

Photochemical Transformation of *p*-Cyanophenol to *p*-Hydroxybenzaldehyde in Aqueous Alkali¹

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Summary Irradiation of *p*-cyanophenol in aqueous alkali gives *p*-hydroxybenzaldehyde: addition of potassium iodide increases the rate of formation and the yield.

DURING the course of our study on the photo-cyanation of *p*-iodophenol with KCN to yield *p*-cyanophenol (I),¹ we have found that *p*-hydroxybenzaldehyde (II) is formed as a

increased both the rate of formation and the yield of (II) (Experiment 2), while addition of KCl or Na₂SO₃ had little effect (Experiment 3). The only minor product detectable in appreciable amounts, other than a resinous material, was *p*-hydroxybenzoic acid (III).

Investigations on the photochemistry of aromatic nitriles have not previously shown the transformation of the

TABLE^a

Experiment	Solvent	Additive (equiv.)	Irradiation time (hr.)	Conversion of (I) (%)	Yields of products (%) ^b	
					(II)	(III)
1	H ₂ O	KOH(10)	138	81	33	ca. 2
2	H ₂ O	KOH(10) KI(35)	26.5	100	80	< 3
3 ^c	H ₂ O	KOH(10) KCl(40)	25	38	44	d
4	EtOH	—	24	36	trace	d
5	EtOH- H ₂ O(1:1)	KOH(10)	22	31	12	d

^a A solution of (I) (ca. 0.2 g.) in a solvent (200 ml) was irradiated with a 40 w low-pressure mercury lamp, Vycor (2537 Å) under N₂ at 30 ± 3°.

^b Yields are based on the starting material consumed.

^c Addition of Na₂SO₃ (40 equiv.) instead of KCl gave similar results.

^d Formed in low yield.

minor product. It prompted us to investigate details of the aldehyde formation, and it has been found that (I) is transformed photochemically into (II) in aqueous alkali.

Photolysis of (I) in ca. 0.09N-KOH gave (II) (33%, Table, Experiment 1). The effects of the additive and the solvent were investigated. Addition of an excess of KI

nitrile group itself; nor has the apparent direct reduction of a nitrile to an aldehyde previously been known, neither photochemically nor thermally. Inorganic iodide, a rarely used photochemical reducing agent, may play an important role in the reductive process.

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¹ Part of the series, "Photoinduced Reactions"; for previous part see: K. Omura and T. Matsuura, *Chem. Comm.*, 1969, in the press.