Use of Crown Ethers for Photochemical Cyanation of Aromatic Hydrocarbons

By RENÉ BEUGELMANS*, MARIE-THÉRÈSE LE GOFF, JACQUES PUSSET, and GEORGES ROUSSI
(*Institut de Chimie des Substances Naturelles, C.N.R.S.,* 91190 *Gif/Yvette, France*)

Summary The photocyanation of the aromatic hydrocarbons naphthalene, anthracene, phenanthrene, and biphenyl occurs easily with potassium cyanide dissolved by means of the cyclic polyether 18-crown-6 in anhydrous acetonitrile.

MANY photochemically induced nucleophilic reactions have been reported;[1] among them, the cyanation of aromatic hydrocarbons (naphthalene, anthracene, phenanthrene, and biphenyl) is one of the simplest, and has therefore been studied extensively.[2–4] This photoreaction is always carried out in a mixture of solvent and various amounts of water in order to dissolve the cyanide. We have found that photocyanation can take place in good yields, without water, under the following conditions: KCN (10^{-3} M) and 18-crown-6 ether (10^{-3} M) were dissolved in methanol (10 ml), solvent was removed *in vacuo*[5] and the resulting complex, with acetonitrile (10 ml), was added to the aromatic hydrocarbon (10^{-4} M). The mixture was then irradiated. After complete transformation of the starting hydrocarbon, classical work up with diethyl ether yielded the expected cyano-compounds, while the 18-crown-6 ether

TABLE

Starting hydrocarbon	This work[a] Product[b]	M.p./°C	% Yield[c]	Literature reports Product	% Yield	Ref.
Naphthalene	1-Cyano	32—33	15	1-Cyano	6	1,2
Anthracene	9-Cyano	176[d]	10[e]	9-Cyano	—[f]	3
	9,10-Dicyano	315—320[g]	10[e]	—	—	—
Phenanthrene	9-Cyano	106—107[h]	25	9-Cyano	—[f]	3
Biphenyl	4-Cyano	87 (decomp.)[i]	50	4-Cyano	28[j]	4
	Dicyano[k]	200—215	10	2-Cyano	14	4

[a] High-pressure lamp (Hanovia 450) and Pyrex filter except for biphenyl (medium-pressure Hanau NK 6/20). [b] Mass spectra are in agreement with the proposed structure. [c] Yields are based on the amount of isolated photoproduct. [d] R. G. Landolt and H. R. Snyder, *J. Org. Chem.*, 1968, **33**, 403, give m.p. 174—176 °C. [e] Large amounts (*ca.* 50%) of anthracene dimer, m.p. 320 °C, are obtained. [f] Yield not reported. [g] Footnote (d) gives m.p. 335 °C (sublimation). [h] C. W. Shoppee, *J. Chem. Soc.*, 1933, 37, gives m.p. 109 °C [i] M. Gomberg, and W. E. Bachman, *J. Amer. Chem. Soc.*, 1924, **46**, 2343, give m.p. 88 °C. [j] After 21 h irradiation. Yield decreases with irradiation time, and is 28% after 10 h. [k] $M^+ = 204$.

remained in the water phase, from which it could be recovered along with other products by work up with $CHCl_3$.† The results are shown in the Table.

Under our conditions, CN^- is present as a non-solvated species in a polar aprotic solvent, whereas this anion is strongly solvated when water is present even in small amounts. For the photochemical nucleophilic addition to occur at least a ten-fold molar excess of CN^- is required when water is present[4] so the enhanced yields we have obtained are probably due to absence of solvation, as in the ground-state S_N2 reaction.[6] Anthracene, which dimerizes easily,[7] probably gives a low yield of substitution products for this reason. In all cases 'α' reactivity is observed.[1b],

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† Control experiments have shown that the 18-crown-6 ether (and other polycyclic ethers including 15-crown-5 and dicyclohexyl-18-crown-6) undergo transformations when irradiated without KCN in the presence of aromatic hydrocarbons. Therefore, reduction, radical addition, and radical coupling products are expected to be present (J. A. Barltrop, *Pure Appl. Chem.*, 1972, **33**, 170). To our knowledge these properties of crown ethers and cryptates have not yet been reported, and we are currently studying these aspects.

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