

Photosensitised Electron Transfer and Anodic Cyanation Reactions of Nitrogen Heterocycles

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Summary The u.v. irradiation of nitrogen heterocycles in methanolic sodium cyanide solution, using 1,4-dicyanobenzene or 1-cyanonaphthalene as a sensitiser, gives good yields of the product resulting from ring substitution with the cyanide ion; analogies with anodic cyanation are drawn.

sensitiser was confirmed by experiments under identical conditions, but in the absence of sensitiser, when reaction did not occur. 1-Cyanonaphthalene can also be used as the sensitiser.

TABLE. Photosensitised electron transfer and anodic cyanation products.^a

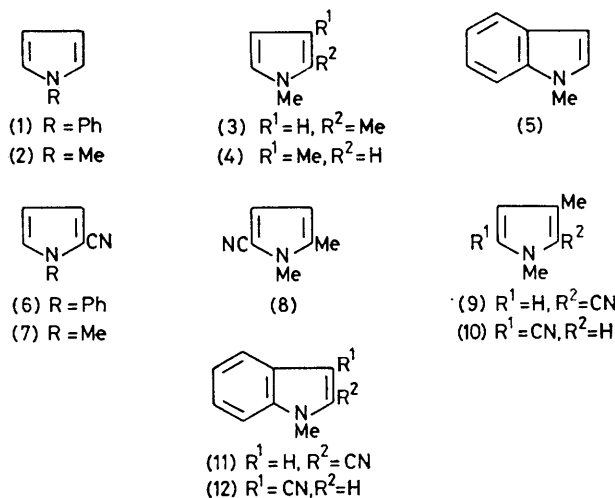
Substrate (λ /nm) ^b	Product	Yield ^c /%	
		Photo-sensitised ^d	Anodic
(1)	(6)	51	82 ^e
(2) (437)	(7)	49	64 ^e
(3)	(8)	40	60 ^e
(4)	(9)	30	74
	(10)	5	13
(5) (440)	(11)	25	50 ^e
	(12)	5	9 ^e

^a All reactions were performed in methanol containing 0.40 M sodium cyanide. ^b Wavelengths of maximum emission for exciplexes with 1-cyanonaphthalene in benzene (data from ref. 1). ^c Yields based on reactant consumed. ^d Sensitiser, 1,4-dicyanobenzene. ^e Data from ref. 4.

I REPORT here an unusual, new substitution reaction by cyanide ion and the first use of photosensitised electron transfer reactions in understanding anodic cyanation. Heterocyclic compounds form fluorescent exciplexes with electron-accepting sensitisers,¹ which dissociate into solvent-separated ion radicals in polar media.^{2,3} The present results for anodic cyanation and the photosensitised electron transfer reactions show that analogies may be drawn between the two reactions.

The following procedure for the photosensitised reactions is typical. Irradiation[†] of 1-phenylpyrrole (1) (5 mmol) in methanolic sodium cyanide solution (0.40 M; 150 ml) with 1,4-dicyanobenzene (10 mmol) present as photosensitiser (electron acceptor) resulted in the formation of the 2-cyano-derivative (6) (51% yield based on substrate consumed).

The Table summarizes the results of photosensitised reactions using other compounds, together with the corresponding data for the electrochemical reaction. The unsymmetrical 1,3-dimethylpyrrole (4) was chosen as a model compound in order to estimate the regioselectivity of the substitution process. The isomer distribution of the resulting products (9) and (10) was similar in both the anodic cyanation and photosensitized reactions. Substitution of 1-methylindole occurred preferentially at position 2. The observation that the same product mixture is formed, and with a similar isomer ratio both electrochemically and *via* photosensitised electron transfer reaction is consistent with the hypothesis that the anodic cyanation involves initial cation radical formation. Net charge distributions calculated by the ω technique (Figure) support the observed reactivity of these cation radicals.



A Pyrex filter was used in all experiments to ensure that direct excitation of the substrate did not occur. Under these conditions light was absorbed only by the sensitiser, which was largely consumed.[‡] The involvement of the

[†] All irradiations were carried out on nitrogen-purged solutions through Pyrex by a 450 W high-pressure mercury vapour lamp at room temperature for 6 h. The product mixture was extracted into methylene chloride.

[‡] Under these experimental conditions 1,4-dicyanobenzene is consumed by a base-catalysed reaction to form the methyl imidate (F. C. Schaefer and G. A. Peters, *J. Amer. Chem. Soc.*, 1961, **26**, 412). During the reduction of alkyl halides with alkali metal derivatives of naphthalenes, a major competing reaction is the coupling of the radical with the anion radical to give ultimately dihydroalkyl-naphthalenes (J. F. Garst, *Accounts Chem. Res.*, 1971, **4**, 400). This type of reaction may account for the consumption of the sensitiser during the reaction (ref. 3).

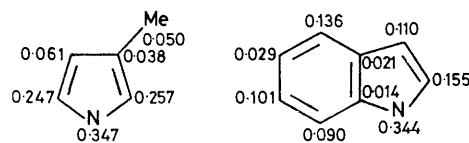


FIGURE. Net charge distributions of cation radicals of pyrrole and indole (ω technique; parameters from ref. 4).

The results obtained indicate a potentially useful reaction which should be general for nitrogen heterocycles. Methanol was used as solvent in order to compare the photochemical and anodic processes; conditions were found under which cyanide ion can serve as the nucleophile, and nucleophilic attack of the solvent was completely suppressed.

The use of photosensitised electron transfer reactions may become a useful method for explaining electrochemical reactivities.

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² M. Ottolenghi, *Accounts Chem. Res.*, 1973, **6**, 153.

³ D. R. Arnold and A. J. Maroulis, *J. Amer. Chem. Soc.*, 1976, **98**, 5931.

⁴ K. Yoshida, *J. Amer. Chem. Soc.*, 1977, **99**, 6111.