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

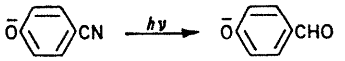
By J. P. FERRIS* and F. R. ANTONUCCI,
(*Rensselaer Polytechnic Institute, Troy, New York* 12181)

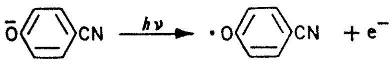
Summary Nitriles are conveniently reduced to aldehydes in aqueous media by photochemically generated hydrated electrons.

IN the course of our investigation of the photochemical conversion of enaminonitriles and enehydroxynitriles into imidazoles and oxazoles, respectively, we discovered the photochemical reduction of nitriles to aldehydes [equation (1)].[1] Here we examine the scope of this novel photochemical reduction.

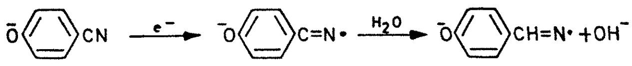
The corresponding aldehydes are formed when 2-, 3-, and 4-cyanophenol are irradiated in 10^{-2}M-NaOH (Table).[2] 4-Cyanoaniline is reduced to 4-aminobenzaldehyde; however, 2-cyanoaniline yielded indazole as the main reaction product along with a trace of 2-aminobenzaldehyde.

It has been demonstrated that the hydrated electron produced by photoexcitation of the phenoxide ion is the reducing agent in the cyanophenoxide reductions [equation (2)];[3] the reduction is quenched in the presence of electron scavengers such as oxygen, nitrate ion, acetone, and protons, and the same reaction products are observed when iodide is the source of the hydrated electrons [equation 3)].[5] Photolysis of the cyanophenols in the presence of iodide ion, with the iodide absorbing 80—95% of the light, gives similar yields of aldehydes (Table). Furthermore, those nitriles which do not yield aldehydes on direct irradiation did so when irradiated in the presence of iodide ion (Table).


(1)


(2)

$$I^- \xrightarrow{h\nu} I\cdot + e^- \qquad (3)$$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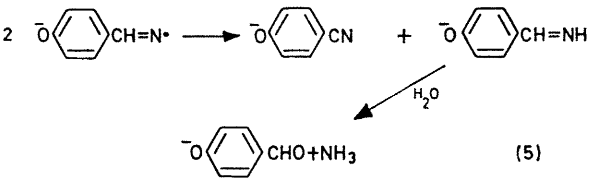
(5)

Photochemical reduction of nitriles to aldehydes

Compound	Product[a]	Yield (%)[b]	
		(I)[c]	(II)[d]
4-Cyanophenol	4-Hydroxybenzaldehyde	62	75
3-Cyanophenol	3-Hydroxybenzaldehyde	67	56
2-Cyanophenol	2-Hydroxybenzaldehyde	32	27
4-Cyanoaniline	4-Aminobenzaldehyde	37	43
2-Cyanoaniline	2-Aminobenzaldehyde	trace	trace
Benzonitrile	Benzaldehyde	0	5
4-Toluonitrile	4-Tolualdehyde		6
3,4,5-Trimethoxybenzonitrile	3,4,5-Trimethoxybenzaldehyde		16[e]
4-Methoxybenzonitrile	4-Methoxybenzaldehyde	0	40

[a] Photolyses were performed for water or methanol–water mixtures with concentration of nitrile varying from 10^{-4}—10^{-1} M. All products were identified by comparison with authentic samples. [b] Maximum yield based on the conversion of every nitrile into an aldehyde. This is probably not the true stoicheiometry of the reaction. [c] Direct irradiation in 10^{-2} M-NaOH. [d] Irradiation in a Rayonet reactor equipped with 254 nm lamps in the presence of KI with I^- absorbing 80—95% of the light. [e] 3,5-Dimethoxybenzonitrile was also obtained (see text).

Finally 3,5-dimethoxybenzonitrile was a reduction product when 3,4,5-trimethoxybenzonitrile was irradiated in the presence of iodide. This observation is consistent with the 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.[6]

It has been reported that cyanophenols react rapidly with solvated electrons.[7] Furthermore, radicals of structure RCH=N· have been detected by e.s.r. in the reaction of solvated electrons with aliphatic nitriles.[8] It has been suggested these radicals are formed by addition of a solvated electron to nitrile followed by a rapid proton transfer [equation (4)].[8] It has also been postulated that disproportionation of the RCH=N· radical yields the aldimine and this hydrolyses to give the aldehyde as the terminal reaction product [equation (5)].[8] Our research provides the first experimental evidence that aldehyde is the end product in the reaction of solvated electrons with nitriles. Further experimental data are required to establish if the aldimine is formed by the disproportionation pathway outlined in equation (5).

This research emphasizes that solvated electron reductions may be commonly involved in photochemical transformations,† and shows that the hydrated electron can be a useful reagent in organic synthesis and that it may have been important in prebiological chemistry.[9]

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† Pyrrole-2-carboxaldehyde has been reported as a minor product in the photochemical rearrangement of 2-cyanopyrrole to 3-cyanopyrrole (H. Hiraoka, *Chem. Comm.*, 1970, 1306). Hydrated electrons are produced when pyrrole is irradiated (H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, 1966, 88, 3261) so that the aldehyde may have been formed by reduction of the nitrile with solvated electrons.[9]

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[2] The reduction of 4-cyanophenol to 4-hydroxybenzaldehyde was discovered independently. T. Omura and T. Matsuura, *Chem. Comm.*, 1969, 1516.

[3] L. Grossweiner, G. Swenson, and E. Zwicker, *Science*, 1963, **141**, 805; H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, 1966, **88**, 3261; E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, 1961, **57**, 1885.

[4] E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, 1970.

[5] J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, 1967, p. 271.

[6] M. E. Kuehne and B. F. Lambert, *J. Amer. Chem. Soc.*, 1959, **81**, 4278.

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[8] P. Neta and R. W. Fessenden, *J. Phys. Chem.*, 1970, **74**, 3362, Ref. 4, pp. 140—141.

[9] Ref. 4, p. 11.