

Use of Tetrabutylammonium Cyanide for Photocyanation of Aromatic Compounds: Phase Transfer Photochemistry

By RENÉ BEUGELMANS,* HÉLÈNE GINSBURG, ALEXANDRA LECAS, MARIE-THÉRÈSE LE GOFF, JACQUES PUSSET, and GEORGES ROUSSE

(Institut de Chimie des Substances Naturelles, C.N.R.S., 91190-Gif/Yvette, France)

Summary Nucleophilic aromatic photosubstitution can be carried out using tetrabutylammonium cyanide in anhydrous acetonitrile or methylene chloride and also under phase-transfer conditions (CH_2Cl_2 -KCN in H_2O).

We have recently reported¹ that photochemical nucleophilic substitution by CN^- can advantageously be made to take place using 18-crown-6 ether to dissolve KCN in anhydrous acetonitrile (Table, conditions A). We now report that this reaction can also be carried out with another phase-transfer agent, tetrabutylammonium cyanide,²

which is, in some cases, even more efficient for aromatic photosubstitution (Table, conditions B, C, and D). In acetonitrile (conditions B) the photoreaction takes place with aromatic hydrocarbons as well as with nitro-derivatives; in comparison with 18-crown-6 ether yields are higher for naphthalene and 9-nitrophenanthrene and lower for 1-nitronaphthalene and 4-nitrobiphenyl.

When the reaction is carried out in methylene chloride (conditions C), the photosubstitution takes place only for the nitro-derivatives. The quantum yield of photosubstitution for 1-nitronaphthalene in acetonitrile, $\Phi(\text{B})$, is *ca.*

TABLE

Starting materials	Conditions (A) ^a		Conditions (B) ^a		Conditions (C) ^a		Conditions (D) ^a		Photoproducts
	Irradiation time/h	% Conversion ^b	Irradiation time/h	% Conversion ^b	Irradiation time/h	% Conversion ^b	Irradiation time/h	% Conversion ^b	
Naphthalene	8	15	8	30	5	0	5	0	{ 1-Cyano-naphthalene { 4-Cyano-biphenyl ^c } d
1-Nitronaphthalene ..	4	30	20	5	1	15	4	68	
Biphenyl	20	50	19	7	5	0	5	0	
4-Nitrobiphenyl ..	1	80	1	25	3	50	3	90	
Phenanthrene ..	3	25	4	20	3	0	3	0	
9-Nitrophenanthrene	3	16	3	87	3	3-5	2	90	

^a Conditions: (A) KCN-18-crown-6 in anhydrous MeCN; molar ratio KCN to substrate 10:1; (B) $\text{Bu}_4\text{N}^+\text{CN}^-$ in anhydrous MeCN; molar ratio $\text{Bu}_4\text{N}^+\text{CN}^-$ to substrate 1.5:1; (C) as for (B) but in CH_2Cl_2 ; (D) $\text{Bu}_4\text{N}^+\text{CN}^-$ in CH_2Cl_2 -2M-KCN in H_2O phase-transfer system; molar ratio $\text{Bu}_4\text{N}^+\text{CN}^-$ to substrate 0.2:1. For (A)-(C), irradiation with a 450 W high-pressure Hg lamp in quartz tubes; for (D), irradiation in a photochemical reaction vessel with an immersed water-cooled quartz finger with rapid argon bubbling and vigorous mechanical stirring. ^b Ratio of photoproduct with respect to starting material measured by g.l.c. ^c Traces (1%) of another monocyano-product were obtained in conditions (B), and a dicyano-product in (D). ^d Mixture of two monocyano-compounds with the 9-cyano-phenanthrene predominant in conditions (A), (B), and (D).

0.001 and in methylene chloride, $\Phi(C)$, is *ca.* 0.1, showing that $\Phi(C)/\Phi(B) = ca. 100$. It is interesting that under both conditions (B) and (C) the molar ratio of CN^- to substrate is 1.5:1 whereas it is 10:1 under conditions (A). The fact that the photoreaction takes place in methylene chloride opens up a pathway to photochemical reaction in a phase transfer system. Indeed, conditions (D) not only give high yields of cyano-derivatives, but are very convenient for work up (the organic layer is separated, washed with water, and evaporated *in vacuo*). Furthermore, only

catalytic amounts of tetrabutylammonium cyanide (0.2 mol for 1 mol of nitro-derivative) are required.

We are now investigating the scope of our finding since other nucleophiles can be extracted from water by phase transfer agents.²

We thank Dr. L. Ebersson, University of Lund, for suggesting the use of tetrabutylammonium cyanide.

(Received, 11th July 1977; Com. 700.)

¹ R. Beugelmans, M. T. Le Goff, J. Pusset and G. Roussi, *J.C.S. Chem. Comm.*, 1976, 377; *Tetrahedron Letters*, 1976, 2305.

² A. Brändström, P. Berntsson, S. Carlson, A. Djurhuus, K. Gustavi, U. Junggren, B. Lamm, and B. Samuelson, *Acta Chem. Scand.*, 1969, **23**, 2202; A. Brändström and U. Junggren, *ibid.*, pp. 2203, 2204; for recent reviews see: M. Makosza, *Pure Appl. Chem.*, 1975, **43**, 439; E. W. Dehmlow, *Angew. Chem. Internat. Edn.*, 1974, **13**, 170; J. Dockx, *Synthesis*, 1973, 441.