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An Electron Spin Resonance Investigation on Intermediates and Products in the Basic Oxidation of Nitrodiphenylethylenes

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Abstract: The anion radicals of 1,1-di(*p*-nitrophenyl)ethylene, 2-ethoxy-1,1-di(*p*-nitrophenyl)ethylene, 1-*p*-nitrophenyl-1-phenylethylene, *cis*- and *trans*-2-bromo-1-*p*-nitrophenyl-1-phenylethylene, 4,4'-dinitrobiphenyl, *p*-*tert*-butoxynitrobenzene, *p*-nitrobenzophenone, *p*-nitrosobenzophenone, *p*-azobenzophenone, 4,4'-dinitrobenzophenone, and *p*-nitrobenzoic acid have been studied by ESR spectroscopy. These radicals are intermediates and products in the basic oxidation of 1,1-di(*p*-nitrophenyl)ethylene and/or 1-*p*-nitrophenyl-1-phenylethylene. Hyperfine splitting constants have been assigned on the basis of MO theories. Intramolecular exchange and relaxation broadenings of ESR lines have been investigated to get information on solution dynamics of these compounds.

Introduction

In a previous work² the anion radicals of a series of mono-nitro derivatives of 1,1-diphenylethylene have been studied by ESR spectroscopy. These radicals were obtained by electrolytic reduction in dimethyl sulfoxide (Me₂SO) and acetonitrile (ACN). Information on the spin densities and the conformation of each radical has been derived through the interpretation of the ESR spectra combined with quantum mechanical calculations based on MO theory.

In this paper the investigation has been extended to anion radicals of 1,1-di(*p*-nitrophenyl)ethylenes electrolytically generated in the same solvents. The anion radicals of 1-*p*-nitrophenyl-1-phenylethylene and 1,1-di(*p*-nitrophenyl)ethylene have been also obtained by reduction with alkali metal alkoxides in Me₂SO. Information on their reactivity has been obtained by means of a detailed study of the paramagnetic intermediates of their basic cleavage and oxidation by traces of molecular oxygen.

In order to get a better understanding of the role of the solvent on reaction mechanism, the investigation was extended

to ESR line shapes, which are affected by the interaction between the radical and the medium. The proton and cation transfers were treated as intramolecular chemical exchanges.³ Rotational diffusion of the paramagnetic species was invoked to explain the relaxation broadening of the ESR lines.⁴ Line shapes were calculated by the density matrix method,^{5,6} either in its whole formalism⁷ or by using some suitable approximation.^{8,9}

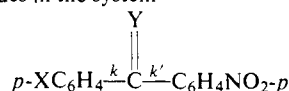
Calculations

Measured hyperfine coupling constants have been assigned on the ground of the theoretical spin densities calculated through the McLachlan method.¹⁰ The starting HMO's have been evaluated adopting the set of parameters¹¹⁻¹⁴ collected in Table I. The cases in which the observed spin distribution appears localized on a molecular fragment and does not reflect the molecular symmetry have been interpreted according to Gutch, Waters, and Symons.¹⁵ These authors suggested that a low-lying excited electronic state, when added to the ground state, can give two equivalent asymmetric structures. The

Table I. Parameter Values Used with Simple McLachlan LCAO Theory

Element	Coulomb integral	Bond integral	Ref
Carbon	$h_C = 0.0$	$k_{C-C} = 1.0^a$	11
	$h_C = 0.335^b$		This work
	$h_C = -0.512^c$	$k_{C-C} = 1.34^d$	This work
		$k_{C-C} = 0.858^e$	This work
Nitrogen		$k_{C-C(\theta)} = k_{C-C(0)} \cos\theta^f$	
	$h_N = 2.2^g$	$k_{C-N} = 1.2^g$	11
		$k_{N-O} = 1.67^g$	11
	$h_N = 0.782^h$	$k_{C-N} = 1.0^h$	12
	$h_N = 1.299^i$	$k_{C-N} = 1.2^i$	This work
Oxygen		$k_{N=N} = 1.1^h$	12
	$h_O = 1.4^g, i$		11
	$h_O = 1.5^j$	$k_{C=O} = 1.6^j$	13
	$h_O = 1.554^k$	$k_{C-O} = 0.93^k$	This work
Bromine		$k_{C-O} = 0.413^l$	This work
	$h_{Br} = 1.5$	$k_{C-Br} = 0.3$	14
	Alkyl (heteroatom model $\equiv C-X$)	$h_X = 1.249^m$	This work

^a An "aromatic" bond of about 1.40 Å length. ^b For one carbon atom at the ortho position with respect to the azo group.¹² ^c For the ortho carbon atom near the oxygen of the nitroso group. ^d For the ethylenic double bond in the 1,1-diarylethylene derivatives. ^e For the inter-ring bond in 4,4'-dinitrophenyl. ^f The following k_{C-C} values in the system



were adopted: $k = k' = 0.719$ for $X = \text{NO}_2$, $Y = \text{CH}_2$; $k = k' = 0.825$ for $X = \text{NO}_2$, $Y = \text{CHOC}_2\text{H}_5$; $k = 0.500$ and $k' = 0.719$ for $X = \text{H}$, $Y = \text{CH}_2$; $k = 0.390$ and $k' = 0.848$ for $X = \text{H}$, $Y = \text{CHBr-trans}$; $k = 0.719$ and $k' = 0.500$ for $X = \text{H}$, $Y = \text{CHBr-cis}$; $k = 0.465$ and $k' = 0.776$ for $X = \text{H}$, $Y = \text{O}$, and for p -nitrosobenzophenone; $k = k' = 0.759$ for $X = \text{NO}_2$, $Y = \text{O}$; $k = k' = 0.819$ for p -azobenzophenone. ^g For the nitro group. ^h For the azo group. ⁱ For the nitroso group. ^j For the carbonyl group. ^k For the ether linkage. ^l Between the oxygen of the nitroso group and the nearby ortho carbon. ^m In the alkoxylic group.

probability that the system will adopt these structures depends on the energy difference between the ground and excited states. Specific solute-solvent interactions, such as hydrogen bonding and ion pairing, can stabilize the asymmetric structures with respect to the symmetric one of the free anion radical.

Calculated spin densities have been translated into proton coupling constants by means of McConnell's relationship.¹⁶ For nitrogen a relationship like that proposed by Karplus and Fraenkel¹⁷ for ¹³C was adopted.

In the case of p -nitrobenzoic acid anion and dianion radicals, where the necessary McLachlan parameters were difficult to assess, the hyperfine coupling constants were calculated by the INDO method.¹⁸⁻²⁰

Refinement of ESR Experimental Data and Line Shape Analysis. The hyperfine coupling constants and line widths of ESR spectra were optimized through a least-squares line shape fitting. The iterative least-squares program ESRCON^{21,22} was used. The optimized parameters were tested by plotting the calculated spectra. However, many spectra were strongly affected by asymmetric variations of line widths, which were reproduced through the following equation:

$$W_j = A + \sum_{\alpha=1}^{N_A} B_{\alpha} \tilde{M}_{j\alpha} + \sum_{\alpha=1}^{N_A} C_{\alpha} \eta(M_{j\alpha}) + \sum_{\alpha>\beta} E_{\alpha\beta} \tilde{M}_{j\alpha} \tilde{M}_{j\beta} \quad (1)$$

(For a justification of eq 1 and related symbols see ref 8, 9). A modified version of the computer program ESRCON, reproducing the relaxation effects on line shape and optimizing parameters A , B_{α} , C_{α} , and $E_{\alpha\beta}$, was written. The actual expression of the first derivative of the Lorentzian line shape function is

$$y(x_n) = S \sum_{j=1}^{N_L} D_j A_{jn} B_{jn}^{-2} W_j^{-2} \quad (2)$$

where the same symbols as in ref 22 are used:

$$A_{jn} = \left(x_0 - \sum_{\alpha=1}^{N_A} A_{\alpha} M_{j\alpha} - x_n \right) W_j^{-1} \quad (3)$$

$$B_{jn} = 1 + 4/3 A_{jn}^2 \quad (4)$$

S is a scaling factor; N_L is the number of allowed transitions with degeneracy D_j and line width W_j ; x_0 defines the symmetry center of the spectrum, and $\sum_{\alpha=1}^{N_A} A_{\alpha} M_{j\alpha}$ the position of a line j , while N_A denotes the number of coupling constants A_{α} . The derivatives of the function $y(x_n)$ with respect to the parameters A_{α} , W_j , and S are

$$\frac{\partial y(x_n)}{\partial A_{\alpha}} = S \sum_{j=1}^{N_L} D_j B_{jn}^{-2} C_{jn} W_j^{-3} M_{j\alpha} \quad (5)$$

$$\frac{\partial y(x_n)}{\partial W_j} = -S A_{jn} B_{jn}^{-2} D_j (2 + C_{jn}) W_j^{-3} \quad (6)$$

$$\frac{\partial y(x_n)}{\partial S} = \sum_{j=1}^{N_L} D_j A_{jn} B_{jn}^{-2} W_j^{-2} \quad (7)$$

where

$$C_{jn} = 1 - \frac{16}{3} A_{jn}^2 B_{jn}^{-1} \quad (8)$$

The derivatives of the function W_j with respect to the parameters A , B_{α} , C_{α} , and $E_{\alpha\beta}$ can be easily calculated from eq 1.

In the case of spectra which are affected by mutual exchange between different sites, with equal probabilities and different resonance frequencies, the density matrix method⁵⁻⁷ reduces to the following expression for the first derivative line shape:

$$y(x_n) = S \sum_{j=1}^{N_L} D_j [2(X_1 + X_2) - X_1^2 - X_2^2 - 2][X_1 X_2 - 1]^{-2} \quad (9)$$

where

$$X_k = -i \left(x_0 - \sum_{\alpha=1}^{N_A} A_{\alpha}^{(k)} M_{j\alpha} - x_n \right) \times \left(\frac{\sqrt{3}}{2} W_{\text{exch}} \right)^{-1} - \left(\frac{W_j^{(k)}}{W_{\text{exch}}} - 1 \right) \quad (10)$$

k indicates the two exchanging sites, and W_{exch} is related to

the rate of the exchange process ($\tau^{-1} = \sqrt{3}|\gamma_e|W_{\text{exch}}/2$). The derivatives of the line shape fitting function **9** with respect to the parameters were calculated analytically. In the fast exchange limit the Freed and Fraenkel theory^{8,9} was applied; it requires the addition of an exchange extra line width contribution to eq 1, and allows us to save computing time markedly. If the nuclei of set α are completely equivalent with respect to the dynamic process, as in proton-transfer equilibria between the anion and dianion radicals of *p*-nitrobenzoic acid, the exchange contribution to the line width is given by

$$W_{\text{exch},j} = \sum_{\alpha=1}^{N_A} F_{\alpha} M_{j\alpha}^2 \quad (11)$$

where

$$F_{\alpha} = \frac{|\gamma_e|}{8\sqrt{3}} \Delta A_{\alpha}^2 \tau \quad (12)$$

Another common situation is one in which two nuclei interchange their coupling constants (complete out-of-phase correlation⁸). This two-site problem occurs, for example, in the intramolecular cation exchange for 1,1-di(*p*-nitrophenyl)ethylene and 4,4'-dinitrobiphenyl. For two ¹⁴N nuclei the outer $M_N = m_1 + m_2 = \pm 2$ lines of the hyperfine quintet are unbroadened, and both components of the $M_N = \pm 1$ lines are broadened by F_N . The component of the central line with $m_1 = m_2 = 0$ is unbroadened, but the other two components have width $4F_N$.

The data points required for the least-squares procedure have been obtained by "digitalizing" the experimental spectra "by hand". Using about 350 experimental points, the calculation usually converged very quickly with standard errors of a few milligauss.

Results and Discussion

Hyperfine Splittings. In Table II experimental and calculated hfsc's of all the anion radicals examined in our work are collected. Q constants (cf. Table II and ref 23, 24), calculated through a least-squares fitting of experimental hfsc's vs. the corresponding spin densities, are in line with values generally accepted in the literature. The assignments accord well with the structure of each π anion radical.

Reaction Course. In view of the similarity of the course of the oxidation reactions of 1,1-di(*p*-nitrophenyl)ethylene, 1-*p*-nitrophenyl-1-phenylethylene, and their halo derivatives, a detailed discussion will be limited to the first compound.

1,1-Di(*p*-nitrophenyl)ethylene (I). The ESR spectra obtained after the electrolytic reduction of I in different solvents are consistent with three pairs of equivalent protons and one nitrogen (Figure 1A). This hyperfine pattern shows that the odd electron is localized on one nitrophenyl fragment. The line widths are affected by asymmetric variations due to the electron spin relaxation, and no alternation effect³ is observed when the temperature is raised.

A 10^{-3} M solution of I in Me₂SO with a large excess of *t*-BuOK is strongly blue colored and exhibits (Figure 1B) the ESR spectrum of the corresponding anion radical, I⁻. However, the spectrum obtained under chemical reduction is consistent with two sets of two and four equivalent protons, and one set of two equivalent nitrogens. Besides, the lines of the ¹⁴N quintet have amplitudes in the ratio 1.0:0.5:1.1:0.5:1.0 instead of 1:2:3:2:1. These data show that (a) the odd electron is delocalized on the whole anion radical, and (b) the two nitro groups interchange the cation. When the temperature is raised, other paramagnetic species contaminate the ESR spectrum of I⁻, so that it was not possible to calculate the activation parameters for the cation exchange.

Electron transfer between 2,2-di(*p*-nitrophenyl)vinyl carbanion and I is responsible for the formation of I⁻ ac-

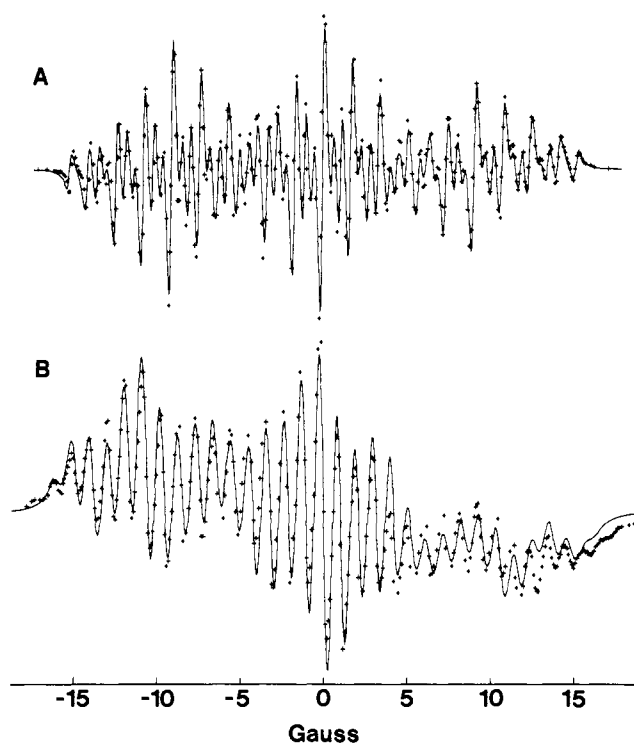
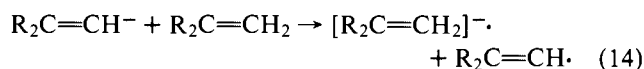
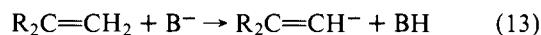


Figure 1. ESR spectra of 1,1-di(*p*-nitrophenyl)ethylene radical anion. Solid lines, simulated spectra; points, experimental spectra. (A) Spectrum observed by electrolytic reduction in ACN at room temperature; simulation was performed with the hfsc's collected in Table II and the following line width parameters: $A = 0.300 \pm 0.012$, $B_N = 0.029 \pm 0.006$, $C_N = 0.044 \pm 0.008$ G. It is consistent with the odd electron localized on one nitrophenyl fragment. (B) Spectrum observed in Me₂SO containing *t*-BuOK at room temperature; it is consistent with the odd electron delocalized on the whole radical. Simulation was performed with the hfsc's collected in Table II and the following line width parameters: $A = 0.614 \pm 0.012$, $B_N = 0.062 \pm 0.011$, $C_N = 0.022 \pm 0.002$, $F_N = 0.567 \pm 0.050$ G. The line broadening is due both to electron spin relaxation and cation exchange between the two nitro groups. A fairly good simulation was also obtained by the density matrix method, assuming that the two nitrogens interchange their coupling constants (10.4 and 0.2 G, respectively), with a rate constant of 2.6×10^8 s⁻¹.

ording to the following scheme:



where $B^- = t\text{-BuO}^-$ or MeO^- and $R = p\text{-O}_2\text{NC}_6\text{H}_4$. A similar reaction scheme was proposed by Russell and co-workers²⁵⁻²⁷ for the disproportionation of *o*- and *p*-nitrotoluenes in basic solution, and by Barton and Jones²⁸ for the autoxidation of 1,1,3-triphenylprop-1-ene. The anion radical I⁻ (as well as $R_2C=CH^-$ and $R_2C=CH\cdot$) is easily oxidized^{28,29} to 4,4'-dinitrobenzophenone (12 h) and successively to *p*-nitrobenzoic acid (24 h) as tested by the observation of the ESR spectra of the corresponding ketyl (Figure 2) and dianion radical (Figure 3).³⁰ However, the recovery of small amounts of 1-methyl-1,3,3-tri(*p*-nitrophenyl)-5-nitroindan (cf. Experimental Section) shows that the anion radical I⁻ dimerizes also, according to the mechanism in Scheme I.

2-Bromo- and 2-Chloro-1,1-di(*p*-nitrophenyl)ethylenes. The reduction of 2-halo derivatives of I both in *t*-BuOK/Me₂SO solutions and in an electrolytic cell gives an ESR spectrum corresponding to that of I⁻. This fact is not surprising when it is considered that the anion radical of benzophenone is observed when 4,4'-dichlorobenzophenone is electrolytically

Table II. Calculated and Experimental Hyperfine Coupling Constants (G)

Molecule	Nucleus and position ^a	2nl + 1	Theor ^b	Exptl ^{c,d}
1,1-Di(<i>p</i> -nitrophenyl)ethylene	N	5	3.824	5.302 ± 0.005
	H _o	5	-1.495	1.036 ± 0.013
	H _β	3	-2.883	3.168 ± 0.012
1,1-Di(<i>p</i> -nitrophenyl)ethylene ^e	N	3	8.426	8.881 ± 0.005 ^f
	H _o	3	-3.217	3.260 ± 0.007
	H _m	3	1.010	1.065 ± 0.005
	H _β	3	-1.389	1.664 ± 0.010
	N	3	9.269	9.713 ± 0.004
2-Ethoxy-1,1-di(<i>p</i> -nitrophenyl)ethylene ^e	H _o	3	-3.392	2.901 ± 0.025
	H _m	3	1.135	0.898 ± 0.026
	H _β	2	-1.160	2.020 ± 0.025
	H _{C₂H₅}	3	0.137	0.282 ± 0.006
	N	3	8.358	8.542 ± 0.003
1- <i>p</i> -Nitrophenyl-1-phenylethylene	H _o	3	-3.198	3.222 ± 0.004
	H _m	3	0.999	1.070 ± 0.005
	H _β	3	-1.485	1.768 ± 0.004
	N	3	8.174	7.881 ± 0.006
<i>trans</i> -2-Bromo-1- <i>p</i> -nitrophenyl-1-phenylethylene	H _o	3	-3.133	3.095 ± 0.017
	H _m	3	0.969	0.993 ± 0.023
	H _β	2	-1.960	2.047 ± 0.030
	N	3	8.789	8.509 ± 0.006
<i>cis</i> -2-Bromo-1- <i>p</i> -nitrophenyl-1-phenylethylene	H _o	3	-3.335	3.160 ± 0.007
	H _m	3	1.090	0.992 ± 0.008
	H _β	2	-0.736	0.826 ± 0.010
	N	5	3.095	3.041 ± 0.001 ^g
4,4'-Dinitrobiphenyl	H _o	5	-1.210	1.269 ± 0.002
	H _m	5	-0.160	0.131 ± 0.006
	N	3	11.143	10.771 ± 0.003
4- <i>tert</i> -Butoxynitrobenzene	H _o	3	-3.654	3.422 ± 0.003
	H _m	3	1.352	1.124 ± 0.003
	N	3	6.160	5.668 ± 0.003
4-Nitrobenzophenone	H _o	3	-2.443	2.647 ± 0.004
	H _m	3	0.244	0.445 ± 0.004
	N	5	2.430	2.372 ± 0.003
4,4'-Dinitrobenzophenone	H _o	5	-0.940	1.138 ± 0.004
	N	3	6.876	6.343 ± 0.006 ^h
	H _o	3	-2.679	2.815 ± 0.005
4,4'-Dinitrobenzophenone ^e	H _m	3	0.459	0.578 ± 0.004
	N	3	6.448	6.883 ± 0.004 ^g
	H _o	3	-2.553	2.991 ± 0.005
Methyl <i>p</i> -nitrobenzoate	H _m	3	0.234	0.703 ± 0.008
	H _{CH₃}	4	-0.062	0.327 ± 0.011
	N	3	6.448	7.048 ± 0.005 ^g
	H _o	3	-2.553	3.005 ± 0.009
Ethyl <i>p</i> -nitrobenzoate	H _m	3	0.234	0.729 ± 0.008
	H _{C₂H₅}	3	-0.062	0.321 ± 0.007
	N	3	6.448	7.094 ± 0.003 ^g
	H _o	3	-2.553	3.013 ± 0.004
<i>tert</i> -Butyl <i>p</i> -nitrobenzoate	H _m	3	0.234	0.735 ± 0.004
	N	3	12.488	11.099 ± 0.027 ⁱ
	H _o	3	-2.711	3.269 ± 0.007
	H _m	3	1.382	1.017 ± 0.007
<i>p</i> -Nitrobenzoic acid	N	3	8.893	8.469 ± 0.025 ⁱ
	H _o	3	-2.447	3.269 ± 0.007
	H _m	3	0.993	1.017 ± 0.007
	H _{COOH}	2	-0.127	
	N	3	6.924 ^j	6.575 ± 0.003
4-Nitrosobenzophenone	H _o ^k	2	-3.299	3.313 ± 0.006
	H _{o'}	2	-2.944	2.666 ± 0.008
	H _m	2	1.302	1.041 ± 0.005
	H _{m'}	2	0.921	0.553 ± 0.007
	N	5	3.952 ^l	3.770 ± 0.002
<i>p</i> -Azobenzophenone	H _o ^m	3	-2.029	2.225 ± 0.003
	H _{o'}	3	-1.711	1.713 ± 0.003
	H _m	3	0.759	0.679 ± 0.002

^a If not otherwise stated, the ortho and meta positions are referred to the nitro group. ^b Hfsc's of the *p*-nitrobenzoic acid anion and dianion radicals were calculated by the INDO method; $a_N^{\text{NO}_2} = K_N \rho_{SN} \rho_N$, where $K_N = 485.935 \text{ G}$.²⁰ Spin densities of the other anion radicals were calculated by the McLachlan method and fitted to the experimental coupling constants in a least-squares procedure according to the relationships $a_H = -(24.743 \pm 0.555) \rho_C$ and $a_N^{\text{NO}_2} = (32.951 \pm 0.727)(2\rho_N - \rho_O) \text{ G}$. ^c If not otherwise stated, the anion radicals were obtained by reduction in Me₂SO with *t*-BuOK. ^d The confidence limits for the hfsc's are calculated through a least-squares fitting of the line shape. ^e The odd electron

Table II. (Continued)

is localized on a nitrophenyl fragment. ^f Obtained by electrolytic reduction in ACN. ^g Obtained by electrolytic reduction in Me₂SO. ^h Obtained by reduction with MeONa in Me₂SO. ⁱ In Me₂SO containing MeONa. The reported hfsc's were obtained through a least-squares line shape fitting including the proton exchange effect (see text and Figure 3B). ^j $a_N^{\text{NO}} = (20.516 \pm 1.303)(2\rho_N - \rho_O)$ G.²⁴ ^k The ortho and meta positions are referred to the nitroso group. ^l $a_N^{\text{azo}} = (13.727 \pm 0.591)\rho_N$ G.²⁴ ^m The ortho and meta positions are referred to the azo group.

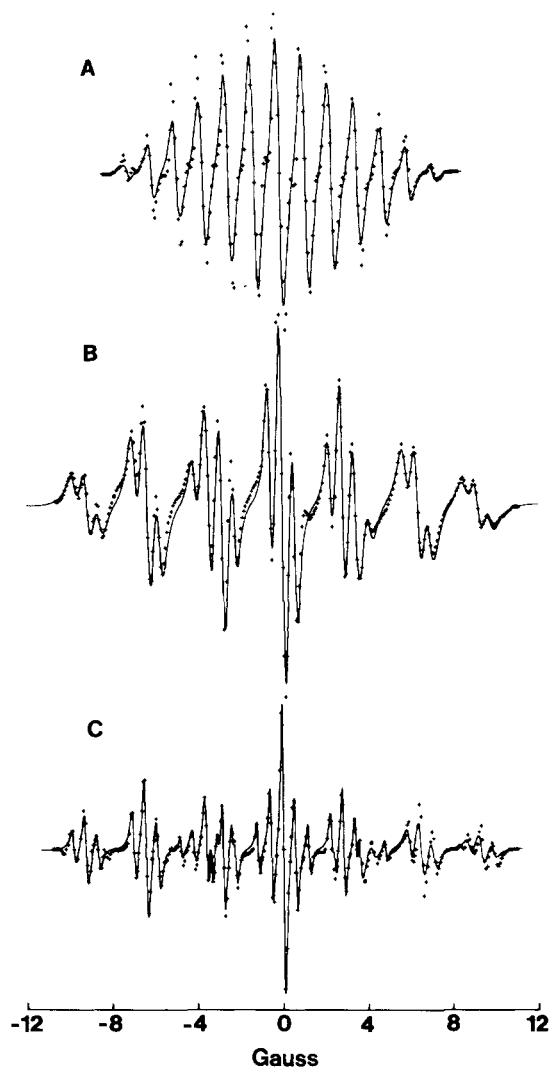


Figure 2. ESR spectra of 4,4'-dinitrobenzophenone anion radicals. Solid line, simulated spectra; points, experimental spectra. (A) Spectrum obtained after oxidation of 1,1-di(*p*-nitrophenyl)ethylene in Me₂SO containing *t*-BuOK; the odd electron is delocalized on the whole radical; the spectrum was simulated with the hfsc's collected in Table II and $W = 0.308 \pm 0.017$ G. (B) Spectrum observed in Me₂SO containing MeONa ($>10^{-2}$ M); the odd electron is localized on one nitrophenyl fragment; the spectrum was simulated with the hfsc's collected in Table II and the following line width parameters: $A = 0.272 \pm 0.005$, $B_N = 0.032 \pm 0.007$, $C_N = 0.139 \pm 0.009$ G. (C) Spectrum obtained by reduction with potassium in DME–Me₂SO (60:40). It was simulated as the superposition of the two spectra (A) and (B) in the ratio 1:10; $a_N^{(A)} = 2.411 \pm 0.007$, $a_{H_o}^{(A)} = 1.176 \pm 0.009$, $W^{(A)} = 0.117 \pm 0.020$, $a_N^{(B)} = 6.460 \pm 0.004$, $a_{H_o}^{(B)} = 2.824 \pm 0.004$, $a_{H_m}^{(B)} = 0.571 \pm 0.003$, $W^{(B)} = (0.148 \pm 0.006) + (0.051 \pm 0.008) \bar{M}_N + (0.092 \pm 0.009) \eta(M_N)$ G.

reduced in aprotic solvents.^{31,32} Likewise the ease with which the halonitrobenzenes are dehalogenated during the electrolytic reduction³³ is well known. The basic dehalogenation of 1,2,3-tribromobenzene³⁴ is also known, even if the dehydrohalogenation³⁵ and alkoxylation³⁶ reactions are usually favored in the *t*-BuOK/Me₂SO system. Obviously the subsequent course of the reaction parallels that observed for I.

2-Ethoxy-1,1-di(*p*-nitrophenyl)ethylene. The first ESR spectrum observed during the chemical reduction of this compound is that of the corresponding anion radical. Hyperfine

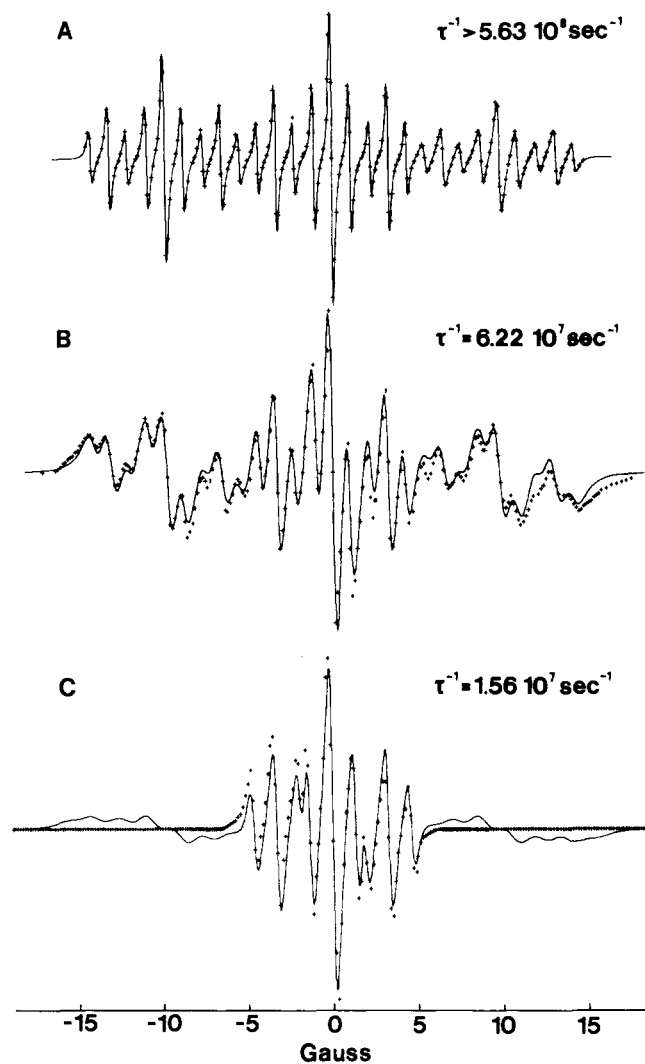
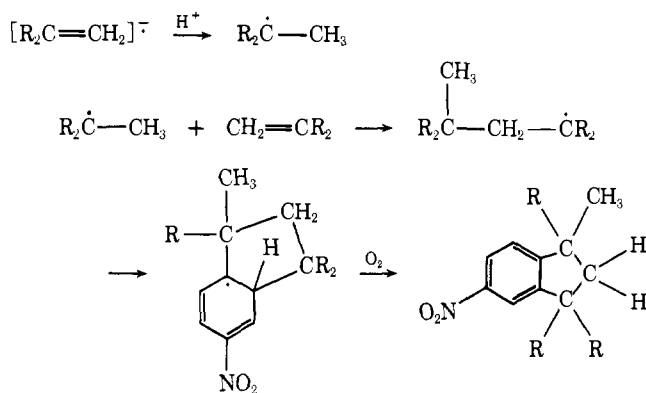


Figure 3. ESR spectra of *p*-nitrobenzoate anion radicals. Solid line, simulated spectra; points, experimental spectra. (A) Spectrum observed in Me₂SO containing *t*-BuOK; it was simulated with hfsc's $a_N = 9.818 \pm 0.000$, $a_{H_o} = 3.304 \pm 0.000$, $a_{H_m} = 1.068 \pm 0.000$ G, and line width parameters $A = 0.195 \pm 0.001$, $B_N = 0.042 \pm 0.001$, $C_N = 0.079 \pm 0.001$ G. (B) Spectrum observed in Me₂SO containing MeONa; it was simulated by the density matrix method (cf. eq 9); a proton exchange between the mono- and dianion radicals was assumed and a rate constant of $(6.22 \pm 0.36) \times 10^7$ s⁻¹ was derived; the hfsc's obtained by the least-squares fitting procedure (see text) are collected in Table II; relaxation broadenings were evaluated assuming the following expression for the line widths: $W^{(1)} = W^{(2)} = (0.553 \pm 0.009) + (0.075 \pm 0.003) \bar{M}_N + (0.064 \pm 0.005) \eta(M_N)$ G. (C) Spectrum observed during the electrolytic reduction in DME. It was simulated as in (B), with rate constant $\tau^{-1} = (1.56 \pm 0.26) \times 10^7$ s⁻¹ and line widths $W^{(1)} = W^{(2)} = 0.462 \pm 0.015$ G. Under electrolytic reduction, spectrum (C) increases its amplitude with time (10–30 min) and after reaching a maximum disappears; then a spectrum equal to (A) is promptly recorded. Apparently, spectrum (A) is a complete average of the spectra of the mono- and dianion radicals in the very fast exchange region ($\tau^{-1} > 5.63 \times 10^8$ sec⁻¹).

pattern indicates that the odd electron is localized on one nitrophenyl fragment. Subsequently the ESR spectra of 4,4'-dinitrobenzophenone ketyl and dianion radical of *p*-nitrobenzoic acid were observed, pointing out that the course of reaction is the same as that of I.

1-*p*-Nitrophenyl-1-phenylethylene and Its Halo Derivatives.

Scheme I



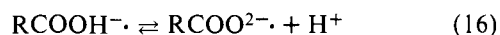
The basic reduction of the neutral substrates gives the corresponding anion radicals as found by electrolytic reduction.² After 1 day the solution changes from blue to the characteristic green color of 4-nitrobenzophenone ketyl, whose ESR spectrum was easily detected.

4,4'-Dinitrobenzophenone (II). *t*-BuOK in Me_2SO is a very strong base³⁷ which enhances significantly the rate of a large number of reactions.^{38,39} In our case this system does not allow us to observe the paramagnetic intermediates of the basic cleavage of II through ESR spectroscopy. In view of this fact we used a less strong base such as MeONa.^{40,41} In this medium four radicals were detected through the corresponding ESR spectra. The first two are associated to different species of 4,4'-dinitrobenzophenone ketyl, IIa^- and IIb^- (Figure 2A,B), and the other spectra to the anion radicals of 4,4'-dinitrophenyl, III^- ,^{42,43} and *p*-nitrobenzoic acid, IV^{2-} ,⁴² respectively. The spectrum of IIa^- is associated to a ketyl in which the odd electron is delocalized on the whole radical; the spectrum of IIb^- is that of a ketyl in which the odd electron is delocalized only on a nitrophenyl fragment, as indicated by the corresponding hyperfine patterns. At high concentration of MeONa (≥ 0.1 M) the species IIb^- prevails, while IIa^- is observed at lower concentrations ($< 10^{-2}$ M). When $NaBPh_4$ (0.28 M) is added to the solution only IIb^- is observed. By electrolytic reduction we observed only the species IIa^- (see also ref 31); on the contrary, the alkali metal reduction in 1,2-dimethoxyethane (DME) gave IIb^- (see also ref 44). When Me_2SO (40%) was added to a potassium ketyl/DME solution the spectrum changed. The new spectrum was simulated as the superposition of IIa^- and IIb^- in the ratio 1:10 (Figure 2C). This result suggests the presence of two different ion pairs. In the DME solution the presence of the metal quartet in the hyperfine pattern indicates the formation of contact ion pairs. In Me_2SO solution the solvated cations allow the formation of solvent-separated ion pairs (IIb^-) and free ions (IIa^-).

In order to verify the role of the base in the cleavage of II, particularly with regard to the formation of esters, methyl, ethyl, and *tert*-butyl *p*-nitrobenzoate were synthesized to check their behavior under electrolytic and chemical reduction. The ESR spectra of electrolytically generated anion radicals were easily observed. But when *t*-BuOK or MeONa were used, the esters immediately hydrolyzed and the observed ESR spectrum was that of IV^{2-} . Therefore the esters, if present, are transient intermediates of the basic cleavage of II. However, Gassman and co-workers⁴⁵ demonstrated that the only feasible mechanism for the cleavage of nonenolizable ketones with *t*-BuOK/water/ether (and by extrapolation in Me_2SO) does not allow ester formation.

***p*-Nitrobenzoic Acid (IV).** The ESR spectrum of the dianion radical of IV is the last detected one in the basic oxidation of I. The ESR spectrum obtained by reduction of IV with *t*-BuOK in Me_2SO exhibits narrow hyperfine lines with a

markedly asymmetric line width variation. A superimposable ESR spectrum was obtained by electrolytic reduction in the same solvent. These spectra were simulated (Figure 3A) by using the line width equation 1 given by Freed and Fraenkel theory.^{8,9} The line width parameters, $B_N = 42 \pm 1$ mG and $C_N = 79 \pm 1$ mG, were obtained by an iterative least-squares line shape fitting procedure (see preceding section) and describe the anisotropic dipolar and *g*-tensor interactions, which are modulated by the rotational diffusion of the anion radical.⁴ The spectrum of the radical obtained from IV by reduction with MeONa in Me_2SO (Figure 3B) was also simulated and the following parameters were optimized: $B_N = 72 \pm 18$ mG, $C_N = 322 \pm 19$ mG. While the difference between B_N values can reasonably be ascribed to slightly different physical properties of the two media, the large variation of C_N can be explained as due to the isotropic interactions of the anion and dianion radicals at equilibrium.⁴⁶



More marked effects due to the same dynamic process are evident in the ESR spectrum of the radical obtained by electrolytic reduction in DME²³ (Figure 3C). ESR spectra were also simulated employing the formalism of the density matrix theory⁵⁻⁷ which needs the knowledge of the hfsc's of the two exchanging species. The satisfactory agreement between calculated and experimental spectra is a further support of our interpretation of the observed line broadenings.

***p*-Nitrobenzophenone (V).** The basic reduction of V gives the same ketyl V^- as obtained by the electrolytic reduction and by the reduction with alkali metals.⁴⁴ The ESR spectrum was simulated with the hyperfine coupling constants of Table II. After a 24 h reaction period the solution of V^- changes from green to dark red color and a new ESR spectrum at higher fields ($g = 2.00481$) with respect to that of V^- ($g = 2.00491$) is observed. Its hyperfine pattern is consistent with two pairs of equivalent protons and one nitrogen, as shown in Table II. The line shape is strongly affected by asymmetric line width variations and was reproduced by using the following parameters in the line width expression (eq 1): $A = 0.283 \pm 0.005$, $B_N = 0.020 \pm 0.003$, and $C_N = 0.070 \pm 0.005$ G. The same ESR spectrum is observed when 4,4'-dinitrophenyl is reduced by *t*-BuOK in Me_2SO . It was assigned to the anion radical of *p*-*tert*-butoxynitrobenzene by comparison with the ESR spectrum obtained after reducing an authentic sample under the same conditions.⁴⁷ When $NaBPh_4$ (0.28 M) is added to the solution of V^- , the ESR spectrum of the anion radical of *p*-*tert*-butoxynitrobenzene is never observed. Instead one observes the ESR spectra of *p*-nitrosobenzophenone (VI) and *p*-azobenzophenone (VII) anion radicals. Attempts to isolate and synthesize the nitroso compound were not successful. However, the ESR spectrum of VI^- is consistent with one nitrogen triplet and four proton doublets (cf. Table II and Figure 4), and accords well with the ESR spectra of a series of nitroso derivatives.²⁴ The hyperfine pattern of VII^- is due to one pair of equivalent nitrogens and three pairs of equivalent protons, as shown in Table II and Figure 5. The large dimensions of the anion radical are responsible for the unusual strong asymmetric line width variations in the spectrum. The assignment was confirmed by the ESR spectrum obtained both by chemical and electrolytic reduction of an authentic sample. Thus *p*-nitrobenzophenone may undergo both the cleavage and the reduction with *t*-BuOK/ Me_2SO , according to Scheme II (see also Experimental Section), and the reaction is controlled by the medium.⁴⁸

Experimental Section

Materials. The 1-*p*-nitrophenyl-1-phenylethylene and *trans*- and *cis*-2-bromo-1-*p*-nitrophenyl-1-phenylethylenes were obtained ac-

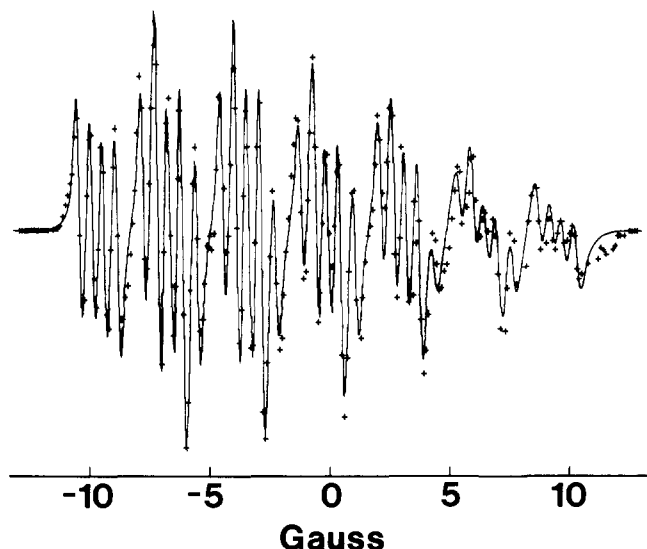


Figure 4. ESR spectrum of *p*-nitrosobenzophenone anion radical obtained by reduction of *p*-nitrobenzophenone in Me_2SO containing *t*-BuOK and NaBPh_4 (0.28 M). Points: experimental spectrum. Solid line: spectrum simulated with the hfsc's collected in Table II and the following line width parameters: $A = 0.280 \pm 0.009$, $B_N = 0.077 \pm 0.009$, $C_N = 0.039 \pm 0.011$ G.

cording to ref 49. For the synthesis of the 1,1-di(*p*-nitrophenyl)ethylene, 2-bromo- and 2-chloro-1,1-di(*p*-nitrophenyl)ethylenes, and 4,4'-dinitrobenzophenone see ref 50. 2-Ethoxy-1,1-di(*p*-nitrophenyl)ethylene was obtained by reaction of 2-bromo-1,1-di(*p*-nitrophenyl)ethylene with potassium *tert*-butoxide in ethanol; in ref 50 sodium ethoxide was used. *p*-*tert*-Butoxynitrobenzene was synthesized using the method described in ref 51. *tert*-Butyl, ethyl, and methyl *p*-nitrobenzoate were obtained by standard procedures.^{52,53} *p*-Azoxybenzophenone and *p*-azobenzophenone were synthesized according to ref 54, 55. 4-Nitrobenzophenone, *p*-nitrobenzoic acid, potassium *tert*-butoxide (*t*-BuOK), sodium methoxide (MeONa), *tert*-butyl alcohol, dimethyl sulfoxide (Me_2SO), and acetonitrile (ACN) were obtained from Merck. Me_2SO was distilled under reduced pressure from calcium hydride before use. Fluka provided 4,4'-dinitrobiphenyl, tetra-*n*-butylammonium perchlorate (TBAP), sodium tetraphenylborate (NaBPh_4), dibenzo-18-crown-6 ether, and 1,2-dimethoxyethane (DME).

Basic Oxidation of 1,1-Di-(*p*-nitrophenyl)ethylene. A solution of 60 mL of Me_2SO , 400 mg of *t*-BuOK, and 300 mg of 1,1-di(*p*-nitrophenyl)ethylene was shaken in a flask at 25 °C. After a 12-h reaction period the solution was treated with aqueous acid, and the resulting precipitate was filtered from a large excess of water. The precipitate was analyzed by liquid chromatography on an alumina column, using benzene as eluent. Removal of the solvent from the first fractions gave unreacted 1,1-di(*p*-nitrophenyl)ethylene and 4,4'-dinitrobenzophenone (mp, mmp 189 °C). Next fractions yielded white needles of 1-methyl-1,3,3-tri(*p*-nitrophenyl)-5-nitroindan, mp 222 °C from benzene, λ_{max} 285.5 nm in ethanol. Its NMR spectrum in CDCl_3 (1.58 s, 3 H_{CH_3} ; 4.93 d, 1 H_A ; 6.72 d, 1 H_X ; 7.32 m, 7 H_m ; 8.25 ppm m, 8 H_o ; $J_{AX} = 12.00$ Hz) is consistent with that of 1-methyl-1,3,3-triphenylindan (see later). Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_8$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.19; H, 3.49; N, 10.06. A solution of 1-methyl-1,3,3-tri(*p*-nitrophenyl)-5-nitroindan and *t*-BuOK in Me_2SO is strongly blue colored but it does not exhibit any ESR spectrum; after a 30-min reaction period the strong ESR signal of *p*-nitrobenzoate dianion radical is observed. The aqueous solution gave slowly a yellow precipitate that was recrystallized from benzene to yield *p*-nitrobenzoic acid (mp and mmp 237 °C).

Scheme II

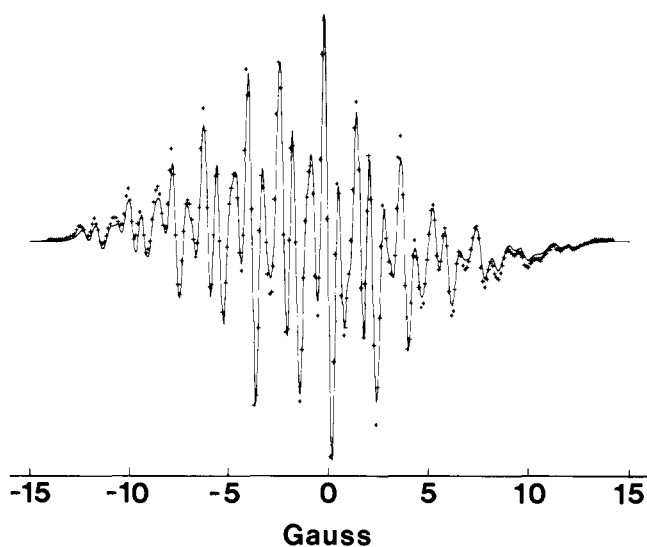
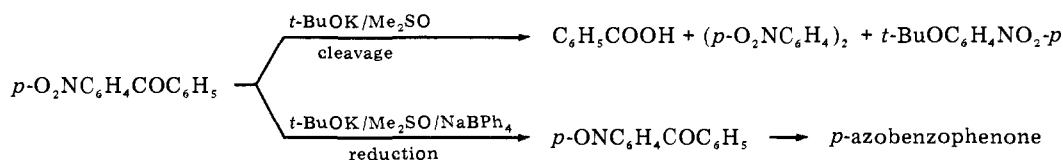


Figure 5. ESR spectrum of *p*-azobenzophenone anion radical in Me_2SO containing *t*-BuOK. Points: experimental spectrum. Solid line: spectrum simulated with the hfsc's collected in Table II and the following line width parameters: $A = 0.333 \pm 0.005$, $B_N = 0.057 \pm 0.003$, $C_N = 0.016 \pm 0.001$ G.

Acid Dimerization of 1,1-Diphenylethylene. Upon heating 2 mL of 1,1-diphenylethylene with 1 drop of oleum (68%) in a water bath for 1 h, 1,1,3,3-tetraphenyl-1-butene was obtained. The crude solid was purified by liquid chromatography on an alumina column, using benzene as eluent, and recrystallized from light petroleum: mp 113 °C (lit.⁵⁶ 113 °C); NMR (CDCl_3) δ 1.46 (s, 3 H_{CH_3}), 7.10 (m, 21 H). On the other hand, heating with 2 drops of oleum for 5 h we obtained 1-methyl-1,3,3-triphenylindan. The product was purified as described for 1,1,3,3-tetraphenyl-1-butene: mp 143 °C (lit.⁵⁶ 143 °C); NMR (CCl_4) δ 1.52 (s, 3 H_{CH_3}), 3.05 (d, 1 H_A), 3.37 (d, 1 H_B), 7.04 (m, 19 H), $J_{AB} = 13.00$ Hz.

Dimerization of 1-*p*-Nitrophenyl-1-phenylethylene. The products of the basic oxidation of 1-*p*-nitrophenyl-1-phenylethylene were analyzed by liquid chromatography. It was not possible to get pure samples; however, the crude solid obtained after removal of the solvent from the first fractions gave mass spectra, in which a strong peak at m/e 450 can be ascribed to the dimer of 1-*p*-nitrophenyl-1-phenylethylene.

Basic Cleavage and Reduction of *p*-Nitrobenzophenone. Two grams of *p*-nitrobenzophenone was stirred with 6 g of *t*-BuOK in 100 mL of methanol at room temperature for 48 h. Evaporation of the solvent, addition of hot benzene to the residue, acidification, and recrystallization of the precipitate from light ether gave benzoic acid (mp and mmp 121 °C). The benzene solution was analyzed by liquid chromatography on an alumina column, using benzene and chloroform as eluents. Removal of the solvent from the first fractions gave shiny red crystals of *p*-azobenzophenone, mp 221–222 °C. A mixture melting point with an authentic sample⁵⁵ showed no depression. Anal. Calcd for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_2$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.18; H, 4.47; N, 7.38.

Last fractions yielded 4,4'-dinitrobiphenyl, mp and mmp 236–237 °C. Anal. Calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4$: C, 59.02; H, 3.30; N, 11.47. Found: C, 57.12; H, 3.12; N, 11.00. No *p*-nitrosobenzophenone and *p*-azoxybenzophenone were obtained.

Preparation of Anion Radicals and Measurements. ESR spectra of 1-*p*-nitrophenyl-1-phenylethylene and its derivatives were recorded with a Varian V-4500 series spectrometer using a 100 Kc/s field modulation, a 9-in. magnet, and a Hewlett-Packard 5340 A frequency counter and 7046 A X-Y recorder. The coupling constants were cal-

Scheme III

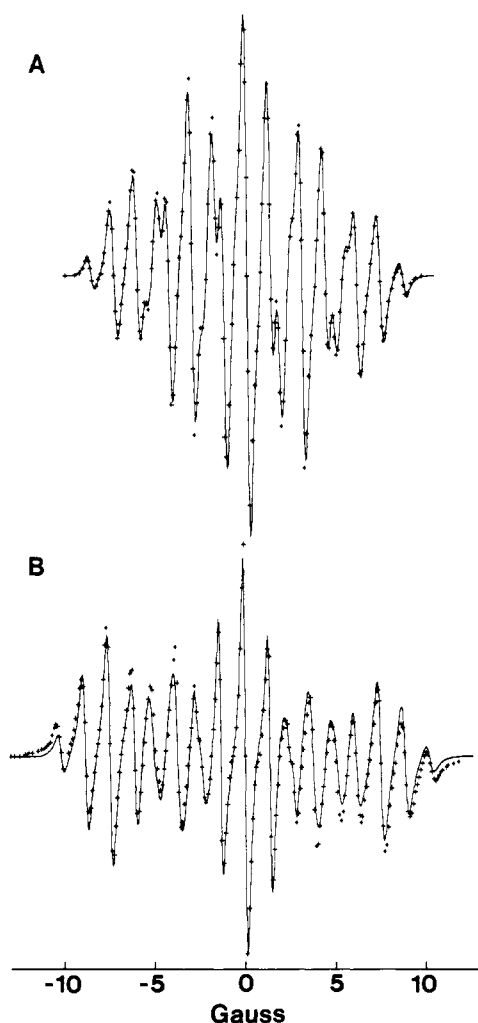
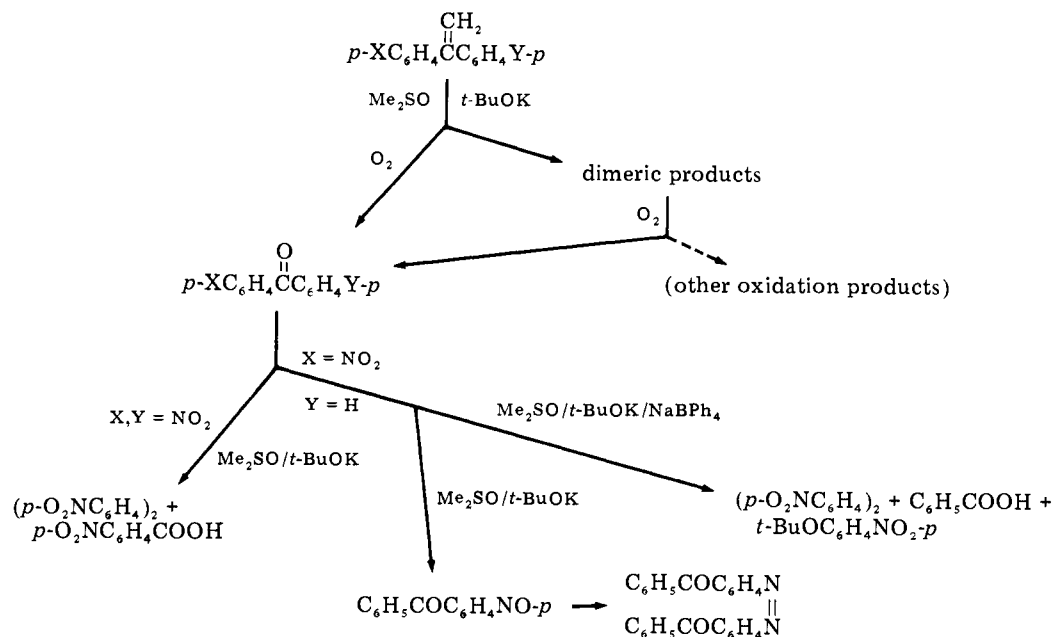


Figure 6. ESR spectra of 4,4'-dinitrophenyl anion radical. Solid line, simulated spectra; points, experimental spectra. (A) Spectrum observed by electrolytic reduction in Me_2SO ; simulation was performed with the hfsc's collected in Table II and $W = 0.267 \pm 0.017$ G. (B) Spectrum observed in Me_2SO containing MeONa and dibenzo-18-crown-6 ether; $a_N = 3.748 \pm 0.002$, $a_{H_o} = 1.364 \pm 0.003$; on comparison with spectrum (A), spectrum (B) shows considerable broadening, due both to electron spin relaxation ($A = 0.278 \pm 0.007$, $B_N = 0.017 \pm 0.003$, $C_N = 0.011 \pm 0.001$ G) and cation exchange between the two nitro groups ($F_N = 0.284 \pm 0.009$ G). The spectrum was also well simulated by the density matrix method, assuming that the two nitrogens interchange their coupling constants (7.3 and 0.2 G, respectively), with a rate constant of $2.4 \times 10^8 \text{ s}^{-1}$.

ibrated by direct comparison with the ESR spectrum of Fremy's salt. The remainder of the work employed a Varian E-Line Century Series spectrometer. The magnetic field sweep was calibrated by a Varian Field/Frequency Lock E-272 B. Both instruments gave identical results.

The electrolytic generation of anion radicals was performed in vacuum cells inside the resonance cavity, as previously described;² however, we substituted for the mercury pool and calomel electrodes two platinum wires. The counter electrode was placed in a compartment separated from the bulk of the solution by a fritted glass disk.²³ The potentials at which the reductions were carried out were chosen from the polarographic half-wave potentials;^{2,57} when no polarographic data were available, the applied voltage was slowly increased in small increments until the first radical was detected. A solution of TBAP in Me_2SO was used as a supporting electrolyte.

In the preliminary part of this work the chemical generation of anion radicals was performed by mixing prepurified nitrogen solutions of the base and each compound in an apparatus similar to that reported by Russell and co-workers.⁵⁸ Successively we modified our apparatus for standard use under vacuum.²³

Concluding Remarks and Summary

The course of basic oxidation of nitroarylethenes can be summarized by Scheme III. All the intermediates and products were isolated and/or observed through the ESR spectra of the corresponding anion radicals.

The ESR spectra, recorded at different times during the course of the reaction, are affected by the changes of the physical properties and the composition of the medium. The proton-extraction reactions described in eq 13, as well as the redox reaction^{59,60}



yield alcohols. This fact affords enhancements in the observed ESR nitrogen hfsc's, due to hydrogen bond formation. The same changes of the nitrogen hfsc's are observed when salts are added to the solutions of anion radicals. The addition of salts results in the formation of ion pairs, which undergo rapid interconversion with the free ions present in solution.⁶¹ Similarly the acid-base equilibria can be studied by changing the base strength of the medium, as done in this work for the anion radical of *p*-nitrobenzoic acid.

Furthermore the details of molecular motion in liquids can be investigated by means of electron spin relaxation which is strongly dependent on molecular dimensions, as shown by the ESR spectra of *p*-azobenzophenone anion radical.

Intramolecular dynamic processes can be visualized, as in the case of 4,4'-dinitrophenyl anion radical. The addition of dibenzo-18-crown-6 ether, which is a complexing agent for

cations, reduces the mobility of the cation, as predicted by Stoke's theory. The spectrum shown in Figure 6 emphasizes this phenomenon through the dramatic line width alternation of the nitrogen hyperfine lines.

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