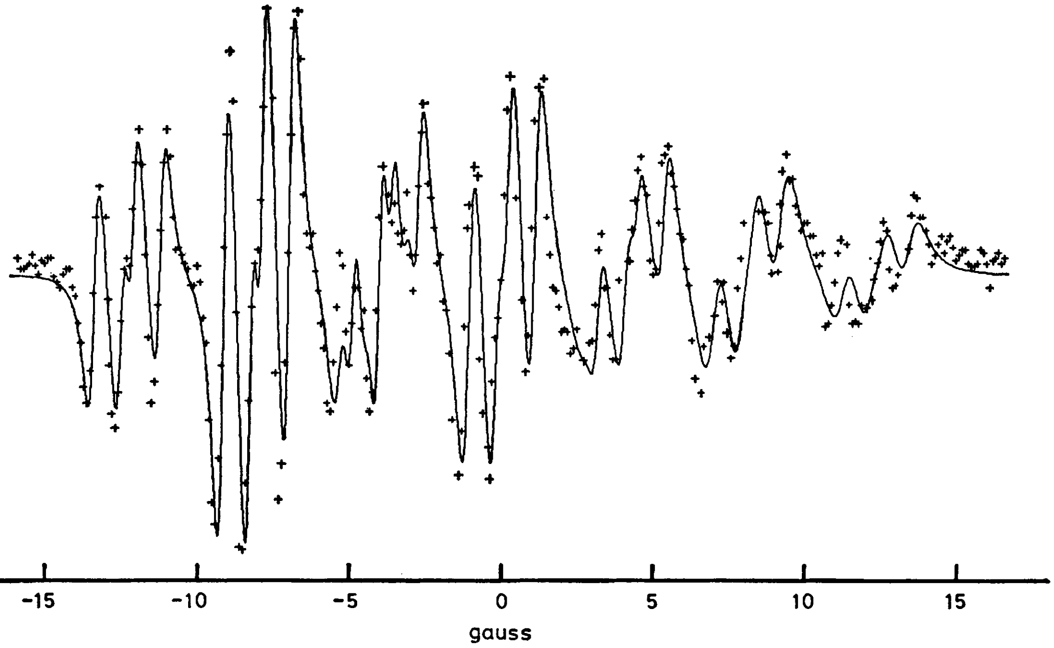

FIGURE 4 E.s.r. spectrum displayed by the ethereal solutions of *o*-dinitrobenzene and 1-nitro-2-nitrosobenzene containing 0.4M-NaBPh$_4$, a few hours after the reduction of the organic substrates on a sodium mirror. Points: experimental spectrum. Solid line: spectrum simulated with the following parameters: a_{N} 8.079 $\pm$ 0.009, $a_{\mathrm{H}}^{\mathrm{triplet}}$ 4.252 $\pm$ 0.011, $a_{\mathrm{H}}^{\mathrm{doublet}}$ 1.290 $\pm$ 0.013, $a_{\mathrm{H}}^{\mathrm{doublet}}$ 0.876 $\pm$ 0.012, W_0 0.461 $\pm$ 0.023, B_{N} 0.151 $\pm$ 0.026, C_{N} 0.078 $\pm$ 0.029 G

sodium in THF containing 0.4M-$NaBPh_4$ gives two different paramagnetic species. The corresponding e.s.r. spectrum shows that one species (present in 25.3% proportion) ($a_{NO_2}^{N}$ 9.89, $a_{doublet}^{H}$ 4.05, $a_{doublet}^{H}$ 3.20, $a_{triplet}^{H}$ 1.30 G; g 2.004 6) is the triple ion of 2-nitrobiphenyl with sodium.* The other (present in 74.7% proportion) has the same hyperfine pattern and g value as the unknown species. The spectral hyperfine splitting coupling constants of the unknown species should be compatible with those of 2-nitrosobiphenyl radical anion. We were not able to obtain any e.s.r. signal from solutions of authentic samples of 2-nitrosobiphenyl reduced under the same experimental conditions. However, reduction of 2-nitrosobiphenyl with a large excess of Bu^tOK in dimethyl sulphoxide containing dibenzo-18-crown-6 ether gave an e.s.r. spectrum which strongly resembles that of the unknown species (a_{NO}^{H} 7.55, $a_{triplet}^{H}$ 3.87, $a_{doublet}^{H}$ 1.21, $a_{doublet}^{H}$ 1.04 G; g 2.006 8). Also, basic reduction of 1-nitro-2-nitrosobenzene with CH_3ONa in dimethyl sulphoxide containing $NaBPh_4$ displayed the same hyperfine pattern (a_{NO}^{N} 7.91, $a_{triplet}^{H}$ 4.26, $a_{doublet}^{H}$ 1.22, $a_{doublet}^{H}$ 0.84 G). Therefore it seems reasonable to identify the unknown species as the triple ion of 2-nitrosobiphenyl. Some slight differences in the observed hyperfine splitting constants are due to the different media used for the experiments. McLachlan calculations,[14] with the parameters reported in refs. 9, 15, and 16, support our assignment (a_{NO}^{N} 7.64, a_3^{H} −4.28, a_4^{H} 1.49, a_5^{H} −3.12, a_6^{H} 0.99 G). Reduction of the nitro- to the nitroso-group in the presence of $NaBPh_4$ has been also observed in the case of the 4-nitrobenzophenone radical anion.[9]

The present results are evidence that $NaBPh_4$ in ethereal solutions may decompose when ion pairs formed by aromatic compounds and alkali-metal cations are present. The role both of the number and position of the substituents in $A^{-\cdot}$ has been clarified, showing that the nature of the substituent (NO_2 or CN) determines the type of the decomposition product (BSQ or BP, respectively).

Both the strong influence of the structure of the radical anion and the likelihood of an intramolecular coupling of two phenyl ring in $NaBPh_4$ suggest that the reactive agents are quadruple $Na^+A^{-\cdot}Na^+BPh_4^-$, rather than triple ions $Na^+A^{-\cdot}Na^+$. Indeed, the presence of quadruples in concentrated ethereal solution of electrolytes has been unequivocally established.[17]

EXPERIMENTAL

Samples of $NaBPh_4$ were obtained from Fluka, Aldrich, and K and K Laboratories. All the samples, used without additional purification, gave BSQ or BP as described in the text above. The presence of traces of BP as an impurity was detected both by t.l.c. and g.l.c.

It is noteworthy that, after thermal pretreatment of $NaBPh_4$ at 100 °C for 48 h, traces of BP were revealed again, but such a treatment avoids formation of $BP^{-\cdot}$ and $BSQ^{-\cdot}$ when the salt is allowed to react with the ion pairs.

The compounds collected in the Table are commercial products with the exception of 3,5-dinitropyridine,[18] 4,4′-dinitrobenzophenone,[9] and 4,4′-dicyanobenzophenone,[19] prepared according the quoted references. 2-Nitrosobiphenyl was synthesised as follows. To an ice-cooled suspension of 2-aminobiphenyl (2.5 g) in H_2O (180 ml) a solution of Caro's acid (45.6 ml) was added dropwise. After stirring for 6 h at room temperature, the suspension was diluted with water, filtered, and the wet material obtained was steam distilled. 2-Nitrosobiphenyl was filtered from the distillate as a yellow-green product, which was air-dried (0.025 g, 1%); m.p. (EtOH) 101—103 °C; $\nu_{max.}$ (Kel-F) 1 480 cm^{-1} (NO). Purification of DME, THF (Fluka), and the reactions of organic substrates with alkali-metals were carried out by standard techniques.

E.s.r. spectra were recorded with a Varian E-line Century Series spectrometer operating at 9.5 GHz and equipped with a 9 in magnet.

Hyperfine coupling constants and linewidths of e.s.r. spectra were optimized by a least-squares line shape fitting procedure.[6,9] The program allows the determination of the relative areas and the position of two different hyperfine patterns. Algorithm (5) was used to compute the spectrum

$$Y(x) = y_1(x) + C_{y_2}(x + \Delta x_0) \tag{5}$$

where $y(x)$ is the first derivative Lorentzian lineshape function, C is the relative amplitude of spectrum (2) with respect to spectrum (1), and Δx_0 is the separation between the symmetry centres of the two spectra; x is the sweep variable which we assume to be sampled for a discrete set of random or equispaced points. Explicit expressions for $y(x)$ as well as its analytical derivatives are given in ref. 9. The experimental e.s.r. spectra were digitalized ' by hand ' over about 350 data points. Calculations usually converged very quickly, with standard errors of a few milligauss (see Figures 1—4).

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* Reduction of 2-nitrobiphenyl with a large excess of Bu^tOK in dimethyl sulphoxide containing dibenzo-18-crown-6 ether shows an e.s.r. spectrum which is consistent with following hyperfine splitting constants: $a_{NO_2}^{N}$ 9.97, $a_{doublet}^{H}$ 3.89, $a_{doublet}^{H}$ 3.19, $a_{triplet}^{H}$ 1.13 G and g 2.0048.

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