# Hydrated Electron in Organic Synthesis. Reduction of Nitriles to Aldehydes

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Abstract: Irradiation of 2-, 3-, and 4-cyanophenol and 2- and 4-aminobenzonitrile in 10^{-2} M NaOH gave 2-, 3-, and 4-hydroxybenzaldehyde and 2- and 4-aminobenzaldehyde in yields of 32, 67, 62, trace, and 37%, respectively. No aldehyde was produced on irradiation of benzonitrile or 4-methoxybenzonitrile. Irradiation of the above compounds in the presence of KI with I^- absorbing 80–95% of the light gave about the same yields of aldehydes. However, irradiation of KI in the presence of benzonitrile, 4-tolunitrile, 3,4,5-trimethoxybenzonitrile, and 4-methoxybenzonitrile gave aldehyde yields of 5, 6, 16, and 40% respectively. Irradiation of KI in the presence of 4-nitrobenzonitrile yielded no aldehyde but 4-aminobenzonitrile, 4-aminobenzaldehyde, 4-cyanophenol, and 4-hydroxybenzaldehyde were found in low yields. These reactions were shown to involve solvated electrons as the reducing agent. The presence of this intermediate was demonstrated by trapping experiments, and phenoxyl radicals were detected by flash photolysis studies. In addition, 3,4,5-trimethoxybenzonitrile was also reduced to 3,5-dimethoxybenzonitrile, a reaction characteristic of solvated electrons. Some mechanistic schemes for these reactions are suggested.

In the course of our investigation of the photochemical conversion of enaminonitriles and enehydroxynitriles to imidazoles[1] and oxazoles,[2] respectively, we discovered the photochemical reduction of nitriles to aldehydes (eq 1). An examination of the scope and mechanism of this novel photochemical reduction is the subject of this paper.[3]

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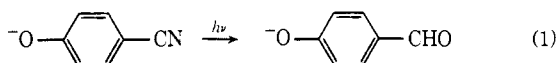
The corresponding aldehydes are formed when 2-, 3-, and 4-cyanophenol are irradiated in 10^{-2} M NaOH (Table I).[4] The conversion of 4-cyanophenol to 4-hydroxybenzaldehyde proceeds cleanly without the formation of significant amounts of other ultraviolet (uv) absorbing products (Figure 1). 4-Cyanoaniline is reduced to 4-aminobenzaldehyde; however, 2-aminobenzonitrile yields indazole[2] as the main reaction product along with a trace of 2-aminobenzaldehyde. The corresponding aldehydes were not produced when benzonitrile and 4-methoxybenzonitrile were irradiated in aqueous base (Table I).

It has been possible to demonstrate by several independent methods that the hydrated electron produced by the photoexcitation of the phenoxide ion is the reducing agent in the cyanophenoxide reductions. First, the reduction is quenched in the presence of electron scavengers such as oxygen, nitrate ion, acetone, and protons.[5] Second, the same reaction products are observed when a different source of hydrated electrons is used. For example, photolysis of iodide ion in the presence of the cyanophenols, with the iodide absorbing 80–95% of the light at 254 nm, gives similar yields of aldehydes (Table I). It is known that the hydrated electron is produced with a quantum yield of 0.29 when iodide ion is irradiated at 254 nm.[6] Furthermore, those nitriles which do not yield aldehydes on direct irradiation did so when irradiated in the presence of iodide ion (Table I). Our failure to observe the corresponding aldehyde from 4-chlorobenzonitrile is consistent with the known chemical reactivity of the solvated electron. Fluorobenzonitriles and 2-chlorobenzonitrile react with solvated electrons by dissociative electron attachment.[7]

$$RX + e^- \longrightarrow R\cdot + X^-$$
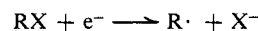
The third line of evidence for the intermediacy of the solvated electron is the observation that 3,5-dimethoxybenzonitrile (II) was also observed as a reduction product when I was irradiated in the presence of iodide (eq 2). This observation is consistent with the

Table I. Photochemical Reduction of Nitriles to Aldehydes

Compound	Product[a]	% yield — I^b	% yield — II^c
4-Cyanophenol	4-Hydroxybenzaldehyde	62[d]	75[d]
3-Cyanophenol	3-Hydroxybenzaldehyde	67[d]	56[d]
2-Cyanophenol	2-Hydroxybenzaldehyde	32[d]	27[d]
4-Cyanoaniline	4-Aminobenzaldehyde	37[d]	43[d]
2-Cyanoaniline	2-Aminobenzaldehyde	Trace[e]	Trace[e]
Benzonitrile	Benzaldehyde	0	5[f]
4-Tolunitrile	4-Tolualdehyde		6[f]
3,4,5-Trimethoxybenzonitrile	3,4,5-Trimethoxybenzaldehyde		16[g]
4-Methoxybenzonitrile	4-Methoxybenzaldehyde	0	40[d]
4-Chlorobenzonitrile	4-Chlorobenzaldehyde		0

[a] Photolyses were performed in water or methanol–water mixtures. All products were identified by direct comparison with authentic samples. [b] Direct irradiation in 10^{-2} M NaOH. [c] Irradiation in the presence of KI with I^- absorbing 80–95% of the light. [d] Yield determined from λ_{max} of the nitrile and the aldehyde when the aldehyde peak reached a maximum. [e] Detected on tlc with 2,4-dinitrophenylhydrazone. [f] Yield of aldehyde determined by glc based on unreacted nitrile. [g] Aldehyde yield based on separation from column (silica:CH_2Cl_2–EtOAc (20:1)).

(1) J. P. Ferris and J. E. Kuder, *J. Amer. Chem. Soc.*, **92**, 2527 (1970).
(2) J. P. Ferris and F. R. Antonucci, *Chem. Commun.*, 126 (1972).
(3) A preliminary communication of some of this work has appeared: J. P. Ferris and F. R. Antonucci, *ibid.*, 1294 (1971).
(4) The reduction of 4-cyanophenol to 4-hydroxybenzaldehyde was discovered independently: T. Omura and T. Matsuura, *ibid.*, 1516 (1969).

(5) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1970.
(6) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1967, p 271.
(7) A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc. A*, 666 (1969).

Table II. Flash Photolysis of Cyanophenols[a]

Compound	Transients, nm	Absorbance $\times 10^2$	Absorbance ($\times 10^2$) in presence of oxygen	$\sim t_{1/2}$, msec
2-Cyanophenol	415	2.57	0.98	1.0
$(8.13 \times 10^{-5}\, M)$	750 (broad)	1.57	0.78	1.2
3-Cyanophenol	410	2.07	0.88	0.7
$(1.08 \times 10^{-4}\, M)$	790	0.39	0.29	1.5
4-Cyanophenol	430	1.17	1.17	3.0
$(4.75 \times 10^{-5}\, M)$	760	0.29	0.20	4.0
4-Cresol[b]	400	8.72	4.57	0.5
$(4.9 \times 10^{-\cdot}\, M)$	750	1.27	0.29	0.5

[a] The measurements were carried out in degassed solutions at pH 11.9 with 0.04 M phosphate buffer. Sodium phosphate (0.2 M) was used as a filter to prevent photolysis of the buffer. Oxygen quenching experiments were done by saturating the solutions with air. The photoflash was of 60-μsec duration and was obtained by discharging 6000 V through the flash lamps; all data from the oscillograms were taken 100 μsec after flash initiation. A more detailed description of the flash apparatus used can be found in V. A. Brosseau, J. R. Basila, J. F. Smalley, and R. L. Strong, *J. Amer. Chem. Soc.*, **94**, 716 (1972). [b] Flash photolysis studies of 4-cresol are described in ref 11a. The experiment was repeated in this study to provide a direct comparison with our data on the cyanophenols. We did not detect the spectrum of the hydrated electron in our investigation of the flash photolysis of 4-cresol. Also, the transient we observe at 750 nm was not reported by Grossweiner, *et al.*[11a]
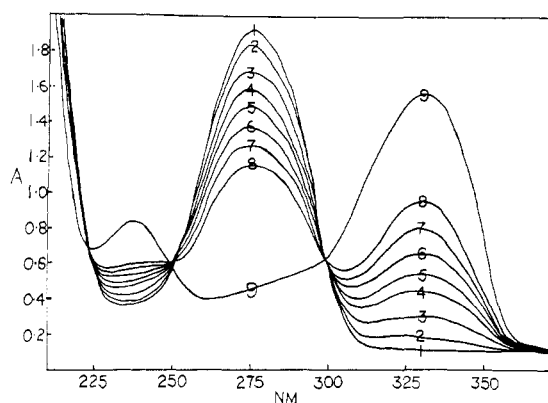

Figure 1. Photolysis of 9 $\times$ 10^{-5} M 4-cyanophenol at 254 nm in degassed 10^{-2} M aqueous NaOH. Curves 1–8 were taken at 5-min intervals, and curve 9 after total irradiation time of 1 hr shows conversion of the 4-cyanophenol ($\lambda_{max}^{OH^-}$ 275 nm) to 4-hydroxybenzaldehyde ($\lambda_{max}^{OH^-}$ 330 nm).

known chemical reactivity of solvated electrons since it has been reported that the reaction of 3,4,5-trimethoxybenzamide with sodium in liquid ammonia, a reagent which is known to generate ammoniated electrons, yields 3,5-dimethoxybenzamide.[8]
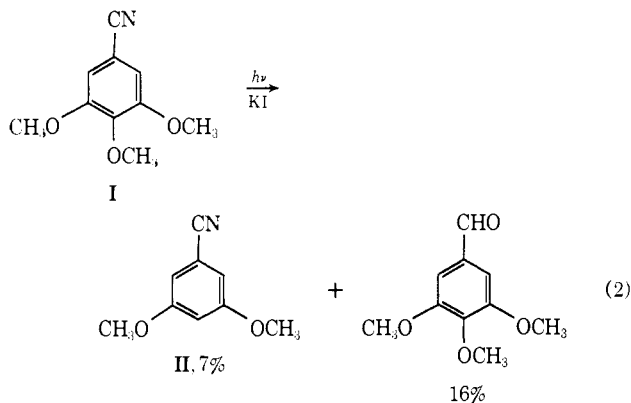
It was of interest to test the selectivity of the hydrated electron as a reducing agent by investigating the re-

(8) M. E. Kuehne and B. F. Lambert, *J. Amer. Chem. Soc.*, 81, 4278 (1959).

duction of a compound containing two reducible functional groups. Selective reduction appeared feasible since we found that it was possible to reduce the nitrile function to an aldehyde; in most instances further reduction of the aldehyde was shown to proceed more slowly. However, a complex series of reaction products was obtained upon reduction of 4-nitrobenzonitrile (eq 3), and it is evident from these products that both the nitro and cyano groupings are reduced. The low yields reflect the competing reduction reactions as well as the competing hydrolysis of the nitrile functionality to the amide and the difficulties involved in separating such a complex mixture.
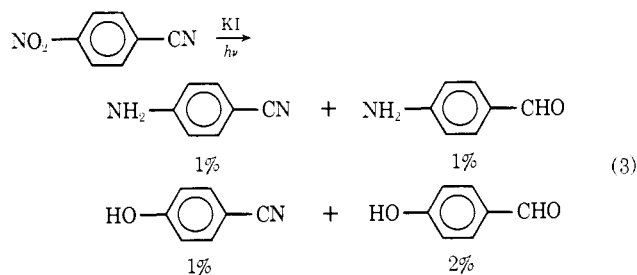
Presumably the two aniline derivatives were formed by reduction of the nitro group *via* the nitroso function.[9] The formation of p-hydroxybenzaldehyde is difficult to rationalize. In a separate experiment it was shown that p-hydroxybenzaldehyde is not produced by the reaction of p-aminobenzaldehyde with solvated electrons. One possibility is the direct displacement of the nitro function from a photoexcited nitro derivative.[10]

Flash photolysis studies provided direct evidence for the formation of phenoxyl radicals from the cyanophenols (Table II). The transient observed in the 410–430-nm region is assigned to the phenoxyl radical. Other phenols exhibit a transient in this spectral region which has been shown to be characteristic of a phenoxyl radical.[11] The transient observed at 750–790 nm is at

(9) K. D. Asmus, A. Wigger, and A. Henglein *Ber. Bunsenges. Phys. Chem.*, 70, 869 (1966).
(10) R. L. Letsinger, O. B. Ramsey, and J. H. McCain, *J. Amer. Chem. Soc.*, 87, 2945 (1965); J. Gold and C. H. Rochester, *J. Chem. Soc.*, 1717 (1964).

the correct wavelength for the hydrated electron; however, the transient is too long-lived to be assigned to the hydrated electron. Hydrated electrons react with nitriles at a diffusion controlled rate ($k \sim 10^{10}$ M^{-1} sec^{-1})[12] and would therefore be expected to have an extremely short lifetime. It appears likely that the 750-nm transient is also associated with the phenoxyl radical since both the 420- and 750-nm transients are quenched to the same extent with oxygen and both have similar half-lives. Furthermore, very similar first-order decay constants were obtained from the transients produced from 2-cyanophenol ($k_{420 nm} = 12.5$ M^{-1} sec^{-1} and $k_{750 nm} = 10$ M^{-1} sec^{-1}), a result which suggests that both absorption bands come from the same species. Weak bands at 500–650 nm have been reported for some phenoxyl radicals in addition to the more intense bands at about 400 nm.[11c]

Mechanism of Reaction

Radicals of structure RCH=N· have been observed by esr spectroscopy in the reaction of hydrated electrons with aliphatic nitriles.[13] It has been suggested these radicals are formed by the addition of the hydrated electron to the nitrile (6) followed by a rapid proton transfer (7). Furthermore, it has been postulated that disproportionation of RCH=N· radical would give the aldimine (8) and this would hydrolyze to give the aldehyde (9) as the terminal reaction product.[14] Our research proves that the aldehyde and ammonia are the end products of the reaction of solvated electrons with nitriles. However, the proposed reaction scheme cannot be completely correct since the stoichiometry required by the disproportionation step predicts that only 33% of the starting nitrile will be converted to aldehyde on direct irradiation. Although a 32% yield was observed for 2-cyanophenol, aldehyde yields of 63 and 67% were obtained on irradiation of 4- and 3-cyanophenol, respectively. We considered the possibility that hydroxide ion might serve as the source of the electrons (10). However, eq 10 is not considered likely because 4-cyanophenol is oxidized much more readily than hydroxide ion; the oxidation potential of 4-cyanophenol (10^{-3} M) is -0.9 V in aqueous NaOH (10^{-2} M) and NaClO$_4$ (10^{-1} M) at a platinum electrode.[15] The oxidation potential for OH$^-$ → ·OH + e$^-$ is -2.0 V.[16] Equation 10 would be of significance only if a very "hot" cyanophenoxyl radical were produced in (4).

Another possibility is that the cyano group of the cyanophenoxyl radical is displaced by hydroxide ion.[17] Equation 4 and the reaction sequence outlined in (11) illustrate how such a substitution reaction could result in the overall donation of four electrons from one cyanophenoxide anion. These four electrons would effect the reduction of two cyano groupings. Such a process

predicts a 66% yield of the aldehyde which is close to the observed value for 4- and 3-cyanophenol. A similar addition of hydroxide to the phenoxyl radical has been proposed for the formation of semiquinones when phenol is photolyzed in aqueous base.[17] Furthermore, hydroxylation products are observed when phenols or anisole are irradiated in aqueous solution.[18] The addition of hydroxide ion to benzoquinones and the subsequent oxidation of these adducts are well documented.[19]

A 1–2% yield of phenol was found in the direct irradiation products of 2- and 4-cyanophenol which indicates that a dissociative electron attachment[7] is a minor reaction pathway (12). This is the first observation of dissociative electron attachment of cyanide from an aromatic nitrile.[13] It is interesting to note that cyanide is not a reaction product but cyanate was found instead. The conversion of cyanide to cyanate provides an additional source of electrons for the reduction of nitriles to aldehydes.[20]

Presumably the irradiations performed in the presence of iodide ion would not proceed by the pathway suggested in (11) since the photolysis of iodide would provide an abundant source of solvated electrons to serve as the reducing agent.

(11) There have been several reports of the formation of phenoxyl radicals and solvated electrons upon irradiation of phenols: (a) L. Grossweiner, G. Swenson, and E. Zwicker, *Science*, 141, 805 (1963); (b) H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, 88, 3261 (1966); (c) E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, 57, 1885 (1961).
(12) M. Anbar and E. J. Hart, *J. Amer. Chem. Soc.*, 86, 5633 (1964).
(13) P. Neta and W. Fessenden, *J. Phys. Chem.*, 74, 3362 (1970).
(14) Reference 5, pp 140–141.
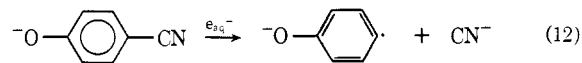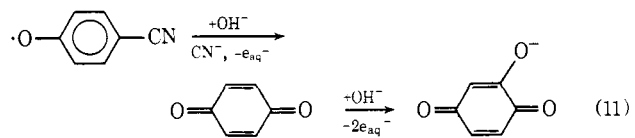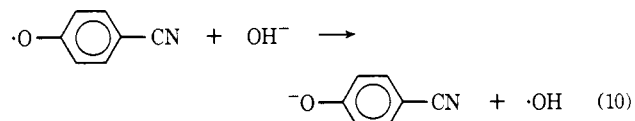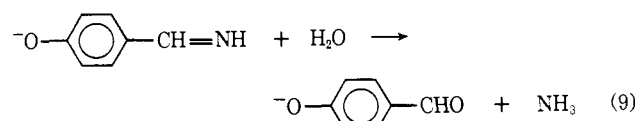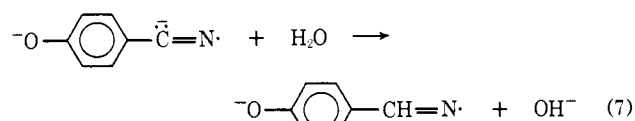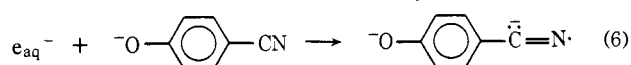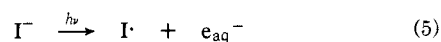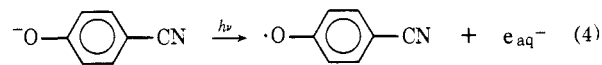(15) We thank Professor D. A. Aikens for this measurement.
(16) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952, p 50.
(17) M. Tomkiewicz, A. Groen, and M. Cocivera, *J. Amer. Chem. Soc.*, 93, 7102 (1971).

(18) H. I. Joschek and S. I. Miller, *ibid.*, 88, 3273 (1966); H. I. Joschek and L. I. Grossweiner, *Z. Naturforsch.*, 246, 562 (1969); K. Omura and T. Matsurra, *Tetrahedron*, 24, 3475 (1968).
(19) V. B. Golubev, L. S. Yaguzhenskii, and A. V. Volkov, *Biofizika*, 11, 572 (1966); T. C. Hollocher, Jr., and M. W. Weber, *Nature (London)*, 195, 247 (1962); C. A. Bishop and L. Tong, *Tetrahedron Lett.*, 3034 (1964).
(20) J. A. J. Vink, J. Cornelisse, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 90, 1333 (1971).

Conclusions

We have demonstrated that nitriles may be reduced readily to aldehydes with photochemically generated hydrated electrons. Photolysis of iodide ion was shown to be a convenient source of hydrated electrons for synthetic reactions. This method of reduction shows considerable promise for use in synthesis because there exists extensive compilations of rate data for the reaction of hydrated electrons with organic compounds.[14] One needs only to utilize these data to predict the course of the reduction of multifunctional organic compounds. Finally, hydrated electron reductions should provide a convenient route to the deuterated organic compound as one would merely have to reduce the appropriate precurser in D_2O. Further applications of the reduction method are under investigation.

Experimental Section

General Procedures. Uv spectra were obtained with a Unicam SP800A ultraviolet spectrophotometer and infrared spectra with a Perkin-Elmer 137. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Glc analyses were conducted on an F & M Model 810 equipped with a flame ionization detector; a 5% Carbowax 20M column was used to analyze the benzonitrile and 4-tolunitrile reductions. The water used was deionized and reagent grade methanol was used without further purification. All ether extracts were dried over $MgSO_4$. Irradiations were carried out in a Rayonet photochemical reactor with fittings for 16 lamps having principal emission at 254 nm. Samples were degassed by the freeze–pump–thaw method. Paper chromatography was done on Whatman 3MM paper and developing with 2-propanol–ethanol–water (9:4:3) (IEW), ethanol–ammonia–water (16:1:3) (EAW), and propanol–ammonia (3:1) (PA). Most of the products were isolated by preparative tlc using silica gel AR. Spots were visualized by uv light or spraying with 2,4-dinitrophenylhydrazine (DNP) or diazotized sulfanilic acid (DSA). Most of the compounds used were obtained commercially except for 4-aminobenzaldehyde and 4-anisonitrile. 4-Aminobenzaldehyde was prepared according to the procedure of E. Campaigne, et al.,[21] by reacting 4-nitrotoluene with sodium sulfide nonahydrate, flowers of sulfur, and sodium hydroxide [mp 70–73° (lit.[21] 71–72°)]. 4-Anisonitrile was prepared according to the procedure of Hunt[22] by reacting 4-anisaldehyde with hydroxylamine hydrochloride [mp 56–58° (lit.[22] 59–60°)].

Irradiation of 4-Cyanophenol. A 250-ml solution of 1.5×10^{-3} M 4-cyanophenol in 10^{-2} M aqueous NaOH was degassed and irradiated at 254 nm for 48 hr. The yellow reaction solution was acidified and extracted with ether, and the ethereal extract was dried and concentrated to dryness. Phenol (1–2% yield) and 4-hydroxybenzaldehyde were isolated by preparative tlc using chloroform–ethyl acetate, 9:1. The absence of phenol in the starting material was ascertained by tlc. Each compound was eluted from the silica gel with ethanol and was identified by comparison of ir (4-hydroxybenzaldehyde), uv (in acid and base), R_f values (three different solvent systems), and color tests (phenol–DSA, (4-hydroxybenzaldehyde–DSA and DNP) with authentic samples.

The concentration of 4-cyanophenol was chosen so that it was absorbing all the light at 254 nm. However, we investigated the possibility that hydroxide ion was the source of the solvated electrons by performing the photolysis with light which had just been passed through a NiSO$_4$, CoSO$_4$, I$_2$, KI filter solution.[23] This filter solution is transparent to light of 254 nm but absorbs the light at shorter wavelengths where OH$^-$ absorbs. The formation of 4-hydroxybenzaldehyde was not inhibited, demonstrating that hydroxide ion is not the source of the hydrated electrons. Photolysis of 9×10^{-5} M 4-cyanophenol is shown in Figure 1.

Irradiation of 3-Cyanophenol. A 100-ml solution of 1.4×10^{-3} M 3-cyanophenol in 10^{-2} M aqueous NaOH was degassed and irradiated at 254 nm for 2.5 hr. The yellow reaction solution was acidified and extracted with ether, and the ethereal extract was

dried and concentrated to dryness. 3-Hydroxybenzaldehyde was isolated by preparative tlc using chloroform–ethyl acetate, 9:1. The aldehyde was eluted from the silica gel with ethanol and was identified by comparison of ir, uv (in acid and base), R_f values (three different solvent systems), and color tests (DSA and DNP) with an authentic sample.

Irradiation of 2-Cyanophenol. A 100-ml solution of 1.4×10^{-3} M 2-cyanophenol in 10^{-2} M aqueous NaOH was degassed and irradiated at 254 nm for 41 hr. The yellow reaction solution was acidified and extracted with ether, and the ethereal extract was dried and concentrated to dryness. Phenol and 2-hydroxybenzaldehyde were isolated by preparative tlc using chloroform. The absence of phenol in the starting material was ascertained by tlc. Each compound was eluted from the silica gel with ethanol and was identified by comparison of uv (in acid and base), R_f values (three different solvent systems), and color tests (phenol–DSA) (2-hydroxybenzaldehyde–DSA and DNP) with authentic samples.

Irradiation of 4-Aminobenzonitrile. A 100-ml solution of 2.7×10^{-3} M 4-aminobenzonitrile in 10^{-2} M aqueous NaOH was degassed and irradiated at 250 nm for 48 hr. The reaction solution was extracted with ether and the ethereal extract was dried and concentrated to dryness. 4-Aminobenzaldehyde was isolated by preparative tlc using methylene chloride. The aldehyde was eluted from silica gel with ethanol and was identified by comparison of ir, uv (in acid and base), R_f values (three different solvent systems), and color test (DNP).

Irradiations of KI in the Presence of Nitriles. The hydrated electron was produced by irradiation of 10^{-2} M KI at 254 nm in degassed 10^{-2} M aqueous NaOH in the presence of the nitrile (10^{-4}–10^{-3} M). 2-, 3-, and 4-hydroxybenzaldehyde, 4-aminobenzaldehyde, and anisaldehyde were identified by tlc, R_f values (at least two different solvent systems), uv spectra in acid and base, and color tests (DNP and/or DSA). Yields were based on λ_{max} of the nitrile and the aldehyde when the aldehyde peak reached a maximum.

4-Chlorobenzonitrile. Four 5-ml methanolic solutions of 5.9×10^{-3} M 4-chlorobenzonitrile and 10^{-1} M KI were degassed and irradiated at 254 nm for 1, 4, 9, and 18 hr. Each reaction solution was concentrated in vacuo and tlc analysis done using methylene chloride. After 18 hr of irradiation no starting material remained and no 4-chlorobenzaldehyde had been detected.

Benzonitrile. A 100-ml aqueous solution of 10^{-3} M benzonitrile and 1 M KI was irradiated at 254 nm for 5.5 days. The solution was extracted with ether; the ethereal extract was dried and concentrated. Benzaldehyde was isolated by preparative tlc using methylene chloride–hexane (5:1) and identified by direct comparison of its uv spectrum, R_f value, glc retention time, and color test (DNP) with that of an authentic sample. It was shown by glc that only 13% of the nitrile had reacted and 5% of that which reacted was converted to aldehyde.

4-Tolunitrile. A 100-ml solution of 3×10^{-4} M 4-tolunitrile and 10^{-2} M KI in aqueous 10^{-2} M NaOH was irradiated at 254 nm for 3 hr. The reaction solution was extracted with ether; the ethereal extract was dried and concentrated. 4-Tolualdehyde was isolated by preparative tlc using methylene chloride–hexane (1:1) and identified by direct comparison of its uv spectrum, R_f value, glc retention time, and color test (DNP). It was shown by glc that 60% of the nitrile had reacted and 6% of that which reacted was converted to aldehyde.

Anthranilonitrile. A 100-ml solution of 5.5×10^{-4} M anthranilonitrile and 10^{-1} M KI in aqueous 10^{-2} M NaOH was degassed and irradiated for 11 hr. The reaction solution was extracted with ether; the ethereal extract was dried and concentrated. Tlc using chloroform showed a compound with similar R_f and DNP as anthranilonitrile, but attempts to obtain a uv spectrum of this compound were unsuccessful. Similar results were obtained by irradiation of anthranilonitrile in basic media.

3,4,5-Trimethoxybenzonitrile. A 100 ml solution of 3.1×10^{-3} M 3,4,5-trimethoxybenzonitrile and 10^{-1} M KI in methanol–water (1:1) was irradiated at 254 nm for 8 days. The methanol–water was removed in vacuo and the residue taken up in base to remove I$_2$. The basic solution was extracted in ether, and the ethereal extract was dried and concentrated for column chromatography using methylene chloride–ethyl acetate, 20:1, as eluent. 3,5-Dimethoxybenzonitrile (7% yield) and 3,4,5-trimethoxybenzaldehyde (16% yield) were isolated from the column and identified by comparison of uv, ir, melting point, and R_f values (two different solvent systems) with authentic samples. 3,4,5-Trimethoxybenzaldehyde reacts very rapidly with the hydrated electron to give an unidentified product which may account for the low yield of aldehyde from nitrile. A solution of 1×10^{-4} M 3,4,5-trimethoxy-

(21) E. Campaigne, W. M. Budd and G. F. Schaefer, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 31.
(22) J. H. Hunt, Chem. Ind. (London), 1873 (1961).
(23) Reference 6, p 729.

benzaldehyde and 10^{-2} M KI in 10^{-2} M NaOH upon irradiation at 254 nm showed a rapid loss of aldehyde absorbance ($t_{1/2}$ = 30 sec). When 3,4,5-trimethoxybenzonitrile and KI solution are irradiated in 10^{-2} M NaOH, no 3,4,5-trimethoxybenzaldehyde was found, but 3,5-dimethoxybenzonitrile was isolated in 24% yield.

4-Nitrobenzonitrile. A 250-ml aqueous solution of 1.35 × 10^{-3} M 4-nitrobenzonitrile and 10^{-1} M KI was degassed and irradiated for 3 days. The reaction solution was basified and extracted with ether; the ethereal extract was dried and concentrated for preparative tlc using chloroform–benzene–ethyl acetate (65: 15:15). 4-Aminobenzonitrile (~1% yield) and 4-aminobenzaldehyde (~1% yield) were eluted from the silica gel with ethanol and identified by comparison of uv spectra in acid and base, R_f values (three different solvent systems), and DNP color test (4-aminobenzaldehyde) with authentic samples.

The reaction solution was then acidified and extracted with ether; the ethereal extract was dried and concentrated for preparative tlc using chloroform–benzene–ethyl acetate (65:15:15). 4-Cyanophenol (<1% yield) and 4-hydroxybenzaldehyde (2% yield) were isolated by eluting from the silica gel with ethanol and were identified by comparison of uv spectra in acid and base, R_f values (three different solvent systems), and DNP color test (4-hydroxybenzaldehyde) with authentic samples. The low yields of products may be due in part to loss of product in the separation scheme and also the fact that a thermal hydrolysis of 4-nitrobenzonitrile to the amide occurs in neutral solution.

Trapping Experiments for the Solvated Electron. Trapping experiments were done using oxygen, NO_3^-, acetone, and protons, respectively, known electron scavengers. (a) Irradiation of 4-cyanophenol (10^{-4} M) in nondegassed aqueous NaOH (10^{-2} M) resulted in only a 20% yield of 4-hydroxybenzaldehyde. (b) 4-Cyanophenol (8.5 × 10^{-5} M) in 10^{-2} M NaOH and NaNO$_3$ (4.1 × 10^{-4} M) was degassed and irradiated at 254 nm for 100 min. Only a slight absorption for the aldehyde was noted at 330 nm. (c) 4-Cyanophenol (6.8 × 10^{-5} M) in 10^{-2} M NaOH and acetone (10^{-3} M) was degassed and irradiated at 254 nm for 40 min during which time most of the nitrile had reacted but no aldehyde absorption was noted. (d) 2-Cyanophenol (10^{-4} M) in 10^{-2} M HCl was irradiated

at 254 nm with no salicylaldehyde absorption noted; only benzoxazole absorption.

Analysis for CNO⁻, CN⁻, and NH₄⁺Cl⁻ upon Irradiation of 4-Cyanophenol in Base. A convenient procedure was developed for the simultaneous detection of CN⁻, CNO⁻, and NH₄⁺. 4-Cyanophenol (10^{-3} M) was irradiated for 31 hr at 254 nm in NaOH (10^{-2} M). The yellow aqueous solution was acidified and extracted with ether. The water layer was concentrated and paper chromatograms were run in three solvent systems with standards to check for the presence of CNO⁻, CN⁻, and NH₄Cl. NH₄Cl gives a pale yellow color with Bromocresol Green while cyanate and cyanide give bright blue colors. No cyanide was detected and only cyanate and ammonium chloride were observed. The observed R_f values are shown in Table III.

Table III. Simultaneous Analysis for Cyanate, Cyanide, and Ammonium Ions

Solvent system[a]	CN⁻	R_f, CNO⁻	NH₄⁺
IEW	0.08	0.31	0.38
EAW	0.17	0.59	0.54
PA	0.16[b]	0.17[b]	0.33

[a] The solvent systems are described under General Procedures.
[b] It is not possible to distinguish between CN⁻ and CNO⁻ in the PA system.

Spiroketal Reductive Ring Opening[1]

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Abstract: Both the direction and mechanism of reductive ring opening with the spiroketal 9,9-dimethyl-1,6-dioxaspiro[4.5]decane (8) have been explored. With dimedone (3) as precursor, synthesis of spiroketal 8 was realized by way of intermediates 4, 5, 6, and 7. Lithium aluminum hydride–aluminum chloride catalyzed reduction of spiroketal 8 was found to yield tetrahydropyran 9 in contrast to the steroidal sapogenins which undergo reductive cleavage of the tetrahydropyran ring. The mechanism of ring opening was examined using deuterium labeling (8 → 9b) combined with mass and proton magnetic resonance spectral measurements. Reductive ring opening of spiroketal 8 was thereby found to proceed by transfer of reagent hydride directly to the spirocarbon. The experimental results also suggested that reductive ring opening of relatively nonhindered spiroketals related to 8 may offer a new synthetic route to certain substituted tetrahydropyrans.

The spiroketal system of steroidal sapogenins will undergo lithium aluminum hydride–aluminum chloride catalyzed opening of the tetrahydropyran ring to afford the corresponding dihydrosapogenin (1 → 2).[2a]

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(2) (a) G. R. Pettit and W. J. Bowyer, *J. Org. Chem.*, **25**, 84 (1960); (b) A. H. Albert, G. R. Pettit, and P. Brown, *ibid.*, in press; (c) P. Brown A. H. Albert, and G. R. Pettit, *J. Amer. Chem. Soc.*, **92**, 3212 (1970).

Subsequent to our initial observation of this convenient route to dihydrosapogenins, several attractive mechanistic pathways were evaluated using deuterium labeling and the stereochemical consequences of this reduction reaction were considered.[2b,c] Direct transfer of hydride from a metal hydride intermediate to the spirocarbon was found to occur and the single epimer produced seemed best represented by structure 2 (see Chart I). Exclusive opening of the tetrahydropyran ring was found in all such reactions viewed. That the steric compression around ring D may present a specialized situation in this reduction reaction was uncovered by extending the study to an analogous but