An Electron Spin Resonance Investigation of the Intermediates and Products in the Basic Reduction of *cis*- and *trans*-*p*-Nitro-β-bromostyrenes

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The mechanism of chemical and electrolytic reduction of *cis*- and *trans*-*p*-nitro-β-bromostyrenes has been studied by e.s.r. spectroscopy. Both isomers undergo dehydrobromination by electrolytic reduction, whereas chemical reduction by potassium t-butoxide also induces debromination. The anion radicals of *cis*- and *trans*-*p*-nitro-β-bromostyrenes, *p*-nitrostyrene, *p*-nitrophenylacetylene, and *p*-nitrobenzoic acid were identified, through the corresponding e.s.r. spectra, as intermediates or products of the reactions investigated. *p*-Nitrophenylacetylene and *p*-nitrobenzoic acid were also isolated from the reaction mixture. The effects of the solvent and the counterion on the yield of electrolytic conversion of *cis*-*p*-nitro-β-bromostyrene to *p*-nitrophenylacetylene are also reported.

IN previous papers,[1,2] the anion radicals of a series of mononitro-derivatives of styrene[1,2] and 1,1-diphenylethylene[1] were studied by e.s.r. spectroscopy combined with quantum mechanical calculations, in order to obtain information on their conformation and spin density distribution. These radicals were obtained by electrolytic reduction in dimethyl sulphoxide (DMSO),[1,2] acetonitrile,[1,2] and liquid ammonia.[2] Recently,[3] the anion radicals of a series of mono- and di-nitro-derivatives of 1,1-diphenylethylene were produced by chemical reduction with alkali-metal alkoxides in DMSO. Information on their reactivity was obtained by means of a detailed study of the paramagnetic intermediates from basic cleavage and oxidation.

In this paper the investigation is extended to chemical reduction of *cis*- and *trans*-*p*-nitro-β-bromostyrenes (BS) by potassium t-butoxide in DMSO. In this medium, both isomers of BS exhibit an e.s.r. spectrum which is consistent with one 1 : 1 : 1 triplet of *ca.* 9.0 G due to the nitrogen, two 1 : 2 : 1 triplets of *ca.* 3.4 and 1.1 G associated with the protons *ortho* and *meta* to the nitro-group, respectively, and a proton doublet of *ca.* 2.2 G (Figures 1A and 2A). The same spectrum is observed when *cis*-BS is reduced electrolytically in DMSO and *NN*-dimethylformamide (DMF). On the other hand, the spectrum obtained by electrolytic reduction of *trans*-BS can be reproduced by including another proton doublet of *ca.* 1.5 G. The different behaviour observed by e.s.r. spectroscopy when basic reduction or electrolytic reduction is employed, prompted us to perform further investigation to obtain more insight into the paramagnetic species involved and the reaction mechanism. Another point of interest is comparison between the spin distribution of the two isomers of BS, which has been determined both experimentally, from the corresponding e.s.r. spectra, and theoretically, by means of approximate MO calculations.

The reactions of both isomers of BS in alkaline media were investigated extensively by Cristol, Norris, and their co-workers.[4,5] It was found that dehydrobromination occurs, the main final products being *p*-nitrophenylacetylene (PA) for both isomers in isopropyl alcohol and for the *cis*-isomer in ethanol. In the latter solvent the *trans*-isomer gives 1,1-diethoxy-2-*p*-nitrophenylethane. In both solvents *cis*-BS eliminates Br *ca.* 1 000 times faster than does *trans*-BS.[4,5]

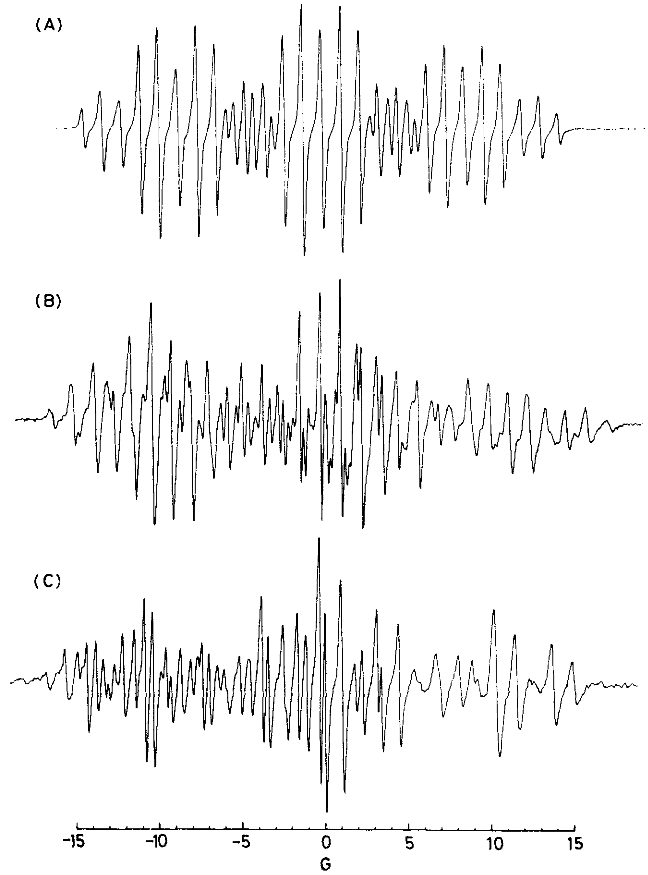


FIGURE 1 Experimental e.s.r. spectra displayed by solutions of *cis*-BS in DMSO–Bu^{t}OH (8 : 2) containing Bu^{t}OK, as a function of time. For comparison with the calculated spectra, see Figure 2. Modulation amplitude 0.8 G; microwave power 5 mW; time constant 0.25 s; scan rate 5 G^{-1} min^{-1}. (A) *t* 3 min; (B) *t* 80 min; (C) *t* 120 h

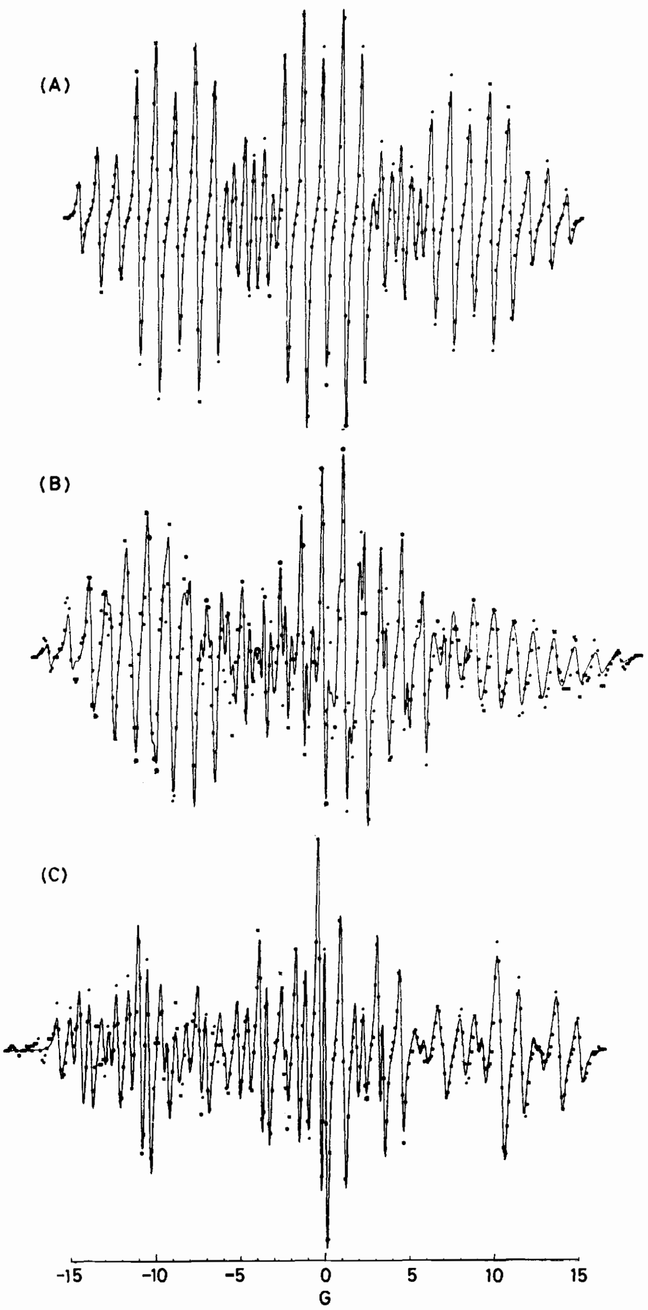
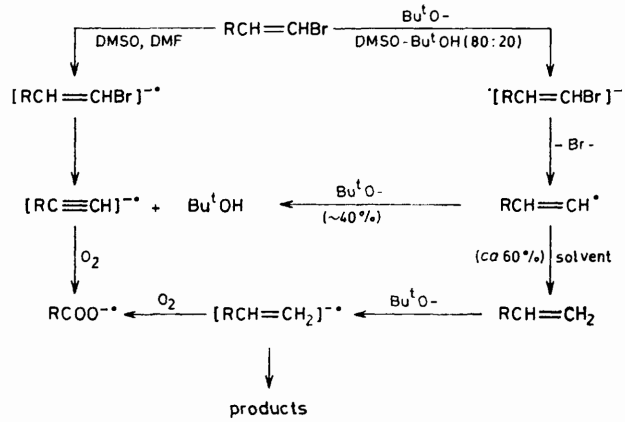


FIGURE 2 E.s.r spectra displayed by solutions of *cis*-BS in DMSO–Bu^{t}OH (8 : 2) containing Bu^{t}OK, as a function of time (*trans*-BS solutions behave in the same way). Solid lines, simulated spectra; points, digitized experimental spectra. The intensity values were scaled by factor of 2, in order to get a better graphic reproduction. (A) *t* 3 min; a_N 8.688 ± 0.002, a_H (triplet) 3.448 ± 0.005, a_H (doublet) 2.313 ± 0.009, a_H (triplet) 1.116 ± 0.006, W_0 0.198 ± 0.004, B_N 0.018 ± 0.003, C_N 0.037 ± 0.004 G; only the hyperfine pattern of the PA anion radical is displayed. (B) *t* 80 min; first hyperfine pattern ($S^{-\bullet}$): a_N 9.039 ± 0.007, a_H (triplet) 3.457 ± 0.005, a_H (triplet) 1.221 ± 0.014, a_H (doublet) 2.503 ± 0.026, a_H (doublet) 2.456 ± 0.022, a_H (doublet) 1.327 ± 0.014, W_0 0.176 ± 0.016 G; second hyperfine pattern ($PA^{-\bullet}$): a_N 9.738 ± 0.037, a_H (triplet) 3.391 ± 0.023, a_H (doublet) 2.046 ± 0.030, a_H (triplet) 0.981 ± 0.033, W_0 0.423 ± 0.011 G; $[PA^{-\bullet}]/[S^{-\bullet}]$ 0.7 ± 0.2; the second hyperfine pattern is at lower fields with respect to the first one (ΔH 0.563 ± 0.017 G). (C) *t* 120 h; first hyperfine pattern ($BA^{-\bullet}$): a_N 10.450 ± 0.004, a_H (triplet) 3.426 ±

It is well known that dehydrohalogenation[6] and alkoxylation[7] reactions usually occur in the Bu^{t}OK–DMSO system. Also, basic dehalogenation can easily occur, as it has been found for 1,2,3-tribromobenzene[8] and 2-bromo- and 2-chloro-1,1-bis-(*p*-nitrophenyl)ethylenes.[3]



SCHEME R = $p\text{-}NO_2C_6H_4$

The reactions investigated are summarised in the Scheme.

RESULTS AND DISCUSSION

On the basis of the results of Cristol, Norris, and their co-workers[4,5] as well as on the basis of the hyperfine structure of the anion radical obtained by chemical reduction of both *cis*- and *trans*-BS (Figures 1A and 2A), the observed e.s.r. spectrum can be assigned to the anion radical of PA. Reduction of an authentic sample of PA confirms the assignment. In the light of the present observations, it appears that the e.s.r. spectrum previously assigned[1] to the *cis*-BS anion radical is that of the PA anion radical. The spectrum of $PA^{-\bullet}$ is to our knowledge, unknown, and in this view the anion radical has been generated in different media and under different conditions. The results are collected in Table 1. It appears that the hyperfine splitting (h.f.s.) constants are significantly dependent on both the solvent and the counterion. Indeed, as a consequence of ion pairing, the nitrogen h.f.s. constant is greater for solvents of low dielectric constant and for counterions of small radius.

Basic Reduction of cis- *and* trans-*BS*.—Since the basic strength of the system Bu^{t}OK–DMSO is stronger[9] than that of the system NaOH–alcohols, no difference between the reaction rates of the two isomers of BS can be observed in the former case. After the addition of Bu^{t}OK, DMSO solutions of both isomers readily display

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FIGURE 2—(*continued*)

0.004, a_H (triplet) 1.113 ± 0.004, W_0 0.181 ± 0.006, B_N 0.033 ± 0.006, C_N 0.076 ± 0.007 G; second hyperfine pattern (unknown): a_N 10.606 ± 0.005, a_H (triplet) 3.493 ± 0.004, a_H (triplet) 1.313 ± 0.005, W_0 0.194 ± 0.005, B_N 0.051 ± 0.007, C_N 0.105 ± 0.008 G; [unknown]/$[BA^{-\bullet}]$ 1.34 ± 0.09; the unknown hyperfine pattern is at lower field with respect to that of $BA^{-\bullet}$ (ΔH 0.331 ± 0.002 G) the uncontaminated spectrum of $PA^{-\bullet}$ (g 2.0050). A possible route for the basic reduction of BS to $PA^{-\bullet}$ follows reactions (1)—(3) where $B^- = Bu^tO^-$ and

$$RCH{=}CHBr \xrightarrow{B^-} [RCH{=}CHBr]^{-\bullet} \qquad (1)$$

$$[RCH{=}CHBr]^{-\bullet} \longrightarrow RCH{=}CH^{\bullet} + Br^- \qquad (2)$$

$$RCH{=}CH^{\bullet} + B^- \longrightarrow [^1RC{\equiv}CH]^{-\bullet} + BH \qquad (3)$$

$R = p\text{-}O_2NC_6H_4$. It is likely that in the case of *cis*-BS reactions (2) and (3) are concerted, because of the high rate constant observed for *trans*-elimination.[4] In *trans*-BS *cis*-elimination probably occurs through a two-step process, *i.e.* equations (2) and (3). An alternative route could involve concertedness of reactions (1) and (2), followed by reaction (3), as the e.s.r spectrum of $BS^{-\bullet}$ is not observed.

After 24 h a solution of $PA^{-\bullet}$ changes from blue to dark red and a new e.s.r. spectrum (g 2.0052) is observed. Its hyperfine pattern is consistent with two pairs of equivalent protons (3.424 ± 0.006, 1.108 ± 0.006 G and one nitrogen (10.493 ± 0.006 G): it was assigned to the dianion radical of *p*-nitrobenzoic acid (BA) by comparison with the e.s.r. spectrum obtained by reduction of an authentic sample under the same conditions.[3]

As Bu^tOK in DMSO significantly enhances the rate of a large number of reactions,[10,11] no other intermediates have been detected by e.s.r. spectroscopy in the course of reaction of BS to PA and BA. In view of this fact we used a less basic system such as Bu^tOK in DMSO–Bu^tOH (8 : 2). In this medium PA is converted into BA in 56% yield within 24 h, and in 88% yield within 190 h, whereas in pure DMSO the reaction goes to completion within 24 h. Conversion yields have been determined through a lineshape least-squares analysis of the e.s.r. spectra displayed by the reaction system. No signal from any other paramagnetic intermediate was observed. It should be noted that the e.s.r. method monitors the conversion of $PA^{-\bullet}$ to $BA^{2-\bullet}$, which may not necessarily correspond to [PA] and [BA]. However, quenching of the mixture by aqueous acid and chemical analysis of the final products showed that the ratio [PA] : [BA] is nearly the same as for the corresponding anion radicals.

In DMSO–Bu^tOH (8 : 2) both *cis*- and *trans*-BS quickly display the e.s.r. spectrum of $PA^{-\bullet}$, which in the early stage of the reaction appears to be free from any other contaminating signal (Figures 1A and 2A). After *ca.* 220—250 h the reaction is complete, the only signal displayed being that of the very stable BA dianion radical. In the intermediate stages of the reaction the e.s.r. spectra detected appear to be due to different radicals, whose relative concentrations change continually. Both the number of paramagnetic intermediates and similarity of their h.f.s. constants prevented us from identifying and assigning all the observed signals. However, we were able to recognize two different hyperfine patterns. The first (Figures 1B and 2B) can be observed after *ca.* 80 min reaction period; it has a g factor of 2.0047 and is consistent with a nitrogen triplet (9.039 ± 0.007 G), two triplets (3.457 ± 0.005 and 1.221 ± 0.014 G) from two pairs of equivalent protons, and three proton doublets (2.503 ± 0.026, 2.456 ± 0.022, and 1.327 ± 0.014 G). It was assigned to the anion radical of *p*-nitrostyrene (S) [2] by comparison with the e.s.r. spectrum obtained by reduction of an authentic sample under the same conditions. The latter hyperfine pattern (Figures 1C and 2C; a_N 10.606 ± 0.005, a_H(triplet) 3.493 ± 0.004, a_H(triplet) 1.313 ± 0.005 G), which can be observed after *ca.* 120 min, strongly resembles that of the BA dianion radical, but it lies at lower fields (g 2.0054) and its assignment is still a puzzle. It appears that the unassigned spectrum of Figure 1C is due to some derivative of BS (or S), as only the signal of $BA^{2-\bullet}$ can be observed by reducing an authentic sample of PA under the same conditions.

The present results are evidence that *cis*- and *trans*-BS in basic media may experience both dehydrobromination according to equations (1)—(3), and debromination according to equations (1), (2), (4), and (5). Reactions

$$RCH{=}CH^{\bullet} \xrightarrow{\text{solvent}} RCH{=}CH_2 \qquad (4)$$

$$RCH{=}CH_2 \xrightarrow{B^-} [RCH{=}CH_2]^{-\bullet} \qquad (5)$$

(3) and (4) are competitive; the ratio $[PA^{-\bullet}]/[^1S^{-\bullet}]$ 0.7 ± 0.2, obtained from the spectrum of Figure 2B after reaction for 80 min, indicates that (4) is slightly favoured.

Electroreduction of cis- *and* trans-*BS*.—A suitable model for the electron-transfer reaction (1) might be electrochemical reduction of the corresponding substrates. In this view, we have investigated the electroreduction (see Experimental section) of *cis*- and *trans*-BS in different media. As noted above, *trans*-BS gives the corresponding stable anion radical (g 2.0060),[1] which slowly dehydrohalogenates, as shown in Figure 3. Conversely, *cis*-BS is promptly converted to $PA^{-\bullet}$. Owing to the fast dehydrobromination of *cis*-BS (*trans*-elimination) the problem of detection and investigation of the h.f.s. constants of its anion radical is still open.

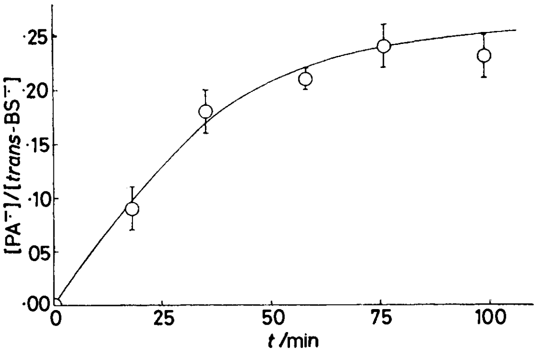

FIGURE 3 Electrolytic dehydrobromination rate of *trans*-BS in DMF containing 0.1M-TBAP

However, when *cis*-BS is reduced by electrolytical techniques using bromide salts as supporting electrolytes, a significant amount of the corresponding anion radical

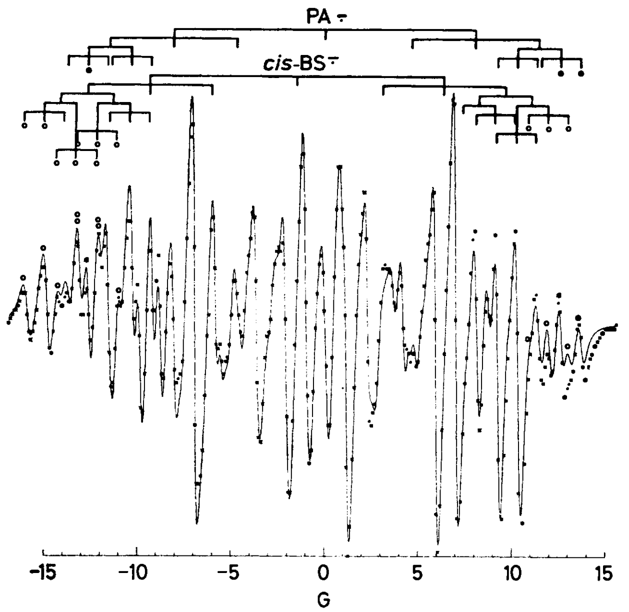

FIGURE 4 E.s.r. spectrum displayed by a solution of *cis*-BS in DMF containing TBAB, under electrolytic reduction. Solid line: simulated spectrum; points: digitized experimental spectrum. The theoretical spectrum has been synthesized as the sum of the hyperfine patterns of the anion radicals of PA (*g* 2.0050) and *cis*-BS (*g* 2.0059), by using the h.f.s. constants and the relative concentration reported in the first column of Table 1. The tree diagrams for the low- and high-field portions of the two hyperfine patterns are reported. The circles provide assignment of non-overlapping lines

is obtained. Indeed the relative e.s.r. spectrum (Figure 4) clearly displays the hyperfine patterns of two different paramagnetic species. One pattern may be promptly assigned to the anion radical of PA (*g* 2.0050). The other was assigned to the anion radical of *cis*-BS (*g* 2.0059), as it consists of one large triplet due to the nitrogen, two triplets characteristic of the *meta*- and *ortho*-protons of the nitrophenyl group, and two doublets due to the vinyl protons. The higher *g*-value measured for the *cis*-BS anion radical is in line with the fact that spin–orbit coupling is more effective in the halogen-substituted anion radicals than in the unsubstituted compounds. The h.f.s. constants of the *cis*-BS anion radical, obtained by electroreduction in DMSO and DMF by using different supporting electrolytes, are collected in Table 1. It appears that higher dielectric constants (DMSO > DMF) favour the debromination reaction (2), whereas the use of bromides as supporting electrolytes stabilizes the *cis*-BS anion radical. As expected, the salt effect is proportional to the dissociation constant of the salt itself (Bu^n_4NBr > KBr), *i.e.* to the concentration of Br^- ion.

Reduction of cis- *and* trans-*BS by Alkali Metals*.—The e.s.r. spectrum obtained by reducing *cis*-BS on a sodium mirror in 1,2-dimethoxyethane (DME) exhibits a well resolved hyperfine pattern, where the quartet typical of the sodium cation is easily recognized (Figure 5B). The signal is stable for about two days and is not contaminated by signals of other paramagnetic species. Computer analysis of the e.s.r. spectrum (Table 1) allows assignment of the signals to the tight ion pair of *cis*-BS anion radical with sodium cation. This finding is somewhat surprising, when compared with the current theories of dissociative electron transfer reactions.[12] However, reduction of *cis*-BS by lithium and potassium, as well as reduction of *trans*-BS by lithium, sodium, and potassium in DME give slowly the ion pairs of PA anion radical. In these cases no e.s.r. signal is observed for bromine derivatives.

Calculations.—Spin density calculations were carried out by means of the McLachlan method,[13] based on the

TABLE 1

Experimental hyperfine coupling constants and linewidth parameters (B_N, C_N) of PA, *cis*- and *trans*-BS anion radicals in different media [a]

Compound	Nucleus	$2nI + 1$	DMF–TBAB	DMF–KBr	DMSO–KBr	DMSO–TBAP	DME–Na	DME–Li
PA	N	3	8.169 ± 0.001	6.833 ± 0.004	9.051 ± 0.001	8.284 ± 0.001	9.900 ± 0.001	10.504 ± 0.003
	H	3	3.364 ± 0.004	3.388 ± 0.009	3.409 ± 0.002	3.367 ± 0.002	3.481 ± 0.002	3.561 ± 0.005
	H	2	2.316 ± 0.007	2.279 ± 0.017	2.234 ± 0.003	2.286 ± 0.005	2.180 ± 0.002	2.149 ± 0.006
	H	3	1.072 ± 0.004	1.138 ± 0.012	1.129 ± 0.002	1.077 ± 0.003	1.194 ± 0.002	1.252 ± 0.004
	Me	4					0.392 ± 0.002	
	B_N		0.019 ± 0.002	0.015 ± 0.004	0.027 ± 0.001	0.023 ± 0.001	0.012 ± 0.002	0.010 ± 0.004
	C_N		0.029 ± 0.002	0.043 ± 0.007	0.045 ± 0.002	0.019 ± 0.001	0.004 ± 0.002	0.019 ± 0.006
cis-BS	N	3	7.902 ± 0.004	8.767 ± 0.005	8.439 ± 0.013	8.198 ± 0.012	9.775 ± 0.002	
	H	3	3.253 ± 0.004	3.316 ± 0.006	3.385 ± 0.017	3.288 ± 0.011	3.434 ± 0.003	
	H	2	2.837 ± 0.009	2.655 ± 0.009	2.551 ± 0.015	2.740 ± 0.020	2.521 ± 0.004	*b*
	H	2	1.721 ± 0.011	1.728 ± 0.008	1.840 ± 0.012	1.756 ± 0.017	1.791 ± 0.005	
	H	3	1.054 ± 0.005	1.111 ± 0.006	1.136 ± 0.012	1.083 ± 0.012	1.202 ± 0.004	
	Me	4					0.386 ± 0.003	
[*cis*-BS$^{-\bullet}$]/[PA$^{-\bullet}$]			3.9 ± 0.3	1.4 ± 0.1	1.3 ± 0.3	0.9 ± 0.1		
trans-BS	N	3	8.053 ± 0.005	8.634 ± 0.004	9.343 ± 0.003	8.266 ± 0.005		
	H	3	3.297 ± 0.008	3.370 ± 0.003	3.399 ± 0.003	3.318 ± 0.006		
	H	2	2.891 ± 0.010	2.744 ± 0.010	2.632 ± 0.006	2.841 ± 0.009	*b*	*b*
	H	2	1.535 ± 0.009	1.592 ± 0.009	1.500 ± 0.007	1.522 ± 0.008		
	H	3	1.111 ± 0.007	1.169 ± 0.006	1.179 ± 0.004	1.132 ± 0.005		
	B_N		0.085 ± 0.010	0.033 ± 0.005	0.104 ± 0.004	0.032 ± 0.008		
	C_N		0.029 ± 0.013	0.063 ± 0.006	0.098 ± 0.005	0.032 ± 0.008		

[a] All values are in gauss. [b] The e.s.r. spectrum of PA$^{-\bullet}$,Me$^+$ is observed.

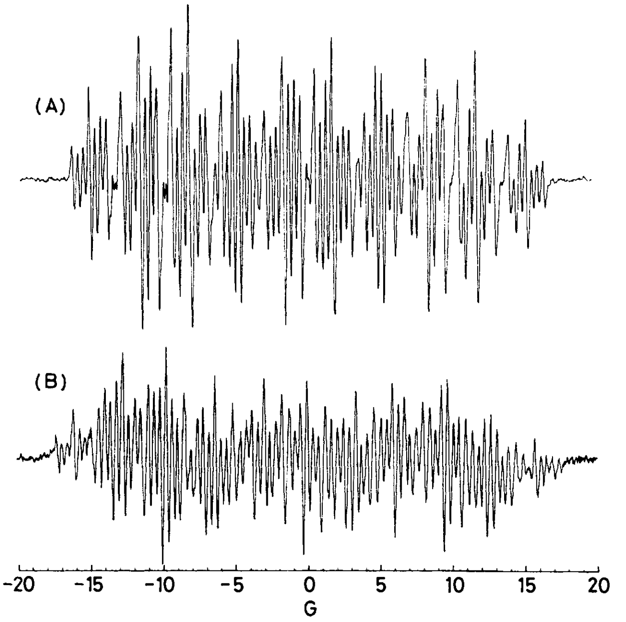

FIGURE 5 (A) Experimental e.s.r. spectrum of PA$^{-\cdot}$Na$^+$ in DME. Modulation amplitude 0.25 G; microwave power 5 mW; time constant 0.25 s; scan rate 5 G min^{-1}. (B) Experimental e.s.r. spectrum of *cis*-BS$^{-\cdot}$Na$^+$ in DME. Modulation amplitude 0.8 G; microwave power 10 mW; time constant 0.25 s; scan rate 5 G min^{-1}. Both spectra were synthesized with the parameters reported in Table 1

σ–π approximation. The required α- and β-integrals were taken from the literature.[13,14] The resonance integrals for the benzene–vinyl bond were adjusted to obtain the best fit between experimental and calculated h.f.s. constants (*cf.* Table 2). According to Honeybourne's recommendation,[15] the original McLachlan procedure has been corrected by forcing the odd α-electron into the perturbed molecular orbitals. The effect of ion pairing on the spin distribution of the anion was calculated by correcting the Huckel parameters for the electrostatic attraction between the anion radical and the cation, according to McClelland.[16] H.f.s. constants were obtained from McLachlan spin densities through the McConnell-type relationships reported in Table 2. It should be noted that, owing to Honeybourne's correction to the McLachlan method, the McConnell parameters of Table 2 differ slightly from the values previously reported.[3] In Table 2 the results of calculations are compared with the experimental values for both free anion radicals and ion pairs. It appears that the McLachlan method gives on the whole a satisfactory interpretation of the experimental spin distribution. In particular the differences in the hyperfine patterns of the two isomers of BS$^{-\cdot}$ are well reproduced. It is noteworthy that Honeybourne's correction gives a better reproduction of the spin density on the α-carbon than the original McLachlan procedure.[1] Also the observed enhancement of the nitrogen h.f.s. constants on changing the counterion from tetra-n-butylammonium to K$^+$ is correctly predicted. The h.f.s. constants of the *cis*- and *trans*-BS$^{-\cdot}$K$^+$ ion pairs are well fitted by using the values of 2.5 and 2.0 Å, respectively, for the distance between the counterion and the nitro-group nitrogen This fact indicates that the ion pair of the *trans*-isomer is tighter than that of the *cis*.

Conclusions.—The course of basic and electrolytic reduction of *cis*- and *trans*-BS is summarized in the Scheme. All the anion radicals indicated in the Scheme

TABLE 2

Experimental and calculated [a, b] h.f.s. constants (G) for magnetic nuclei in the investigated anion radicals and ion pairs

			Free ion		Ion pairs			
Compound	Nucleus	Position	DMF–TBA$^+$	calc.	DMSO–K$^+$	calc. [c]	DME–Na$^+$	calc. [d]
PA	N	1	8.17	8.21	9.05	9.07	9.90	9.66
	H	2,6	3.36	−3.31	3.41	−3.40	3.48	−3.46
	H	3,5	1.07	1.16	1.08	1.24	1.19	1.29
	H	α	2.32	−2.34	2.23	−2.22	2.18	−2.13
cis-BS	N	1	7.90	8.02	8.44	8.93	9.77	9.54
	H	2,6	3.25	−3.24	3.38	−3.36	3.43	−3.42
	H	3,5	1.05	1.14	1.14	1.24	1.20	1.30
	H	α	1.72	1.13	1.84	1.11	1.79	1.08
	H	β	2.84	−3.03	2.55	−2.84	2.52	−2.71
trans-BS	N	1	8.05	8.04	9.34	9.23		
	H	2,6	3.30	−3.25	3.40	−3.39		
	H	3,5	1.11	1.14	1.18	1.27		
	H	α	1.54	1.11	1.50	1.09		
	H	β	2.89	−2.97	2.63	−2.73		
S	N	1	8.31 [e]	8.16	9.04	9.03		
	H	2,6	3.18	−3.29	3.46	−3.39		
	H	3,5	1.11	1.14	1.33	1.23		
	H	α	1.31	0.97	1 22	0.96		
	H	β,β′	2.46	−2.52	2.48	−2.37		

[a] Spin densities calculated by McLachlan method (see text) and translated into h.f.s. constants according to the relationships $a_H = -27.5\rho_c$ and $a_{N(NO_2)} = 27.2(2\rho_N - \rho_0)$. [b] $k_{C-C} = 1.1$, $k_{C=C} = 1.2$, $k_{C\ ring\text{–}C\ vinyl} = 0.87$, 0.90, 0.89, and 0.81, for PA, *cis*-BS, *trans*-BS, and S, respectively. The remaining parameters were taken from the literature.[3,14] [c] The cation is in the molecular plane at r 2.5 Å from the nitrogen of the nitro-group, along the C–NO$_2$ bond, with the only exception of *trans*-BS for which r is 2.0 Å. [d] The cation is in the molecular plane at 1.5 Å from the nitrogen of the nitro-group, along the C–NO$_2$ bond. [e] In DMSO containing tetraethylammonium perchlorate as a supporting electrolyte.[2]

were identified through the corresponding e.s.r. spectra. *p*-Nitrophenylacetylene and *p*-nitrobenzoic acid were also isolated from the reaction mixture. The basic dehydrobromination involves the formation of the free radical RCH=CH$^\bullet$, which is the natural precursor of the observed anion radical of *p*-nitrostyrene [*cf.* equations (4) and (5)]. On the other hand, the anion radical of *p*-nitrostyrene is never observed during the electrolytic reduction of both *cis*- and *trans*-BS. Therefore it is likely that electrolytic dehydrobromination involves concertedness of reactions (2) and (3). The presence of the anion radical *cis*-BS$^{-\bullet}$ as an intermediate of the electrolytic dehydrobromination of the parent compound has been established. It is favoured by addition of bromides as supporting electrolytes (*cf.* Table 1).

It should be noted that the e.s.r. spectra, recorded at different times during the course of the reaction, appear to be affected by changes in physical properties and composition of the medium. The proton-extraction reaction described in equation (3) yields t-butyl alcohol. This fact affords enhancement in the observed nitrogen h.f.s. constants, due to hydrogen bond formation. Therefore, an increase in the nitrogen h.f.s. constant with time could be considered as a very sensitive test for the formation of proton donors in the reaction mixture.

EXPERIMENTAL

Materials.—*cis*- and *trans*-*p*-nitro-β-bromostyrenes were synthesized and separated according to ref. 17. *p*-Nitrophenylacetylene was obtained according to ref. 4. *p*-Nitrostyrene was high-purity K & K product. *p*-Nitrobenzoic acid, potassium t-butoxide, t-butyl alcohol, dimethyl sulphoxide, *NN*-dimethylformamide, 1,2-dimethoxyethane, potassium bromide, tetra-n-butylammonium bromide (TBAB), and tetra-n-butylammonium perchlorate (TBAP) were obtained from Fluka. Potassium t-butoxide was purified by sublimation before use. DMSO was distilled at reduced pressure from calcium hydride. DMF was purified by drying (K_2CO_3) followed by distillation at reduced pressure and storing under vacuum.

Preparation of Anion Radicals and Measurements.—Electrolytic generation of anion radicals was performed in vacuum cells inside the resonance cavity, as previously described.[3] A solution of 0.1M-TBAP, -TBAB or -KBr was used as supporting electrolyte. The chemical generation of anion radicals was performed by mixing deoxygenated solutions of Bu^{t}OK and each compound in the apparatus as previously described.[3] [18] The sodium salt of *cis*-BS and the lithium and sodium salts of PA were produced by chemical reduction of the parent compounds by the alkali metals in a vacuum degassed solution of DME.

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 lineshape fitting procedure.[3] [19] The program allows the determination of the relative areas and the position of two or more different hyperfine patterns. The experimental spectra were digitalized by hand over *ca.* 350 data points. Calculations usually converged very quickly, with standard errors of a few milligauss. A few results of this procedure are collected in Table 1 and Figures 2 and 4. The digitized experimental spectra and the calculated spectra were displayed by a Calcomp plotter (Figures 2 and 4).

Electroreduction of cis-*BS.*—A solution of *cis*-BS (0.032 g) in anhydrous DMF (1 ml) in the presence of TBAP (0.045 g) was submitted to electrolytic reduction in a 1 ml potentiometric cell (3.5 V) at room temperature. When the reaction was complete (g.l.c. analysis), the cathodic solution (0.5 ml) was diluted with water (5 ml) and extracted by ether ($n \times n$ ml). Evaporation of the solvent gave pure *p*-nitrophenylacetylene (0.013 g), m.p. 140—142 °C (lit., 140 °C); δ ($CDCl_3$) 7.90 (4 H, m) and 3.36 (1 H, s).

Basic Reduction of cis-*BS.*—*cis*-BS (40 mg) was stirred with Bu^{t}OK (40 mg) in DMSO or DMF (10 ml) at room temperature for 12 h. The mixture was then diluted with water and extracted with ether. The aqueous solution, after acidification, slowly gave a yellow precipitate which was recrystallized from benzene to yield *p*-nitrobenzoic acid, m.p. and mixed m.p. 237 °C. The ethereal solution was analysed by g.l.c. It was not possible to obtain pure samples; however, the corresponding mass spectra suggest that the higher *m/e* values observed could be ascribed to the fragmentation of some dimeric product of *p*-nitrostyrene and/or *p*-nitrophenylacetylene.

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