

## Photocyanation of Anisole in the Presence of Polyethylene Glycol

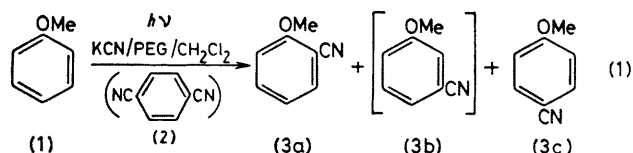
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**Summary** Polyethylene glycol can replace crown ether as a co-solvent in the photochemical substitution reaction of anisole with KCN in  $\text{CH}_2\text{Cl}_2$ .

PHOTOCHEMICAL nucleophilic substitutions of aromatic ring systems in protic solvents have been well documented.<sup>1</sup> When a crown ether is present the photocyanation proceeds

better in aprotic solvents than in protic solvents,<sup>2</sup> while addition of an electron acceptor, such as terephthalonitrile (**2**) improves both the yield of the photocyanation products and the specificity of substitution.<sup>3</sup> This report concerns the photochemical cyanation of anisole (**1**) with KCN in an aprotic solvent, in the presence and absence of (**2**), when polyethylene glycol (PEG) is present instead of a crown ether (CE) (equation 1).



The general experimental procedure was as follows. A solution of (1) (10 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) with KCN (30 mmol) and PEG [200 (2 g) or 1000 (3 g)] or 15-crown-5 was irradiated externally with a high pressure mercury lamp (Eikosha PIH-300, 300 W) through a water-cooled quartz or Pyrex cell. Experiments were carried out in the presence or absence of (2) (20 mol equiv). The irradiated solution was analysed by glc† and the results are given in the Table.

tightly and therefore liberates a naked anion ( $^-\text{CN}$ ) which may react efficiently with electrophiles, while PEG, which is assumed to have a complex spiral structure,<sup>4</sup> incorporates the cation less effectively.

While a mixture of (1) and (2) gave no extra absorption in its u.v. spectrum, a new fluorescence emission band was present. This suggests that a charge-transfer complex between (1) and (2) is formed, which may explain both the enhancement of the yields of (3) and the higher preference for *para*-substitution.<sup>1,3</sup>

The total conversion yields of (3) decreased with the irradiation time. This implies that further reactions [*e.g.* cyanation of (3)]<sup>1,6</sup> which may be faster than cyanation of (1) may be occurring.<sup>7</sup> In addition cyanoanisoles (3) decompose photochemically under the experimental conditions above. The photochemical decay rate of (3a)

TABLE Photocyanation of anisole (1) in PEG or CL

Co-solv <sup>a</sup>	Yield <sup>g</sup> and conv. yield <sup>h</sup> of (3)/%									<i>p</i> CN/ <i>o</i> -CN <sup>i</sup>	<i>m</i> -CN
	1 h			3 h			6 h				
PEG 200 <sup>b</sup>	5.7	32	(18)	11.4	24	(47)	10.8	17	(64)	0.90	trace
PEG 200 <sup>c</sup>	5.3	20	(26)	8.8	19	(47)	9.6	16	(61)	1.00	— <sup>j</sup>
PEG 200 <sup>d</sup>	3.2	46	(7)	6.9	38	(18)	8.9	25	(36)	1.33	— <sup>j</sup>
PEG 200 <sup>e</sup>	—	—	—	2.8	15	(19)	5.8	20	(29)	1.36	— <sup>j</sup>
PEG 200 <sup>f</sup>	—	—	—	7.6	31	(24)	18.0	46	(39)	2.77	— <sup>j</sup>
PEG 1000 <sup>b</sup>	6.5	41	(16)	9.1	22	(42)	9.2	14	(64)	0.39	trace
PEG 1000 <sup>d</sup>	2.9	73	(4)	7.4	41	(18)	9.2	38	(24)	0.85	— <sup>j</sup>
CE <sup>b</sup>	9.4	47	(20)	26.5	58	(46)	26.2	39	(67)	0.38	trace
CE <sup>d</sup>	7.6	29	(26)	10.9	20	(54)	13.6	20	(68)	0.75	trace

<sup>a</sup> PEG (Nakarai Chem. Co.) was dried azeotropically with benzene before use. CE = 15-crown-5-ether (Nakarai Chem. Co.).

<sup>b</sup> Quartz cell, no (2). <sup>c</sup> Quartz cell, 50 mmol of (2). <sup>d</sup> Quartz cell, 200 mmol of (2). <sup>e</sup> Pyrex cell, no (2). <sup>f</sup> Pyrex cell, 150 mmol of (2).

<sup>g</sup> Yield of (3) based on initial amount of (1). <sup>h</sup> Conversion yield based on (1) consumed. Consumption of (1) is given in parentheses. <sup>i</sup> After 3 h irradiation. <sup>j</sup> Not detected.

In a quartz cell, when (2) was absent, consumption of (1) with PEG present was comparable to that with CE. However, the conversion yields of (3) decreased in the order CE > PEG 1000 > PEG 200 present. The ratio of yields of (3c) : (3a) (*p*-CN/*o*-CN) decreased in the order PEG 200 > PEG 1000 > CE.

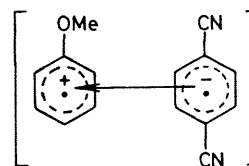
In the absence of (2) with PEG present, (1) gave *o*-, *p*- and a trace of *m*-cyanoanisole [(3a), (3c), and (3b)] as substitution products but, in the presence of (2), (1) gave only the *o*- and *p*-cyanoanisoles (3a) and (3c) in yields that increased with irradiation time. However, the consumption of (1) was lower than in the absence of (2); in CE the consumption of (1) in the presence of (2) was higher than that in the absence of (2). Conversion yields of (3) and the *p*-CN/*o*-CN ratio with PEG present were higher than those in CE. These yields were excellent with PEG 200 (PEG 200 > PEG 1000 > CE). With CE the *meta*-isomer (3b) was also formed even when (2) was present.

These results reveal that PEG activates the  $^-\text{CN}$  anion in an aprotic solvent, as does CE, by forming a complex with the  $\text{K}^+$  cation. In PEG, the acceptor (2) forms a complex with (1) and then activates the *para*-position of (1) rather than the *ortho*-position, and totally deactivates the *meta*-position. These are useful properties of PEG.

The lower yields obtained with PEG than with CE may be explained as follows. The CE incorporates the  $\text{K}^+$  cation

was much faster than that of the *meta*- and *para*-isomers in quartz cells and this tendency is more marked in Pyrex cells. The fact that the *p*-CN/*o*-CN ratio was much larger in Pyrex cells than in quartz cells may be explained by the facts above. Since the decay rate of the *meta*-isomer (3b) was comparable with that of the *para*-isomer (3c), the absence of (3b) in the reaction reflects the fact that the rate of its formation was very low.

Quenching and fluorescence experiments showed that the present reaction proceeds through the  $\text{T}_1$  excited state of (1), in agreement with Nilsson's work,<sup>5</sup> when (2) is absent, and the  $\text{S}_1$  state of the charge-transfer complex (4) when (2) is present. The charge distribution described in the literature<sup>1,6,7</sup> of (1) in the  $\text{S}_1$  and  $\text{T}_1$  excited states cannot, however, explain the different reactions in the presence and absence of (2) which suggests at least that (4) has a different electron distribution to that described.



(4)

† Glc: Yanagimoto Model G 80FP, with a flame-ionisation detector. Column A (5.0 mm × 2.0 m, 5% PEG-20M on 60–80 mesh Gasport in a stainless steel column) was used for product analysis. Column B (5.0 mm × 2.0 m, 25% Apiezon L on 30–60 mesh fire brick in a glass column) was used to analyse the degradation of (1) after being washed with water to remove PEG and KCN.

The mechanism in the absence of (2) can be explained by Havinga's theory<sup>7</sup> that the  $\pi-\pi^*$  triplet excited state of (1), produced photochemically *via* successive intersystem crossing, is attacked by the  $-\text{CN}$  anion and then liberates an electron to give a cation radical. This radical reacts with one more  $-\text{CN}$  anion to afford monocyanoanisoles (3). In

the presence of (2), (1) may react through (4).<sup>3</sup> The formation of (4) may result in the higher conversion yields of (3) than those obtained in the absence of (2).

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<sup>6</sup> G. Lodder and E. Havinga, *Tetrahedron*, 1972, **28**, 5583.

<sup>7</sup> J. D. Heijer, O. B. Shadid, J. Cornelisse, and E. Havinga, *Tetrahedron*, 1977, **33**, 779.