

## Some Reactions of the Nitrobenzene Radical-anion and of its Halogenated Derivatives

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A technique for preparing and handling stable solutions of the nitrobenzene radical-anion,  $(\text{PhNO}_2\cdot)^-$ , in dry methyl cyanide is described. The first-order decay of this radical in the presence of a small percentage of an aqueous buffer is ascribed to the diffusion-controlled rate of neutralisation of the anion.

E.s.r. measurements show that the electron-transfer reactions of  $(\text{PhNO}_2\cdot)^-$  with quinones, diketones, and aromatic nitro-compounds of higher oxidation potential than nitrobenzene are rapid. The anions of *ortho*-chlorinated nitrobenzenes are unstable and undergo a first-order decay in which the labile chlorine is replaced by hydrogen.

SOLUTIONS of the radical-anion of nitrobenzene,  $(\text{PhNO}_2\cdot)^-$  (I) can be prepared in oxygen-free methyl cyanide by electrolytic reduction at a controlled potential.<sup>1</sup> They are quite stable and consequently, by manipulation under nitrogen, the reactions of (I) can be studied by e.s.r. spectroscopy outside an electrolytic cell. New features of our observations are described below.

**Proton Donors.** These destroy (I) by converting it into the unstable neutral radical  $(\text{PhNO}_2\text{H}\cdot)$  (II) which rapidly decomposes, eventually to yield phenylhydroxylamine and nitrobenzene, or, in alkali, azoxybenzene. This decomposition has been studied in detail in aqueous solution, using combined techniques of polarography, e.s.r. spectroscopy, and also pulse radiolysis and u.v. spectroscopy.<sup>2-6</sup> Evidently (II) is a very unstable acid of *pK* about 3.2.<sup>2,3</sup> The earlier experiments<sup>4,5</sup> indicated that the decay of (I) in equilibrium with (II) was a first-

order process up to about pH 9 but became a second-order reaction with respect to (I) in stronger alkali. However later studies,<sup>6</sup> especially that depending on pulse radiolysis,<sup>2</sup> accord with the view that second-order decompositions alone are involved and that they require both (I) and (II) since the decay of the radicals has an inverse acidity dependence even in alkali.

We have found that in dry methyl cyanide (I) is stable for days and is not affected by anhydrous bases such as triethylamine. Though the e.s.r. signal is immediately destroyed by the addition of anhydrous acids (chloroacetic,  $K_a = 2.86 \times 10^{-3}$ ; benzoic,  $K_a = 6.5 \times 10^{-5}$ ), when (I) was originally taken in excess then a weak signal of undecomposed material persisted over a long period. The addition in excess of alkylated phenols ( $K_a$ ,  $10^{-10}$ — $10^{-11}$ ), acetylacetone ( $K_a$   $10^{-9}$ ), or ethyl acetoacetate ( $K_a$ ,  $2.1 \times 10^{-11}$ ) also effected the destruction of (I) but less acidic ketones, *e.g.* acetone ( $K_a$   $10^{-20}$ ), acetophenone, and 1,2-dibenzoylthane as

<sup>1</sup> D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, 1960, **82**, 2671; 1961, **83**, 1852; D. H. Geske, J. L. Ragle, M. A. Bambanck, and A. L. Balch, *ibid.*, 1964, **86**, 986.

<sup>2</sup> K.-D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 862.

<sup>3</sup> G. Farnia, G. Mengoli, and E. Vianello, *Ricerca Sci.*, 1967, **37**, 668.

<sup>4</sup> L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, 1961, **83**, 3909.

<sup>5</sup> P. Koopmann and H. Gerischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1966, **70**, 127.

<sup>6</sup> B. Kastening and S. Vavřička, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 27.

well as alcohols ( $K_a < 10^{-16}$ ) such as benzhydrol and triphenylcarbinol and also benzophenone oxime had no effect. *p*-Nitrobenzyl cyanide behaved as an acid and gave its magenta-coloured anion.

The addition of a drop of water effected a gradual decay of the e.s.r. signal of (I). Measureable decay rates could be studied by addition of a small percentage of an aqueous borate buffer of pH 10.5<sup>7</sup> and then operating the e.s.r. spectrometer at constant power while maintaining the magnetic field strength at a value corresponding to one of the main signal peaks of (I). As shown from Table 1 the diminution of peak height with time accords with a first-order process for the whole of the decay. Table 2 gives pseudo-unimolecular velocity constants

TABLE 1

Rate of decay of  $(\text{PhNO}_2)^-$  in an alkaline buffer

Time (min.)	Signal height (cm.)	$\log_{10}$ height	Time (min.)	Signal height (cm.)	$\log_{10}$ height
0	6.23	0.80	12	1.89	0.28
2	5.18	0.71	14	1.51	0.18
4	4.19	0.62	16	1.25	0.097
6	3.50	0.54	18	1.04	0.017
8	2.78	0.44	20	0.86	-0.05
10	2.25	0.35			

Aqueous borate buffer (pH 10.5, ionic strength 0.048 $\text{M}$ ) (15 ml.) was diluted to 100 ml. with methyl cyanide containing enough  $\text{Pr}_4\text{NClO}_4$  to give an overall 0.1 $\text{M}$ -solution of dissolved salts: this solution (0.15 ml.) was then added to a solution (1.0 ml.) of (I) at room temperature (22°). The resulting solution contains 5.4 mole % of water.

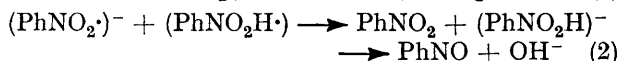
TABLE 2

First-order decay rates of  $(\text{PhNO}_2)^-$  in aqueous methyl cyanide

Mole fraction of water (%)	$a_N$ of Spectrum (gauss)	First-order rate constant $k_1$ (sec. <sup>-1</sup> )	Half life (min.)
0.00	10.20	—	—
3.83	11.1	$0.45 \times 10^{-3}$	25.7
5.42	11.55	$1.69 \times 10^{-3}$	6.85
6.80	11.7	$2.52 \times 10^{-3}$	4.59

The addition of buffer was made as reported for Table 1; temperature 22°.

together with values of  $a_N$  for the various solutions; the latter change in the expected manner as water is added to the methyl cyanide.<sup>8</sup>



Our results can accord with the view that the radical decay is the bimolecular interaction (2) between (I) and (II) only if, under our conditions, the hydrogen ion activities of the solutions are so small that the forward reactions (1), *i.e.* the neutralisation of the radical-anion (I), are rate-determining.

<sup>7</sup> R. G. Bates, 'Determination of pH — Theory and Practice,' J. Wiley and Co., New York, 1964, p. 162.

<sup>8</sup> L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, 1964, **86**, 2568.

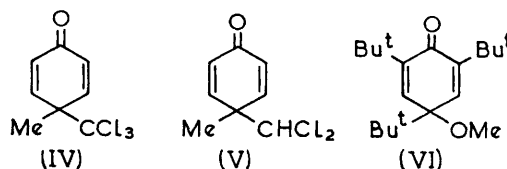
<sup>9</sup> J. M. Fritsch, T. P. Layloff, and R. N. Adams, *J. Amer. Chem. Soc.*, 1965, **87**, 1724.

*Quinones, Unsaturated Ketones, and Related Compounds.* Fritsch, Layloff, and Adams<sup>9</sup> have found that in dimethylformamide solution (I) rapidly reduces quinones and similar compounds which have lower (negative) polarographic half-wave reduction potential than nitrobenzene. We have confirmed this for solutions of (I) in methyl cyanide and have extended considerably the list of reducible compounds. Phenanthraquinone, anthraquinone, and acenaphthaquinone immediately yield the known spectra<sup>10</sup> of their semiquinone radical-anions. As expected from the related work of Russell, Janzen, and Strom,<sup>11</sup> benzil when added in 10-fold excess to a solution of (I) gave a deep blue solution, the e.s.r. spectrum of which showed the superimposition of the spectrum of the blue radical-anion of benzil,  $\text{PhCO}(\dot{\text{C}}-\text{O})\cdot\text{Ph}$  (III), on that of (I). Both spectra disappeared during 5–10 minutes after admixture and the eventual solution became yellow. Since (III) is known to disproportionate<sup>12</sup> to benzil and its diamagnetic dianion we suggest that the electron transfer (3) is reversible.



A much more transient blue colour was noticed on the addition of (I) to *trans*-1,2-dibenzoyl ethylene but the eventual yellow solution gave no e.s.r. signal. We conclude that the intermediate  $\text{PhCO}\cdot\text{CH}:\text{CH}(\dot{\text{C}}-\text{O})\cdot\text{Ph}$  had been formed but was irreversibly destroyed. Biacetyl also effected the disappearance of the signal of (I).

As expected from their redox potentials<sup>9</sup> (I) was not affected by benzophenone, cinnamaldehyde, methyl crotonate, 3-phenylhex-2-enone, or  $\alpha$ -benzoyl-*cis*-stilbene. Its signal however was destroyed by (IV) and (V) but not by (VI). It would appear that the electron



delocalisation of  $\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot$  approaches that of quinones and that the electrophilic  $\text{CCl}_3$  and  $\text{CHCl}_2$  groups enhance the reducibility of this system.

Nitrogenous analogues of quinones and unsaturated ketones are less easily reduced since phenazine, benzalazine, and *O*-benzoylbenzil mono-oxime had no action on (I).

*Aromatic Nitro-compounds.* Electron exchange between aromatic nitro-compounds and corresponding radical-anions is rapid. As expected from measurements of polarographic redox potentials<sup>1</sup> the introduction of electrophilic groups (F, Cl, Br,  $\text{CO}_2\text{Et}$ , and OH) were all

<sup>10</sup> 'Landolt-Börnstein Numerical Data *etc.*,' New Series, Group II, vol. I; 'Magnetic Properties of Free Radicals,' ed. H. Fischer, Springer-Verlag, Berlin-Heidelberg-New York, 1965.

<sup>11</sup> G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.

<sup>12</sup> A. G. Evans, J. C. Evans, and E. H. Godden, *Trans. Faraday Soc.*, 1967, **63**, 136.

tested as *para*-substituents) favours the transfer of an electron from (I) whereas *p*-nitrotoluene, *p*-nitroanisole, and nitromesitylene are not reduced by it.

All three monochloronitrobenzenes, the dichloronitrobenzenes, and 2-chloro-4-nitrotoluene give characteristic

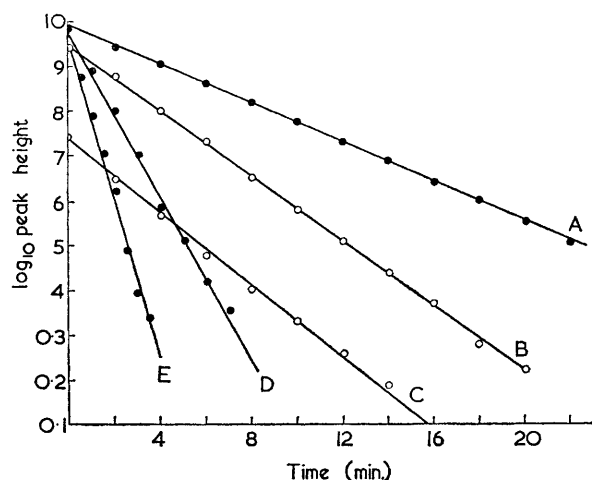


FIGURE 1 First-order decay rates of halogenated nitrobenzene radical-anions (22°). A, 4-Bromonitrobenzene; B, 2,3,5-trichloronitrobenzene; C, 2-chloronitrobenzene; D, 2,4-dichloronitrobenzene; E, 2,3,5,6-tetrachloronitrobenzene

solutions of their radical-anions when treated with (I) but, as Figure 1 shows, the e.s.r. signal strengths of the radicals formed from the *ortho*-chlorinated nitrobenzenes slowly diminish in intensity by a first-order decay

The course of the decomposition described above can be followed by e.s.r. spectroscopy for when 2,3,5,6-tetrachloronitrobenzene (VII) is treated with a solution containing an equivalent of (I) the e.s.r. spectrum of its radical-anion (VIII), which promptly appears, decays and a radical-free solution remains. Addition of another equivalent of (I) to this gives the e.s.r. spectrum of the radical-anion of 2,3,5-trichloronitrobenzene (IX) which clearly shows the extra hyperfine splitting of one *ortho*-hydrogen. This spectrum again decayed, after which the addition of a third equivalent of (I) gave the e.s.r. spectrum of the stable radical-anion of 3,5-dichloronitrobenzene. The two *ortho*-chlorines from 2,4,6-trichloronitrobenzene have been removed in similar stages.

Two pathways for the decay of (VIII) and its analogues can be formulated; (a) loss of a chloride anion to give an organic radical (X), which like a phenyl radical should be capable of abstracting a hydrogen atom from an organic solvent (here, methyl cyanide) or (b) loss of a chlorine atom to give an anion (XI) which could abstract a proton from the solvent. The Scheme shows that both routes (a) and (b) involve the conversion of a  $\pi$ -type radical (VIII) to a  $\sigma$ -type radical (X) or to an anion (XI) by a relaxation process in which the axial orientation of an unpaired  $p_z$  electron must change by 90° and take up an  $sp^2$ -hybridised orbital. From consideration of enthalpies route (a) which leads to the formation of chloride anion and not of atomic chlorine would be the favoured pathway. To test for the possible formation of chlorine atoms the reaction of (I) with 2,4-dichloro-

TABLE 3

Hyperfine splitting constants (gauss) and first-order rate constants ( $\text{sec}^{-1}$ ) for the decay of halogenated nitrobenzene radical-anions in methyl cyanide at 22° (ionic strength  $\text{ca. } 5 \times 10^{-2}\text{M}$ )

	$g$ value	$a_N$	$a_2 = a_6$	$a_3 = a_5$	$a_4$	$k_1$
4-Chloronitrobenzene .....	2.0048	9.62	3.42	1.13	—	(Stable)
3-Chloronitrobenzene .....	—	9.43	3.47	0.96	4.07	(Stable)
2-Chloronitrobenzene .....	2.0051	9.72	3.16	1.17	4.03	$1.6 \times 10^{-3}$
3-Chloro-4-methylnitrobenzene .....	—	9.88	3.42	1.05	( $a_{\text{CH}_3}$ , 4.26)	(Stable)
3,5-Dichloronitrobenzene .....	—	8.45	3.35	—	4.26	(Stable)
3,4-Dichloronitrobenzene .....	—	8.84	3.42	0.94	—	(Stable)
2,5-Dichloronitrobenzene .....	—	8.69	3.41	1.14	4.36	(Stable)
2,4-Dichloronitrobenzene .....	—	8.99	3.35	1.26	—	$3.6 \times 10^{-3}$
2,4,6-Trichloronitrobenzene .....	—	14.1	—	1.01	—	$\text{ca. } 1 \times 10^{-2}$
2,3,5-Trichloronitrobenzene .....	2.0049	7.90	3.43	—	4.46	$1.4 \times 10^{-3}$
2,3,5,6-Tetrachloronitrobenzene .....	2.0054	13.4	—	—	2.31	$7.1 \times 10^{-3}$
4-Bromonitrobenzene .....	—	9.43	3.43	1.14	—	$0.84 \times 10^{-3}$

process. The radical-anion spectra from both *p*-fluoro- and *p*-chloro-nitrobenzene did not decay appreciably; that from *p*-bromonitrobenzene decayed slowly and that from *o*-bromonitrobenzene too rapidly for measurement. Table 3 shows that *para*-chlorine substitution enhances the lability of the radical-anion of *o*-chloronitrobenzene. The splitting constant,  $a_N$ , for these solutions of chlorinated nitrobenzene radical-anions in methyl cyanide are also listed. They show that two *ortho*-chlorine atoms greatly enhance values of  $a_N$  by causing the nitro-group to twist out of the plane of the ring<sup>8</sup> though one *ortho*-chlorine has surprisingly little effect.

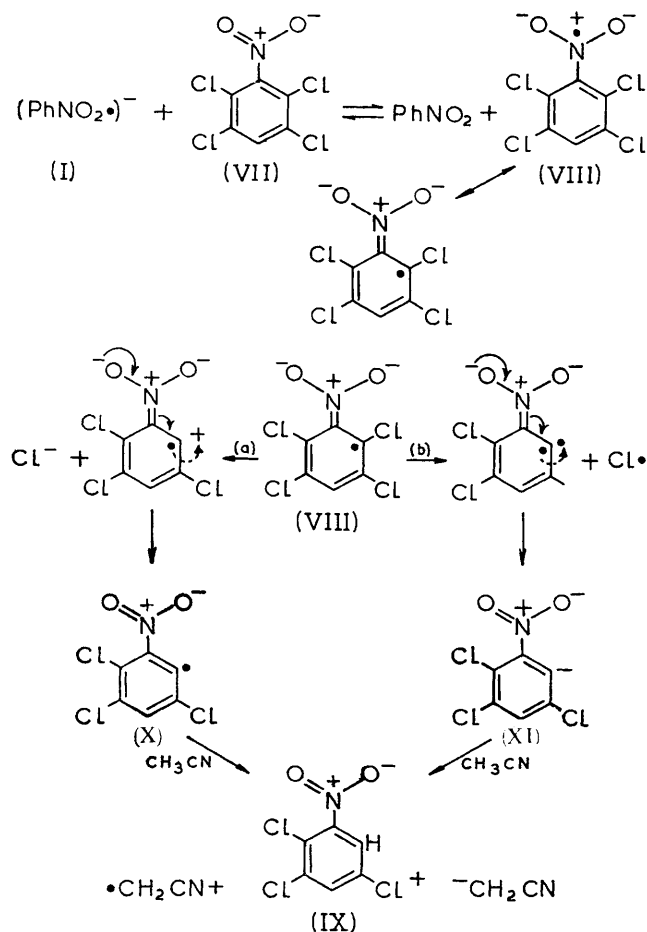
<sup>13</sup> T. Kitagawa, T. P. Layloff, and R. N. Adams, *Analyt. Chem.*, 1963, **35**, 1086.

nitrobenzene was effected in the presence of a 10-fold excess of cyclohexene to act as a chlorine scavenger. After removal of the bulk of solvent, less volatile reaction products were examined by vapour-phase chromatography; nitrobenzene and *p*-chloronitrobenzene were detected but neither cyclohexyl chloride nor dichloro-cyclohexane.

Our conclusions accord with the findings of Kitagawa, Layloff, and Adams<sup>13</sup> who found that *o*- and *p*-iodo- and bromo-nitrobenzenes lose their halogens on polarographic reduction in dimethylformamide and with those of Wawzonek and Wagenknecht<sup>14</sup> who demonstrated

<sup>14</sup> S. Wawzonek and J. H. Wagenknecht, *J. Electrochem. Soc.*, 1963, **110**, 420.

similar halogen loss with *o*-dibromobenzene, though both groups of investigators consider that they had been dealing with two-electron reductions. However a clear case of one-electron reduction of aryl iodides, with expulsion of iodide anions,  $(\text{ArI}\cdot)^- \rightarrow \text{Ar}\cdot + \text{I}^-$ , has been described by Bunnett and Wamser.<sup>15</sup>



SCHEME Mechanisms for decomposition of the radical-anion of 2,3,5,6-tetrachloronitrobenzene

Coulson<sup>16</sup> has pointed out that the single-stage dissociation of the radical-ion of chlorobenzene in the vapour phase should give a chlorine atom and a phenyl anion and would be endothermic.

Consequently, as Clarke and Coulson<sup>17</sup> point out, the exothermic reaction  $(\text{PhCl})\cdot^- \rightarrow \text{Ph}\cdot + \text{Cl}^-$  requires a significant amount of activation energy and probably an intermolecular collision. Reactions in solution would thus tend to follow route (a) and not route (b).

A similar transition to route (a) in the Scheme, in which an electron from a  $\pi$ -orbital shifts to a  $sp^2$  orbital or to an *ortho*-carbon has been suggested by Abramovitch and Gadallah<sup>18</sup> to occur in the thermal decomposition of benzenediazonium tetrafluoroborate.

## EXPERIMENTAL

**Electrolytic Preparation of (I).**—The electrolytic cell (Figure 2) comprised a 50 ml. conical flask with a mercury pool cathode C on which floated a magnetically driven stirrer S. Tubes Y and Z for the admission of reagents or dry nitrogen were sited at right angles to a sloping side-arm (not shown in the Figure) closed by a serum cap through which could be inserted a syringe or, alternatively, a capillary leading to a small reference electrode consisting of a silver wire immersed in 0.1M-silver perchlorate and 0.1M-tetrapropylammonium perchlorate in methyl cyanide.<sup>19</sup> The anode compartment, which fitted by a ground joint B into the neck of the cell, was separated from the cathode by a fritted glass plate and contained a platinum black anode plate A and separate nitrogen inlet and outlet leads.

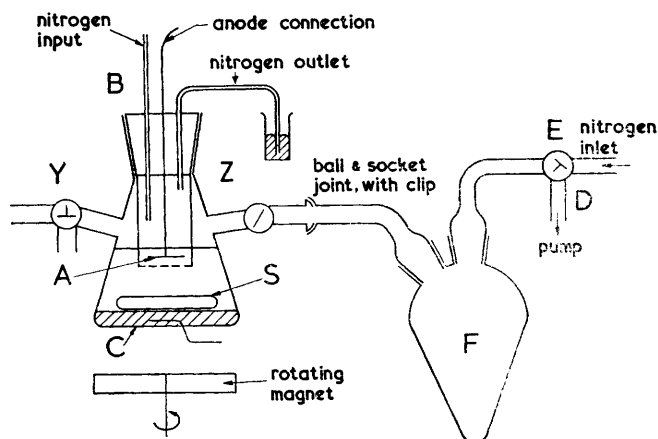


FIGURE 2 Electrolytic cell

To operate, a solution of  $5 \times 10^{-3}\text{M}$ -nitrobenzene and 0.1M-tetrapropylammonium perchlorate in purified methyl cyanide (35 ml.) was placed in F in which air was then replaced by nitrogen. Tap Z was closed, F was cooled in liquid nitrogen and evacuated by pumping at D, and then nitrogen was readmitted at E as the solution in F was allowed to thaw. After repeating this freeze-evacuate-thaw cycle 3 times the oxygen-free solution was transferred to the electrolytic cell under nitrogen until the anode plate A was just covered by rotating the ball joint near Z.

Electrolysis was then carried out, with the reference electrode fitted, using an applied voltage of up to 8.5 v between A and C but controlling it so that the potential difference between C and the reference electrode never exceeded 1.8 v. The initial current was *ca.* 1 milliamp but after about 10 min. it rose sharply to *ca.* 10 milliamp and the solution then turned yellow. As electrolysis proceeded under this steady current the solution gradually became red. When the current started to drop (*ca.* 30 min.) the electrolysis was stopped since over-electrolysis yielded unstable solutions. The nitrogen pressure in the cell was then increased slightly, the reference electrode was replaced by a

<sup>15</sup> J. F. Bunnett and C. C. Wamser, *J. Amer. Chem. Soc.*, 1967, **89**, 6712.

<sup>16</sup> C. A. Coulson, *Chem. in Britain*, 1968, **4**, 113.

<sup>17</sup> D. D. Clarke and C. A. Coulson, *J. Chem. Soc. (A)*, 1969, 169.

<sup>18</sup> R. A. Abramovitch and F. F. Gadallah, *J. Chem. Soc. (B)*, 1968, 497.

<sup>19</sup> P. H. Rieger, I. Bernal, W. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1963, **85**, 683.

nitrogen-flushed syringe, and samples were withdrawn slowly enough to prevent any of the acidic anodic liquid from diffusing down to the cathode compartment. Lithium and sodium perchlorates were not satisfactory supporting electrolytes since during electrolysis a film then forms on the mercury surface, probably due to amalgam formation and its reaction with the solvent.

*Reactions.*—Reagent solutions were prepared in a flask similar to F with nitrogen inlet and outlet leads (as D and E) and a side-arm closed with a serum cap. All solutions were deoxygenated, as described above, before admixture with (I) and reacted mixtures were transferred by a syringe to a nitrogen-flushed e.s.r. sample cell for examination on a Varian V4500 instrument.

*Measurements of Reaction Velocities.*—These were performed using a 'Fieldial' to set the applied magnetic field at a value corresponding to one of the main resonance lines of the specimen under examination and running the chart paper at a constant known speed. By keeping the micro-

wave power well below the saturation level, as indicated by line broadening, the signal response, at constant power is then proportional to the radical concentration. Radicals with half-life times of the order of minutes can conveniently be examined in this way.

*Reagents.*—Methyl cyanide was purified as described by Cooper and Waters<sup>20</sup> and the nitrobenzene as described by Masson.<sup>21</sup> Tetrapropylammonium perchlorate was recrystallised from 20% aqueous methyl cyanide, powdered, and then dried thoroughly in a vacuum ( $P_2O_5$ ). The other reagents were crystallised to authentic m.p. and dried before use. We thank Mr. H. Browning of this laboratory for the samples of the cyclohexadienones (IV)—(VI).

One of us (A. R. M.) thanks the S.R.C. for a research studentship.

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<sup>20</sup> T. A. Cooper and W. A. Waters, *J. Chem. Soc.*, 1964, 1538.

<sup>21</sup> I. Masson, *Nature*, 1931, **128**, 726.