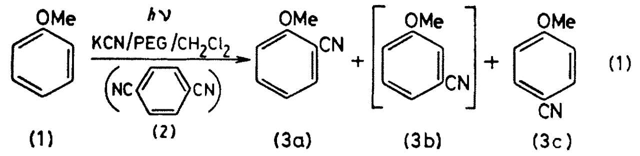
Photocyanation of Anisole in the Presence of Polyethylene Glycol

By Nobutaka Suzuki*, Kazuo Shimazu, Toshikuni Ito, and Yasuji Izawa
(*Chemistry Department, Faculty of Engineering, Mie University, Tsu, Mie* 514, *Japan*)

Summary Polyethylene glycol can replace crown ether as a co-solvent in the photochemical substitution reaction of anisole with KCN in CH_2Cl_2.

Photochemical nucleophilic substitutions of aromatic ring systems in protic solvents have been well documented.[1] When a crown ether is present the photocyanation proceeds better in aprotic solvents than in protic solvents,[2] while addition of an electron acceptor, such as terephthalonitrile (**2**) improves both the yield of the photocyanation products and the specificity of substitution.[3] 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 CH_2Cl_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 g l c † and the results are given in the Table

tightly and therefore liberates a naked anion (^-CN) which may react efficiently with electrophiles, while PEG, which is assumed to have a complex spiral structure,[4] 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 [1,3]

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

TABLE Photocyanation of anisole (**1**) in PEG or CE

Co-solv [a]	Yield[g] and conv yield[h] of (**3**)/%									*p* CN/*o*-CN[i]	*m*-CN
	1 h			3 h			6 h				
PEG 200[b]	5 7	32	(18)	11 4	24	(47)	10 8	17	(64)	0 90	trace
PEG 200[c]	5 3	20	(26)	8 8	19	(47)	9 6	16	(61)	1 00	—[j]
PEG 200[d]	3 2	46	(7)	6 9	38	(18)	8 9	25	(36)	1 33	—[j]
PEG 200[e]	—	—	—	2 8	15	(19)	5 8	20	(29)	1 36	—[j]
PEG 200[f]	—	—	—	7 6	31	(24)	18 0	46	(39)	2 77	—[j]
PEG 1000[b]	6 5	41	(16)	9 1	22	(42)	9 2	14	(64)	0 39	trace
PEG 1000[d]	2 9	73	(4)	7 4	41	(18)	9 2	38	(24)	0 85	—[j]
CE[b]	9 4	47	(20)	26 5	58	(46)	26 2	39	(67)	0 38	trace
CE[d]	7 6	29	(26)	10 9	20	(54)	13 6	20	(68)	0 75	trace

[a] PEG (Nakarai Chem Co) was dried azeotropically with benzene before use CE = 15-crown 5-ether (Nakarai Chem Co) [b] Quartz cell, no (**2**) [c] Quartz cell 50 mmol of (**2**) [d] Quartz cell 200 mmol of (**2**) [e] Pyrex cell no (**2**) [f] Pyrex cell 150 mmol of (**2**) [g] Yield of (**3**) based on initial amount of (**1**) [h] Conversion yield based on (**1**) consumed Consumption of (**1**) is given in parentheses [i] After 3 h irradiation [j] Not detected

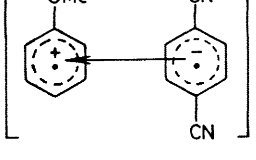
In a quartz cell, when (**2**) was absent consumption of (**1**) with PEG present was comparable to that with CE However, the conversion yields of (**3**) decreased in the order CE > PEG 1000 > PEG 200 present The ratio of yields of (**3c**) (**3a**) (*p*-CN/*o*-CN) decreased in the order PEG 200 > PEG 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 ^-CN anion in an aprotic solvent, as does CE, by forming a complex with the 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 K^+ cation

Quenching and fluorescence experiments showed that the present reaction proceeds through the T_1 excited state of (**1**), in agreement with Nilsson's work,[5] when (**2**) is absent, and the S_1 state of the charge-transfer complex (**4**) when (**2**) is present The charge distribution described in the literature[1,6,7] of (**1**) in the S_1 and 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**)

---

† G l c 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[7] that the π–π^* triplet excited state of (**1**), produced photochemically *via* successive intersystem crossing, is attacked by the $^-$CN anion and then liberates an electron to give a cation radical. This radical reacts with one more $^-$CN anion to afford monocyanoanisoles (**3**). In the presence of (**2**), (**1**) may react through (**4**).[3] The formation of (**4**) may result in the higher conversion yields of (**3**) than those obtained in the absence of (**2**).

(*Received, 22nd September* 1980; *Com.* 1041.)

[1] For reviews see J. Cornelisse and E. Havinga, *Chem. Rev.*, 1975, **75**, 353; J. Cornelisse, *Pure Appl. Chem.*, 1975, **41**, 433.

[2] R. Beugelmans, M. T. L. Goff, J. Pusset, and G. Roussi, *J. Chem. Soc., Chem. Commun.*, 1976, 377.

[3] K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1975, 553.

[4] F. E. Bailey, Jr., and J. V. Koleske, 'Poly(ethylene oxide),' Academic Press, New York, 1976; S. Yanagida and M. Okahara, 'Chemistry of Crown Ethers,' *Kagaku* (Special Issue), eds. R. Oda, T. Shono, and I. Tabushi, 1978, **74**, 149; F. Vögtle and E. Weber, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 753; for CE, see J. S. Bradshaw in 'Synthetic Multidentate Macrocyclic Compounds,' eds. R. M. Izatt and J. J. Christensen, Academic Press, New York, 1978, ch. 2.

[5] S. Nilsson, *Acta Chem. Scand.*, 1973, **27**, 329.

[6] G. Lodder and E. Havinga, *Tetrahedron*, 1972, **28**, 5583.

[7] J. D. Heijer, O. B. Shadid, J. Cornelisse, and E. Havinga, *Tetrahedron*, 1977, **33**, 779.