Exiplex Involvement in the Photoaddition of Acrylonitrile to Indoles

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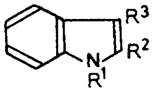
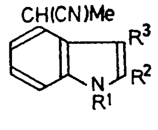
Summary Irradiation of indoles in the presence of acrylonitrile produces the corresponding α-cyanoethylated indoles; a mechanism involving exiplex formation is discussed.

In view of increasing interest in the chemistry of exiplexes, the photochemical additions of acrylonitrile to aromatic hydrocarbons[1] and heteroaromatic systems[2] have drawn considerable attention. Recently we reported the photoaddition of acrylonitrile to an *N*-unsubstituted imidazole resulting in α-cyanoethylation.[3] We now report that indoles undergo ready photochemical reactions with acrylonitrile to yield the corresponding α-cyanoethylated products *via* exiplex formation.†

In a typical run, irradiation‡ of indole (0·02 M) and acrylonitrile (0·2 M) in methanol followed by preparative t.l.c. yielded 3-(2-cyanoethyl)indole (**1**)[5] (31%), m.p. 56°. Under similar conditions, 2-methylindole and 1,2-dimethylindole gave the corresponding 3-(2-cyanoethyl) derivatives



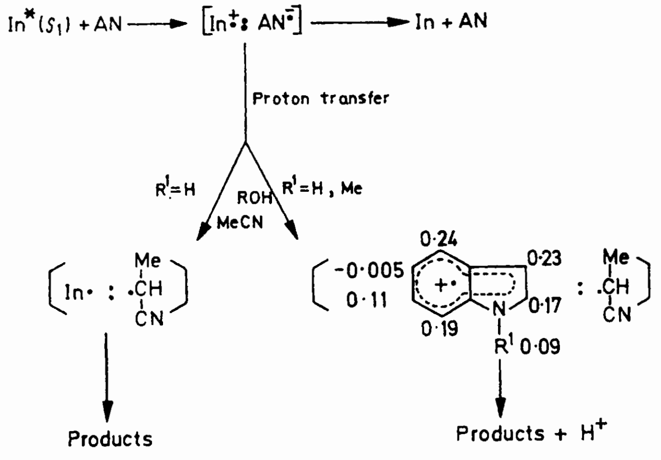


(**1**) $R^1 = R^2 = H$, $R^3 = CHCNMe$
(**2**) $R^1 = H$, $R^2 = Me$, $R^3 = CHCNMe$
(**3**) $R^1 = R^2 = Me$, $R^3 = CHCNMe$
(**6**) $R^1 = H$, $R^2 = CHCNMe$, $R^3 = Me$
(**4**) $R^1 = R^3 = H$, $R^2 = Me$
(**5**) $R^1 = R^2 = Me$, $R^3 = H$
(**7**) $R^1 = R^2 = H$, $R^3 = Me$

† Acylindoles have been reported to undergo photocycloaddition with electron-deficient olefins *via* triplet states.[4]

‡ Irradiation was carried out with a 200 W medium-pressure mercury lamp at room temperature.

(**2**) (10%)§ and (**3**) (13%), m.p. 125° together with comparable amounts of 4-(2-cyanoethyl) derivatives (**4**) (8%) and (**5**) (11%), respectively. Similarly, 3-methylindole yielded (**6**) (11%), m.p. 133° and (**7**) (7%).



SCHEME

Noteworthy characteristics of these photochemical reactions are; (i) NH-indoles undergo photocyanoethylation in both methanol and acetonitrile, whereas *N*-methylindole reacts with acrylonitrile only in protic solvents such as methanol, indicating that proton transfer either from the solvent or from the NH group of indoles to acrylonitrile may be involved in the formation of these products; (ii) added piperylene inhibits the polymerization of acrylonitrile but has no significant effect on the photocyanoethylations.

We also observed that the fluorescence emissions of the indoles were strongly quenched by acrylonitrile at room temperature. From the Stern–Volmer plots half-quenching concentrations of acrylonitrile for quenching of the indole fluorescences were obtained (Table). From the slope ($k_q\tau$) of the Stern–Volmer plots and the known life time for indole fluorescence[6] (τ = 4·3 ns in methanol) the rate constant for the indole fluorescence quenching was estimated to be *ca.* $1{\cdot}2 \times 10^{10}$ mol^{-1} s^{-1}, close to the diffusion limit ($1{\cdot}5 \times 10^{10}$ mol^{-1} s^{-1}). In the case of 1,2-dimethylindole a new fluorescence emission located at 540 nm, presumably an exiplex emission, was observed in acetonitrile solution.

TABLE

Fluorescence quenching of indoles by acrylonitrile

Fluorescer	Solvent	$k_q\tau$/ mol^{-1} l	10^{-2} $C_{\frac{1}{2}}$/ mol l^{-1} [a]
Indole	MeOH	51·3	1·95
	MeCN	64·2	1·56
2-Methylindole	MeOH	53·8	1·86
3-Methylindole	MeOH	39·2	2·55
1,2-Dimethylindole ..	MeOH	65·8	1·52
	MeCN	109	0·99

[a] $C_{\frac{1}{2}}$ = half-quenching concentration.

These observations suggest that these reactions may proceed *via* exiplexes as intermediates and an important step in the decay of the exiplexes may involve proton transfer to the acrylonitrile group. The observed high reactivities of 3- and 4-positions of the indole nuclei to the photocyanoethylations can be interpreted in terms of the calculated spin densities of indole cation radical reported by Naruto and Yonemitsu (Scheme).[7]

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§ Structure assignments of these new compounds were supported by i.r., u.v., n.m.r. (100 M Hz), and mass spectral data.

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