

Photoinduced Reactions of Some Aromatic Hydrocarbons with Cyanide Ion¹

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Summary Biphenyl, azulene, and naphthalene are found to react with cyanide ion on irradiation, leading to cyano-substituted products.

WE report that certain aromatic hydrocarbons undergo photosubstitution reactions upon irradiation in the presence of cyanide ion. To our knowledge this is the first example

of unsubstituted aromatic hydrocarbons undergoing photo-substitution with a nucleophile.

Irradiation of biphenyl (200 mg) in Bu^tOH-H₂O (1:2, 1:5 l) with KCN (5 g) in a Rayonet photochemical reactor RPR-208 (2537 Å) afforded 2-cyanobiphenyl, 4-cyanobiphenyl, and at least two dicyano-substituted biphenyls which were not further identified. After 10 h 67.5% of the biphenyl had reacted.

The yield of 2-cyanobiphenyl is practically independent of the time of irradiation (13.8% after 10 h, 14.3% after 21 h†). The yield of 4-cyanobiphenyl, however, decreases upon increasing irradiation times (28.6% after 10 h, 17.5% after 21 h), while the yield of disubstituted compounds increases (10.6% and 22.6%, respectively). From the observation that the sum of the yields of 4-cyanobiphenyl and the disubstituted biphenyls remains constant, it may be concluded that the dicyanobiphenyls are formed in a photochemical reaction from 4-cyanobiphenyl. Allowing

† Percentage yields are based on the amount of converted starting material.

¹ The investigations will be described in greater detail in the theses of J. A. J. Vink and C. M. Lok, University of Leiden, to be published, 1972.

for the statistical factor, the ratio of the rates of reaction at the *ortho* versus the *para* position is *ca.* 1:6.

Irradiation of azulene (244 mg) Bu^tOH-H₂O (1:5 l, 2:3) in the presence of KCN (10 g) for 120 h in the Rayonet reactor (3000 Å) afforded 1-cyanoazulene (32.3%).

From naphthalene (300 mg) in Bu^tOH-H₂O (1:5 l, 1:2) with KCN (10 g) upon irradiation for 12 h in the Rayonet reactor (2537 Å) 1-cyanonaphthalene (20.4 mg, 6%) was obtained. Moreover, 39.2 mg of a mixture of cyanodihydro- and dicyanotetrahydro-naphthalenes were isolated.

Irradiation of benzene under similar conditions did not lead to detectable amounts of benzonitrile.

It is noteworthy that with these hydrocarbons reaction starting from the excited state with a nucleophile leads to substitution at the same positions as electrophilic substitution in the ground state.

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