Reaction of I with Triphenylphosphine. A.—To a solution of 2.28 g (8.7 mmol) of triphenylphosphine (Carlisle Chemical Co.) in 100 ml of benzene stirred under nitrogen was added a solution of 3.00 g (8.7 mmol) of the bromoenamine I in 20 ml of benzene. After 1 hr of stirring at room temperature, tlc showed the absence of unreacted I. A white, hygroscopic precipitate, mp 128–130°, was filtered from the reaction mixture. An oil was obtained from the filtrate after removal of solvent. Hydrolysis of the oil with undried methanol gave 0.86 g (37%) of enamine III and 0.56 g (27%) of deoxybenzoin after fractional recrystallization from methanol. The white precipitate could not be purified, as it hydrolyzed rapidly in air to give enamine III, deoxybenzoin, and triphenylphosphine oxide.

B.—The same reaction was carried out in a carefully dried system. Instead of filtration of the precipitate, a different work-up procedure was employed. A mild exothermic reaction took place with the dissolution of the original precipitate when 1.8 times the equimolar amount of absolute ethanol was added to the reaction mixture. After having been stirred overnight, the mixture was fractionally distilled. Comparison of the nmr spectra of the distillate fractions with that of authentic ethyl bromide showed a 50% yield of ethyl bromide. An 85% yield of *cis*-III, a 9% yield of deoxybenzoin, and a 92% yield of triphenylphosphine oxide were obtained from the residue by fractional recrystallization from methanol.

Reaction of II with Triphenylphosphine.—The reaction was carried out in a manner similar to A above. After 24 hr of stirring tlc showed the presence of unreacted II. Column chromatography yielded 70% unreacted triphenylphosphine and 29% deoxybenzoin.

Registry No.—*cis*-I, 20735-65-3; *trans*-I, 20735-66-4; *cis*-II, 20735-67-5; *trans*-II, 20735-68-6; phenyllithium, 591-51-5; triphenylphosphine, 603-35-0.

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The Coupling of Nitrophenyl Radicals and Anions To Form Anion Radicals

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Dimerization, disproportionation, and atom abstraction are among frequently reported reaction pathways for organic free radicals.[1] Evidence has been presented recently which shows that still another reaction pathway, the coupling of a radical with an anion, predominates for nitrobenzyl radicals in the presence of certain anions.[2] Similarly, the coupling of a phenyl radical with an anion has been suggested to rationalize the formation of biphenyl in the photolysis of a phenyllithium in ether solution.[3]

In the course of some of our earlier work we reported that the presence of iodide ion markedly altered the rate of halogenated nitrobenzene anion radical decomposition.[4] That observation suggested that further studies should be made into the reactions of phenyl radicals in the presence of anions. The results of such a study are reported herein.[5]

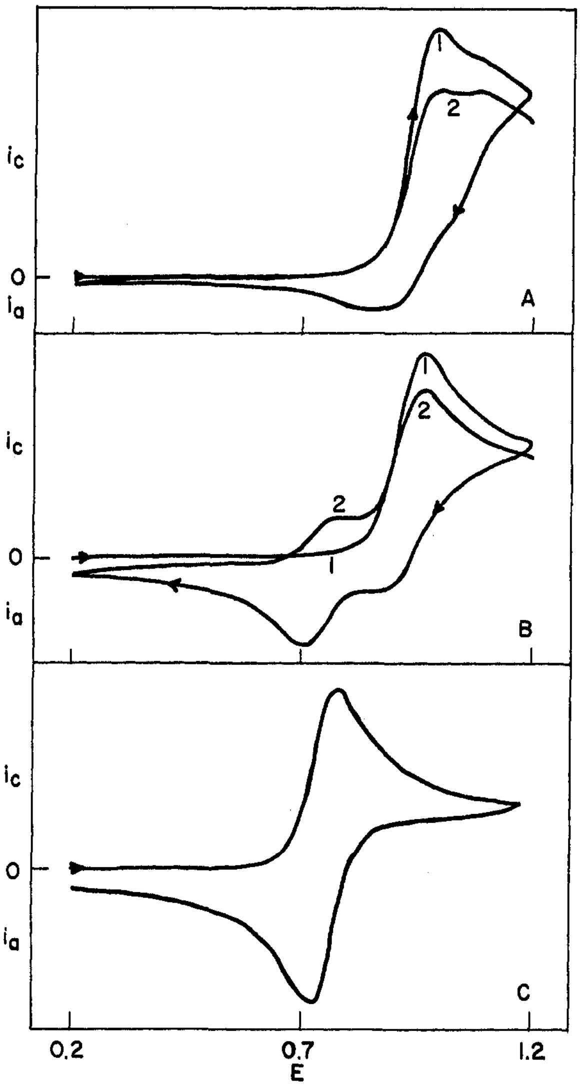

Figure 1.—Cyclic voltammograms in 0.1 *M* TEAP–DMSO at a scan rate of 80.6 mV/sec: (a) 7.32 × 10^{-3} *M* *p*-iodonitrobenzene; (b) 7.32 × 10^{-3} *M* *p*-iodonitrobenzene and 0.1 *M* NaCN; (c) 5.82 × 10^{-3} *M* *p*-nitrobenzonitrile. Numbers 1 and 2 represent cycles 1 and 2, respectively.

Evidence for a phenyl radical–anion reaction is shown in Figure 1. In the absence of a reactive anion, such as cyanide (Figure 1a), the nitrophenyl radical formed by the electrochemical reduction of *p*-iodonitrobenzene (cathodic peak near −1.0 V) abstracts a hydrogen atom from the solvent to form nitrobenzene. The nitrobenzene is then reduced in a one-electron process at slightly more negative potential (cathodic peak near −1.09 V) to its anion radical.[6] The absence of appreciable anodic current on the reverse, anodic sweep is the result of a solution oxidation–reduction reaction involving nitrobenzene anion radical and *p*-iodonitrobenzene.[4]

Hydrogen atom abstraction is virtually eliminated as a reaction pathway in dimethyl sulfoxide (DMSO)

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[1] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966.

[2] G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968); N. Kornblum, R. E. Michel, and R. C. Kerber, *ibid.*, **88**, 5660 (1966).

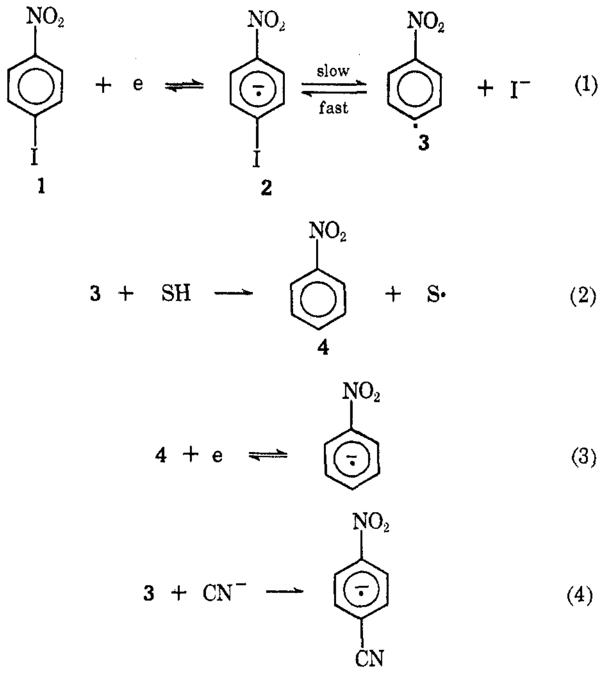
[3] E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **87**, 4964 (1965).

[4] J. G. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

[5] Since the completion of this work, the coupling of phenyl radical and nitrite ion was observed by esr spectroscopy in aqueous solution: A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc., B*, 403 (1969).

[6] For additional applications of cyclic voltammetry to organic systems, see, *e.g.*, R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969.

when cyanide ion is present. In the presence of cyanide ion (Figure 1b), only the reduction wave owing to the one-electron reduction of *p*-iodonitrobenzene to its anion radical is readily discernible on the first cathodic sweep. After reversal of the potential scan at −1.2 V, an anodic wave not seen in Figure 1a is observed at −0.72 V. Subsequent cathodic sweeps show an additional reduction process at −0.78 V. A comparison of the cyclic voltammograms of authentic *p*-nitrobenzonitrile (Figure 1c) and the present system clearly shows that the new redox couple is due to *p*-nitrobenzonitrile-*p*-nitrobenzonitrile anion radical. The absence of a reduction wave at −0.78 V on the first cathodic scan shows unequivocally that the anion radical of *p*-nitrobenzonitrile cannot result unless the reduction of *p*-iodonitrobenzene is first made to occur. A reaction scheme consistent with this interpretation is shown by eq 1–4.



Confirmation of *p*-nitrobenzonitrile anion radical formation was obtained by esr spectroscopy. The esr spectrum of the anion radical obtained in this manner was identical with the spectrum of the anion radical of an authentic sample of *p*-nitrobenzonitrile. As expected, the hyperfine splitting constants ($a^{N}_{NO_2}$ = 7.15, a^{H}_{O} = 3.06, and $a^{H}_{M} = a^{N}_{CN}$ = 0.76 G) differ only slightly from those reported previously for the anion radical in acetonitrile.[7]

Formation of *o*-nitro- and *m*-nitrobenzonitrile anion radicals from the corresponding nitrophenyl radicals and cyanide ion is observed similarly by cyclic voltammetry. In the presence of 0.1 *M* sodium cyanide in DMSO, thin-layer coulometry[8] results (Table I) show that the yields of the nitrobenzonitrile anion radicals are greater than 90% from each of the nitrophenyl radicals.

As expected, increasing the ease with which a hydrogen atom can be abstracted from the solvent decreases the amount of coupling with cyanide ion. Thus, as the solvent is varied from DMSO to AN (acetonitrile) to DMF (dimethylformamide), nitrobenzene formation is observed qualitatively to increase in the order DMSO < AN < DMF.[9] Since ion-pair formation is probably extensive (but unknown) in these solvents, a quantitative study of the relative rates in the several solvents was not attempted.

TABLE I

COULOMETRIC REDUCTION OF IODONITROBENZENES IN DMSO[a]

Nitrobenzene substituent	Anion added	$-E_{\text{applied}}$	*n* value[b]
4-Iodo-		1.2	1.93
4-Iodo-	CN⁻	1.2	1.04
3-Iodo-		1.2	1.93
3-Iodo-	CN⁻	1.2	0.92
2-Iodo-		1.4	1.89
2-Iodo-	CN⁻	1.2	0.96

[a] Supporting electrolyte is 0.1 *M* tetraethylammonium perchlorate. When cyanide ion is indicated to be present, its concentration is 0.1 *M*. [b] The theoretical number of electrons (*n* value) for the reduction of an iodonitrobenzene to nitrobenzene anion radical and iodide ion is 2.0; see eq 1–3 for a description of the electrochemical and chemical process. The formation of a nitrobenzonitrile anion radical corresponds to a one-electron process; see eq 1, 2, and 4 for a description of these processes. Relative average deviation is less than 5% of an *n* value.

Coupling of phenyl radicals with nitrite ion was also observed. Phenyl radical, prepared by the thermal decomposition of phenylazotriphenylmethane in DMSO in the presence of 0.1 *M* NaNO$_2$, yielded a product which upon electroreduction gave a strong esr spectrum of nitrobenzene anion radical; glpc showed the presence of approximately 5% nitrobenzene and 75% benzene. Coupling of electrochemically generated *p*-nitrophenyl radical with nitrite ion nearly eliminates hydrogen atom abstraction as a reaction pathway, as evidenced by the absence of a nitrobenzene reduction wave (Figure 2). The pair of reduction waves near −0.59 and −0.73 V arises from the stepwise reduction of the coupled reaction product, dinitrobenzene, to its dianion. The anodic peak remaining at −0.90 V represents the reoxidation of unreacted *p*-iodonitrobenzene anion radical.

Attempts to prepare other anion radicals by coupling a nitrophenyl radical with an anion were not successful. As observed previously by Parker and coworkers,[10] thiophenoxide reacts rapidly with *p*-iodonitrobenzene to form *p*-nitrophenylthiophenyl ether prior to the electrochemical reduction. A similar reaction occurred between thiophenoxide and *m*-iodonitrobenzene.[11] Coupling of either *m*- or *p*-nitrophenyl radical with either chloride or bromide ion to form the corresponding halonitrobenzene anion radical was not observed. Although coupling of a nitrophenyl radical with iodide ion has been reported previously,[4] the resulting anion radical (as used in the present study) readily dissociates to regenerate the nitrophenyl radical.

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(7) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

(8) A. T. Hubbard, R. A. Osteryoung, and F. C. Anson, *Anal. Chem.*, **38**, 692 (1966).

(9) The ease of hydrogen atom abstraction by phenyl radical decreases in the order DMF > AN > DMSO. See R. F. Bridger and G. A. Russell, *J. Amer. Chem. Soc.*, **85**, 3754 (1963); J. D. Hunt, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1966.

(10) B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc., B*, 152 (1966).

(11) This substitution reaction may also proceed by a free-radical chain process with coupling of the nitrophenyl radical with thiophenoxide to form an anion radical intermediate. See ref 2 for a complete discussion of this mechanism with nitrobenzyl halides.

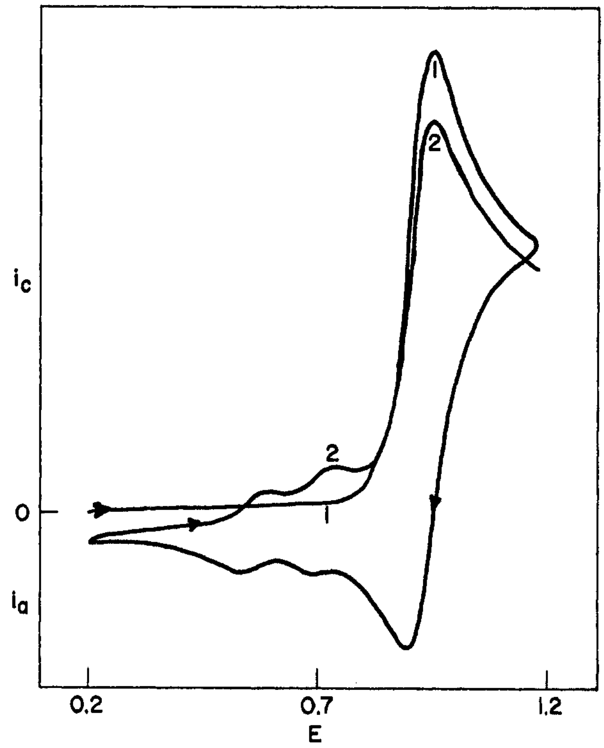

Figure 2.—Cyclic voltammogram of 5.52×10^{-3} M *p*-iodonitrobenzene and 0.1 M $NaNO_2$ in 0.1 M TEAP–DMSO at a scan rate of 80.6 mV/sec.

This work illustrates the facile nature of the coupling process of an organic free radical and anion. In contrast to the earlier reported work utilizing relatively stable benzyl free radicals,[2] the results reported herein illustrate that reactive phenyl radicals can be effectively scavenged by various anions even in the presence of reasonably good hydrogen-donating solvents. Such a low-energy reaction pathway available to free radicals is understandable, since only bond-formation and no bond-cleavage processes are involved.

Experimental Section

Instrumentation.—The cyclic voltammetric and thin-layer coulometric studies were performed on a transistorized, three-electrode potentiostat–galvanostat described previously.[4] The techniques suggested by Brown, Smith, and Booman[12] for stabilization of the potentiostat with 100% *iR* compensation were incorporated into this instrument.

Electron spin resonance spectra were obtained on a Varian V-4502 spectrometer. The anion radicals were produced *in situ* by the electrochemical reduction of the required iodonitrobenzene in the presence of the reacting anion.

The gas chromatograph was a Hewlett–Packard Model 700 equipped with flame ionization detection.

Cells and Electrodes.—The working electrode in the cyclic voltammetric experiments was a planar platinum button (Beckman No. 39273) with a geometric area of *ca.* 0.23 cm². The auxiliary electrode, a platinum foil, and the reference electrode, a saturated calomel electrode (sce), were isolated from the working electrode compartment by means of porous vycor glass (Corning No. 7930) and a bridge containing the solvent and 0.1 M supporting electrolyte.

A thin-layer electrode similar to the one described by McClure and Maricle[13] was used for the rapid determination of n values. The working electrode was a 3-mm length of 0.25-cm-diameter platinum rod attached to a stainless steel spindle (L. S. Starrett Co.) by means of electrically conducting epoxy. The sides of the spindle and the platinum rod were covered with a thin layer of epoxy cement (Devcon WR-2) in order to render them electroinactive. While the electrode functioned well in solutions of DMSO and AN, degradation of the epoxy covering occurred within several hours after placement in DMF solutions.

In the thin-layer experiments the potential of the working electrode was set sufficiently cathodic so as to reduce iodonitrobenzene and nitrobenzene (the product of hydrogen atom abstraction), but not so cathodic as to further reduce the product of the coupling reaction with cyanide ion. The method is not applicable in the case of nitrite ion, since the product of the coupling reaction, a dinitrobenzene anion radical, is further reduced at the applied potential to the corresponding dianion.

Chemicals.—All organic compounds were commercially available samples. The purity of each was checked by gas chromatography, cyclic voltammetry, and melting point; impure samples were recrystallized repeatedly until at least 99% purity was obtained.

Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee;[14] the method of Pocker and Kevill[15] was used for the preparation of tetraethylammonium nitrite. All supporting electrolytes were stored in a vacuum desiccator prior to their use. In a typical experiment, data were obtained first for the particular electrochemical system with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. The experiment was then repeated with the sodium salt of the desire anion added (0.1 M). Because of the insolubility of sodium nitrite in AN, tetraethylammonium nitrite was used as the anion source in this solvent.

DMF, AN, and DMSO were purified by previously described procedures[4] and stored over Linde Type 4A molecular sieves. All electrochemical experiments were performed in a glovebag under a nitrogen atmosphere. The solutions were deaerated with purified nitrogen for at least 20 min prior to the electrochemical measurements. All work was conducted at room temperature (22.5 ± 0.5°).

In the thermal generation of phenyl radicals, phenylazotriphenylmethane (0.005 M) was decomposed at 60.0 ± 0.1° with DMSO containing 0.10 M $NaNO_2$. Gas phase chromatography analysis showed formation of both benzene and nitrobenzene.

Registry No.—**1**, 636-98-6; **3**, 2395-99-5; *p*-nitrobenzonitrile anion radical, 12402-47-0; 3-iodonitrobenzene, 645-00-1; *m*-nitrophenyl radical, 3522-58-5; *m*-nitrobenzonitrile anion radical, 12402-46-9; 2-iodonitrobenzene, 609-73-4; *o*-nitrophenyl radical, 23209-57-6; *o*-nitrobenzonitrile anion radical, 12402-45-8.

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(13) J. E. McClure and D. L. Maricle, *ibid.*, **39**, 236 (1967).

(14) I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 870 (1957).

(15) Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965).

The Reaction of Benzyne with 1,3-Cyclohexadiene

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The recent report by Grisdale, *et al.*,[2] describing the synthesis and characterization of the series of phenyl-

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[1] J. R. Geigy A. G., 1061.419 Grundlagenforschung, 4000, Basel 21, Switzerland.

[2] P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, *J. Org. Chem.*, **33**, 1116 (1968).