

Photochemical Reactions in Polyethylene Glycol. 2.¹⁾ Photo-induced Nucleophilic Substitution of Dimethoxybenzenes in the Presence of Polyethylene Glycol

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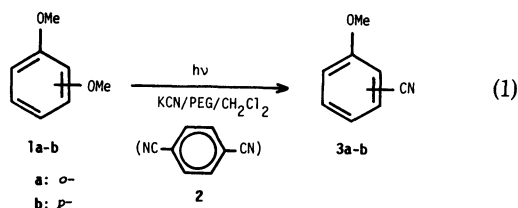
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Synopsis. Polyethylene glycol can replace crown ether as co-solvent for photochemical substitution reactions of dimethoxybenzenes with KCN in CH₂Cl₂ in either the presence or the absence of terephthalonitrile.

The chemistry of cyclic polyethers (crown ethers) is attracting keen interests of many investigators²⁾ because of the high selectivity of reaction by activated anion species in their circumstances. Many interesting photochemical reactions have been found to proceed in crown ether.²⁾

In a previous report,¹⁾ we described the first example of photochemical reaction that a much higher selectivity is obtained in PEG employed in place of crown ether in a photochemical nucleophilic substitution of anisole to give *o*- and *p*-methoxybenzonitriles (**3**). There have been known a few photochemical reactions in PEG or acyclic polyethers,^{3,4)} though photochemical nucleophilic substitutions of aromatic systems in protic solvents have been well documented.^{1,5-8)}

When a crown ether is present, photocyanation proceeds in aprotic solvents more easily than in protic solvents,⁹⁾ while addition of electron acceptor, such as terephthalonitrile (**2**), improves both the yield of photocyanation products and the specificity of substitution.¹⁰⁾ This report is concerned with photochemical cyanation of *o*- and *p*-dimethoxybenzenes (**1a** and **1b**) with KCN in an aprotic solvent, in the presence and absence of **2** when PEG is used as co-solvent (Scheme 1).



Scheme 1.

Results and Discussion

Photoreaction in a Quartz Cell in the Absence of **2**.

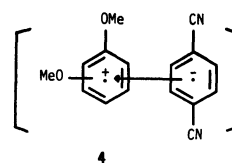
Consumption of **1** in the presence of PEG was slightly slower than in the presence of crown ether. However, conversion yields¹¹⁾ of **3** with PEG were comparable to that for **3a** and superior to those with crown ether for **3b** (see runs #1, 5, 7, and 12 in Table 1).

In comparison with the results obtained by Heijer *et al.*⁸⁾ in *t*-BuOH-H₂O, both the consumption and the conversion yield were worse for **1a** with PEG, but those for **1b** were much better.

Both the conversion of **1** and the formation of **3** were neither quenched by 1,3-pentadiene (≈ 50 mM) (1 M = 1 mol/dm³) nor sensitized by acetone (≈ 50 mM) whose E_T (≈ 78 kcal/mol)¹²⁾ is high enough for sensitizing **1**

to their triplet states. Fluorescence of **1** was not affected by either 1,3-pentadiene or acetone. These data suggest that the cyanations proceed through comparatively short-lived intermediates (probably S₁ state).¹²⁾

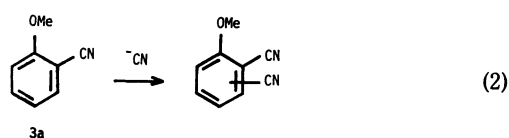
Photoreaction in the Presence of **2.** Both the consumption of **1a** and conversion yield of **3a** with PEG were half as much as those with crown ether. However, those with PEG for the reaction of **1a** were similar to these with crown ether. Photolyses of **1b** with PEG were superior to those with crown ether and could be used for the preparation of **3b**. Both the conversion of **1** and the formation of **3** were quenched by 1,3-pentadiene¹²⁾ ($k_q\tau_0/\text{dm}^3 \text{ mol}^{-1}$: 11 for **1a** and 6 for **1b**; 6 for **3a** and 16 for **3b**) and slightly sensitized with acetone.¹²⁾ These data suggest that the cyanations in the presence of **2** proceed through comparatively long-lived intermediates¹²⁾ (probably the T₁ state of **1** and/or of a charge transfer complex of **1** and **2** like **4**).⁸⁾



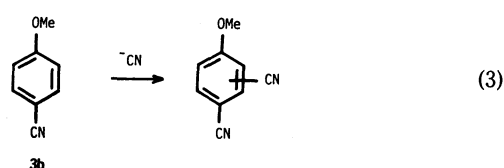
Photoreactions in the Presence/Absence of **2.** Substitution of KCN with NaCN did not affect the consumption of **1** but did the conversion yields of **3a** (increased) and **3b** (decreased). This reflects the tolerance of PEG for the size of the cationic guests incorporated in it compared with crown ether.

Prolonged irradiation caused a slight decrease in the conversion yield of **3**. This implies that further reactions, *e.g.*, the cyanation of **3**,¹³⁾ may be faster than cyanations of **1**.⁸⁾

Although, in Pyrex cells with PEG, consumption of **1** was much slower than in quartz cells, conversion yields of **3** increased remarkably, especially for **1b** (see runs #1 through 4 and 8 through 11 in Table 1). This phenomenon may result from a further photocyanation of **3**⁸⁾ in a quartz cell (see Table 2).



Scheme 2.

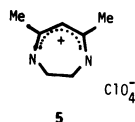


Scheme 3.

TABLE 1. PHOTOSUBSTITUTION OF DIMETHOXYBENZENES (**1a** AND **1b**) WITH CN⁻

Run	1	Cell ^{a)}	Co-solv. ^{b)}	MCN ^{c)}	2 used (mM)	Yield ^{d)} & C.Y. ^{e)} of 3/%		
1	1a	Q	PEG	K	—	20.2	31.7	(63.8)
2		Q			150	7.6	28.5	(26.6)
3		P			—	7.2	45.9	(15.7)
4		P			150	5.5	67.9	(8.1)
5		Q	CE		—	35.5	39.6	(89.7)
6		Q			150	33.4	57.5	(58.1)
7		Q	PEG	Na	—	22.8	37.2	(61.3)
		Q ^{f)}	BH		—		73.2	(30.2) g)
8	1b	Q		K	—	29.1	32.5	(89.7)
9		Q			150	63.5	72.6	(87.5)
10		P		P	—	27.1	41.6	(65.1)
11		P		P	150	71.5	96.6	(74.0)
12		Q	CE		—	26.5	28.4	(93.3)
13		Q			150	57.9	73.9	(78.3)
14		Q	PEG	Na	—	23.6	27.7	(85.0)
		Q ^{f)}	BH		—		22.2	(61.6) g)

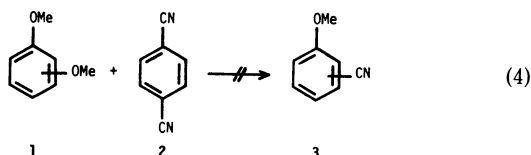
a) Q: Quartz cell; P: Pyrex cell. b) PEG: PEG #200/CH₂Cl₂; CE: 18-Crown-6/CH₂Cl₂; BH: *t*-BuOH/H₂O (3:1). c) K: KCN; Na: NaCN. d) Yield of **3** based on initial amount of **1**. e) Yield based on **1** consumed.¹¹⁾ Consumption of **1** is given in parentheses. f) Filter: 1 cm of a solution of **5** in water (100 mg dm⁻³). g) See Ref. 8.

TABLE 2. PHOTODEGRADATION OF METHOXYBENZONITRILES (**3a** AND **3b**) IN PYREX CELLS

Run	3	2 used (mM)	Conv. of 3/%		
			2 h	4 h	6 h
1	3a	—	10.7	12.3	19.9
2		150	41.0	59.7	69.2
3	3b	—	0	0.3	0
4		150	10.4	13.0	13.3

The photochemical decay rate of **3a** was much higher than that of **3b** in Pyrex cells and this tendency is more marked in quartz cells, especially in the presence of **2** (Schemes 2 and 3).

Suspected transformation of **1** and **2** to yield the corresponding **3** was excluded for these photocyanation reactions (Scheme 4).



Scheme 4.

Experimental

Instrumentation. All mps were taken with a microscope hot stage and are uncorrected. UV-visible spectra were recorded on a Shimadzu UV-200, fluorescence/phosphorescence spectra on a Hitachi MPF-2A, and GLC on a Yanagimoto Yanaco G-80F (FID). The GLC conditions used: 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 analyses; column B (3.8 mm × 3.0 m, 25% Apiezon L on 30—60 mesh fire brick in a glass column) was used to analyse the degradation of **1**.

Materials. Dimethoxybenzenes (**1a** and **1b**), terephthalonitrile (**2**), 18-crown-6, and KCN were purchased. CH₂Cl₂ was distilled from CaH₂. PEG #200 (Nakarai Chem. Co.) was dried azeotropically by toluene. Methoxybenzonitrile (**3a**¹⁴⁾ and **3b**¹⁴⁾ were prepared according to the literature methods. 1,3-Pentadiene (bp 42—44 °C) and acetone were distilled before use.

General Experimental Procedures. A solution of **1** (10 mM), KCN (30 mM), and PEG (1 M) or 18-crown-6 in CH₂Cl₂ (10 cm³) in the presence or absence of **2** (150 mM) was irradiated externally with a high-pressure mercury lamp (Eikosha PIH-300, 300 W) through a water-cooled quartz or Pyrex cell. The irradiated solution was analysed by GLC after washing with water to remove PEG and KCN. The results are given in Table 1.

Degradation of 3. Photodegradation of **3a** and **3b** (10 mM) was observed under conditions similar to those used for **1** (see Table 2).

Attempt of Photochemical Transformation of 1 and 2 to 3.

A solution of **1** (10 mM) and **2** (10 mM) was irradiated and the mixture was analysed by GLC. No formation of cyananisoles (**3**) was observed.

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