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GENERATION OF AROMATIC RADICAL-ANIONS BY PHOTOREDUCTION AND ELECTRON TRANSFER PROCESSES

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RECENTLY Ayscough and Sargent[1] **reviewed some of the standard methods of** generation of aromatic radical-anions (reduction by alkali metals, electroreduction, reduction by zinc or glucose in basic media) and pointed out that photolysis of basic solutions of aromatic ketones or aromatic nitro compounds was an alternate and often convenient route to radical-anions. They presumed an electron transfer mechanism,

$$\mathrm{Ph_2C{=}O} \xrightarrow{h\nu} \mathrm{Ph_2C{=}O^*} \xrightarrow{\mathrm{OR^-}} \mathrm{Ph\dot{C}{-}O^-} + {}^{\bullet}\mathrm{OR}$$

$$\mathrm{PhNO_2} \xrightarrow{h\nu} \mathrm{PhNO_2} \xrightarrow{\mathrm{OR^-}} \mathrm{PhNO_2^{\overset{-}{\bullet}}} + {}^{\bullet}\mathrm{OR}$$

These observations can be explained in an alternate manner, particularly in view of some of the newer methods reported for the preparation of radical-anions. In addition to the standard reductive methods mentioned by Ayscough and Sargent can be added the following processes, (1) electron transfer between anions and unsaturated systems,[2,3] and particularly between dianions ($\pi^=$) and their unsaturated analogues (π),[3]

$$\pi\mathrm{H_2} \overset{B^-}{\rightleftharpoons} \pi^=$$

$$\pi^= + \pi \rightleftharpoons 2\pi^{\bullet -}$$

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(1) P.B. Ayscough and F.P. Sargent, Proc. Chem. Soc., (London), 94 (1963).
(2) G.A. Russell and E.G. Janzen, J. Am. Chem. Soc., 84, 4153 (1962).
(3) G.A. Russell and E.G. Janzen and E.T. Strom, J. Am. Chem. Soc., 84, 4155 (1962).

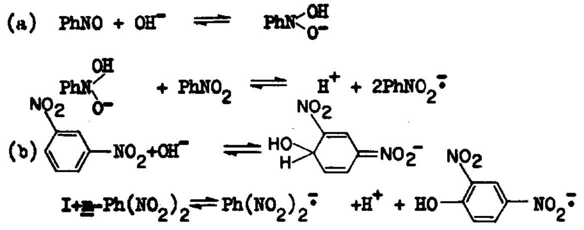
(2) Homolytic dissociation of 1,4-dianions,[3]

$$H\text{-}\pi-\pi\text{-}H \xrightarrow{B^-} {}^-\pi-\pi^- \rightleftharpoons 2\,\pi\cdot^-$$

(3) Electron transfer between dianions and molecular oxygen,[3]

$$H_2\pi \xrightarrow{B^-} \pi^= \xrightarrow{O_2} \pi\cdot^- + O_2\overset{-}{\cdot}$$

(4) Formation of radical-anions in basic solution from hydroxide addition products of unsaturated systems and electron acceptors, e.g.[1,4]



$$\text{(a)}\quad PhNO + OH^- \rightleftharpoons PhN{<}^{OH}_{O^-}$$

$$PhN{<}^{OH}_{O^-} + PhNO_2 \rightleftharpoons H^+ + 2PhNO_2\cdot^-$$

$$\text{(b)}\quad I + m\text{-}Ph(NO_2)_2 \rightleftharpoons Ph(NO_2)_2\cdot^- + H^+ + HO\text{-}C_6H_3(NO_2)\text{-}NO_2\cdot^-$$

Production of ketyl radical-anions by photolysis of aromatic ketones in alcoholic base[1] undoubtedly involves the well known formation of benzpinacol followed by reaction 2. Significant concentrations of ketyl radical-anions are also formed when benzophenone is first irradiated in methanol or ethanol solution and the resulting photolysate basified with sodium hydroxide. Table I summarizes pertinent results.

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(4) G.A. Russell and E.G. Janzen, Reprints of Papers, Div. of Petroleum Chemistry of American Chemical Society, **7**, 81 (1962).

TABLE I

Photoreduction of Benzophehone

Treatment [a,b]	Conc. of ketyl, 2 min. after mixing or after the cessation of photolysis
Irradiation with NaOH/MeOH in Cavity[c]	4.2×10^{-5} *M* (light on)
Irradiation with NaOH/EtOH in Cavity[c]	20.0×10^{-5} *M* (light on)
Irradiation in NaOH/MeOH for 20 min. before transfer to Cavity[c]	2.7×10^{-5} *M*
Irradiation in NaOH/EtOH for 10 min. before transfer to Cavity[c]	6.4×10^{-5} *M*
Irradiation in MeOH (20 min.) followed by addition of NaOH	5.8×10^{-5} *M*
Irradiation in EtOH (10 min.) followed by addition of NaOH[d]	10.4×10^{-5} *M*
Benzpinacol (0.02 *M*) in EtOH, 50% saturated with NaOH	16.0×10^{-5} *M*

[a] In cavity irradiations involved use of an unfocused 100 watt, General Electric AH-4 UV bulb about 3" from Varian V-4531 cavity. [b] Other irradiations were performed in a 15 mm. fused silica tube 4" removed from the AH-4 bulb in a water bath, solutions were continuously degassed by oxygen-free nitrogen. [c] 0.1 *M* benzophenone, 50% saturated NaOH. [d] 0.2 *M* benzophenone diluted with an equal volume of saturated NaOH.

The e.s.r. spectra were recorded with a Varian V-4500 spectrometer with 100 kc/sec. field modulation, and using a Varian aqueous sample cell. Those solutions which required mixing after irradiation were transferred to a two bulbed container attached to the cell, thoroughly degassed by a stream of oxygen-free nitrogen, mixed and allowed to flow directly into the cell. Concentrations of benzophenone ketyl were estimated by comparing the recorded spectra with those of diphenylpicrylhydrazyl at known concentrations. The concentration of the ketyl decreased fairly rapidly with time.

Reduction products of nitrobenzene, such as nitrosobenzene or phenylhydroxylamine, generate nitrobenzene radical-anions when added to basic solutions of nitrobenzene (reactions 4a,5)

$$\begin{tikzcd}
\text{(5) } PhNHOH+B^- \arrow[r, shift left] & \left[PhN{-}O\right]^{=} \arrow[l, shift left] \arrow[r, "\underline{PhNO_2}"] & PhNO_2^{\overline{\cdot}} + PhNO^{\overline{\cdot}} \arrow[d] \\
& PhN{=}N(O)Ph & \left[PhN(O)N(O)Ph\right]^{=} \arrow[l]
\end{tikzcd}$$

However, attempted photolyses of nitrobenzene in methanol or ethanol followed by basification yielded little $PhNO_2^{\overline{\cdot}}$ although photolysis in the presence of base yielded the radical-anion in significant amounts.[1] We feel the reaction is most readily formulated as follows,[5]

$$\text{(6) } PhNO_2 \xrightarrow{h\nu} PhNO_2^{*} \xrightarrow{CH_3CH_2O^-} PhNO_2H + CH_3CH\overset{\cdot}{=}O^-$$

$$\text{(7) } PhNO_2 \longrightarrow PhNO_2^{\overline{\cdot}} + H^+$$

$$\text{(8) } \left[CH_3CH\overset{\cdot}{=}O\right]^- + PhNO_2 \longrightarrow CH_3CHO + PhNO_2^{\overline{\cdot}}$$

Alternately, 7 and 8 might be replaced by 9 followed by 4a.

$$\text{(9) } Ph\dot{N}O_2H + CH_3CH\overset{\cdot}{=}O^- \longrightarrow \begin{array}{l} PhNO_2H^- + CH_3CHO \\ \qquad\qquad\quad PhNO+OH^- \end{array}$$

Another source of $PhNO_2^{\overline{\cdot}}$ is electron transfer from the enolate anion ($CH_2{=}CHO^-$) to nitrobenzene a process which occurs readily. Some typical experiments are summarized in Table II.

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(5) NOTE ADDED IN PROOF. The abstraction of α-hydrogens has been observed in irradiated solutions of nitrobenzene in THF (R.L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

TABLE II

Photolysis and Electron Transfer to Nitrobenzene

Treatment [a,b]	Conc. of $PhNO_2^{\cdot -}$
Irradiation in Cavity, NaOH/EtOH[c]	3.1×10^{-4} M (light on)
Irradiation in Cavity, NaOEt/EtOH[c]	3.9×10^{-4} M (light on)
Irradiation in methanol (30 min.) followed by addition of base[d]	None detected
Irradiation in NaOH/Methanol for 10 min.[c]	1.3×10^{-5} M
Irradiation in ethanol (40 min.) followed by addition of base[d]	1.6×10^{-5} M
Irradiation in NaOH/ethanol (1 hr.)[c]	7.7×10^{-5} M
C_6H_5NO(0.005 M) + $C_6H_5NO_2$(0.1 M)[e]	2.5×10^{-4} M
C_6H_5NHOH(0.005 M) + $C_6H_5NO_2$(0.1 M)[e]	2.6×10^{-4} M
CH_3CHO(0.1 M) - $C_6H_5NO_2$(0.1 M)[e]	1.7×10^{-4} M
C_6H_5NHOH(0.005 M) + C_6H_5NO(0.005 M)[e]	None detected

[a,b] See footnotes a and b, Table I. [c] 0.1 M Nitrobenzene, 50% saturated NaOH. [d] 0.2 M Nitrobenzene diluted with an equal volume of saturated NaOH. [e] In the presence of 50% saturated NaOH in ethanol.

The absence of radical-anions in the solution on phenylhydroxylamine—nitrosobenzene in the presence of base is interesting. We had expected that this would be another example of a $\pi^{=} + \pi \rightleftharpoons 2\,\pi^{\cdot -}$ system. The absence of radicals indicates that the well known condensation of these substances to give azoxybenzene cannot proceed by the intermediacy of any significant concentrations of $C_6H_5NO^{\cdot -}$[6]

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(6) In aprotic systems where reversible dimerization is possible, the equilibrium

$$C_6H_5N(ONa)C_6H_5 \rightleftharpoons 2\ C_6H_5NONa$$

is significant (T, Kauffmann and S.M. Hage, *Agnew, Chem. Internal. Edit.*, 2, 156 (1963).