Tetrahedron Letters No.28, pp. 2417-2422, 1965. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTOCHEMICAL REACTION OF MERCURIC CYANIDE WITH CYCLOHEXENE*

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(Received 24 May 1965)

A number of nitriles have been prepared by nucleophilic substitution reactions. However, until recently little was known about the use of cyano radical. Müller (1) has showed that the cyano group was introduced into saturated hydrocarbons and ethers by the photolysis of cyanogen chloride. However, in their reactions, alkyl radicals, produced by the abstraction reaction, reacted with cyanogen chloride, making it difficult to estimate the reactivity of the cyano radical. Cyano radicals have two reaction points based upon the following resonance forms, $\cdot C\equiv N| \longleftrightarrow |\overset{\ominus}{C}\equiv\overset{\oplus}{N}\cdot$ Under suitable conditions, therefore, not only nitrile but also isonitrile might be expected to be produced.

It is known that mercuric cyanide was decomposed by light, and ultraviolet irradiation of diphenylmercury produced phenyl radicals (2). The absorption spectrum of mercuric cyanide (3) showed increasing absorption without a maximum in the region 210-360 mμ.

It would be expected from the above facts that the cyano radical may be produced by the irradiation of mercuric cyanide with ultraviolet light. With this view, the photochemical reaction of mercuric cyanide with cyclohexene was investigated.

The photolyses were conducted with the unfiltered radiation from a high pressure mercury lamp at temperatures between 30 and 40°. In the first place, the behavior of mercuric cyanide in simple solvents was ascertained. Methanol reacted slightly to form ethylene glycol. The gaseous fraction consisted of hydrogen, methane, and hydrogen cyanide. Mercuric cyanide reacted with tetrahydrofuran. A mixture of 2-cyanotetrahydrofuran (a 15.0% yield based on the mercuric cyanide photolyzed) and 3-cyanotetrahydrofuran (1.5% yield) was obtained. The accompanying product was 2,2'-bitetrahydrofuryl (51.4% yield). In no case was any isonitrile formed.

Secondly, the photolysis of mercuric cyanide (12.6 g.) with cyclohexene (32.8 g.) in methanol (150 ml.) was studied. The irradiated mixture was worked up as usual to give mercury (6.5 g.), hydrogen cyanide, cyclohexyl cyanide (6.8% yield), 3-cyanocyclohexene (3.5% yield), and 3,3'-bicyclohexenyl (49.5% yield). The accompanying products were a small amount of methoxycyclohexane, 3-methoxycyclohexene, and cyclohexylcarbinol. The gaseous fraction (50 ml.) consisted of hydrogen and methane.

These products were identified by infrared spectroscopic and gas chromatographic measurements and preparation of derivatives. The hydrolysis[+] of a mixture of nitriles, the infrared spectrum of which showed an absorption band at 2250 cm^{-1} (-CN), yielded the carboxylic acids, b.p. 125-130°/15 mm. The p-bromophenacyl esters of the carboxylic acids were prepared and were separated into two parts by chromatography on silica gel. One melted at 89-90° and was identified as p-bromophenacyl cyclohexanecarboxylate by a mixed melting point measurement. Anal. Calcd. for $C_{15}H_{17}BrO_3$: C, 55.40; H, 5.27. Found: C, 55.21; H, 5.19. The other melted at 108-109° and was identified as p-bromophenacyl cyclohexene-1-carboxylate by a mixed melting point measurement. Anal. Calcd. for $C_{15}H_{15}BrO_3$: C, 55.74; H, 4.68. Found: C, 55.64; H, 4.80.

2- and 4-cyanocyclohexene were not detected from the results

[+] It has been already reported that the hydrolysis of 3-cyanocyclohexene by means of alkalies yielded cyclohexene-1-carboxylic acid: (a) W. Braren and E. Buchner, Ber., 33, 3455 (1900); (b) M. Mousseron, F. Winternitz, J. Jullien, and R. Jacquier, Bull. soc. chim. France, 79 (1948).

of infrared spectroscopic and gas chromatographic measurements.

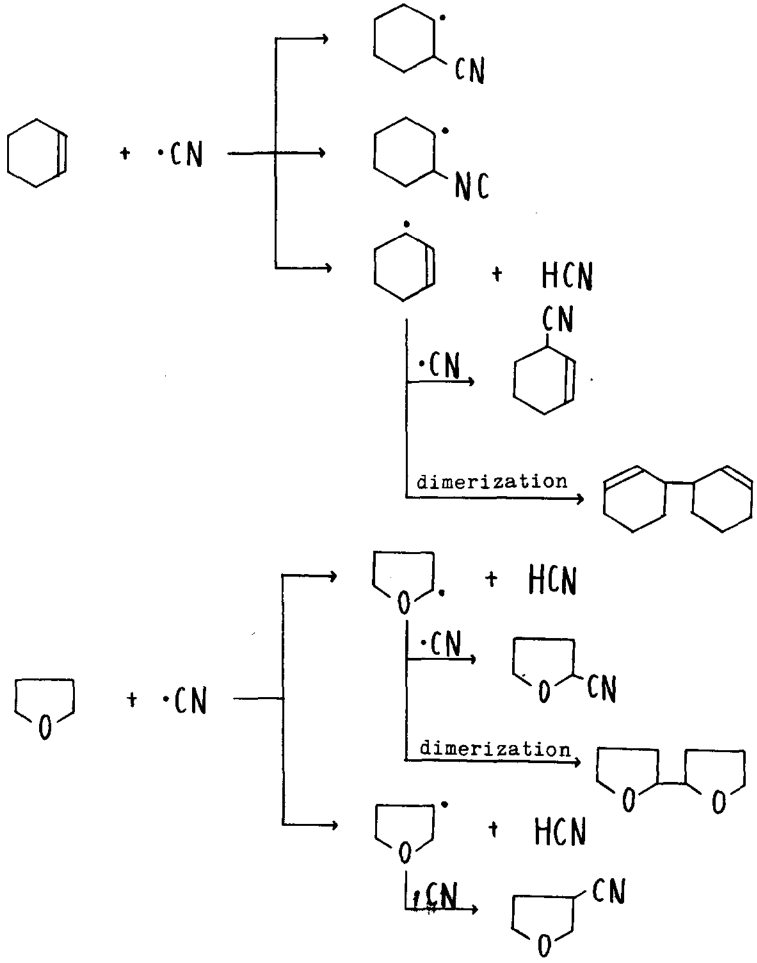
When tetrahydrofuran was used as a solvent, in addition to mercury (5.0 g.), hydrogen cyanide, cyclohexyl cyanide (8.3% yield), 3-cyanocyclohexene (3.0% yield), and 3,3'-bicyclohexenyl (49.5% yield), 2-cyanotetrahydrofuran (4.1% yield), 2,2'-bitetrahydrofuryl (a small amount), and cyclohexyl isocyanide (1.8% yield) were produced. The fraction of isonitrile, the infrared spectrum of which showed a strong absorption band at 2150 cm^{-1} (-NC), was hydrolysed to form amine. The benzamide was prepared, m.p. 147-148°, and was identified as benzamide of cyclohexylamine by a mixed melting point measurement. Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.90; H, 8.45. 3-isocyanocyclohexene was not detected.

We tentatively posturate on the basis of the reactivities of substrates and the stoichiometries of the reactions that the primary step in the photolysis is :

$$Hg(CN)_2 \xrightarrow{h\nu} \cdot CN \ + \ \cdot HgCN$$
$$\hookrightarrow Hg \ + \ \cdot CN$$

Cyanide radicals (HgCN radicals (4)) react with cyclohexene or cyclohexenyl radical to form nitriles, dissociate to mercury and cyano radical, or as is known in inorganic chemistry, disproportionate to mercury and mercuric cyanide (5).

The following reactions of cyano radicals can then occur.



Because the solubility of mercuric cyanide in organic solvents is small, it is difficult to study the solvent effects systematically. It is not clear why the corresponding isonitrile was formed when the reaction was carried out in non-hydroxylic solvents such as tetrahydrofuran and acetonitrile but not in methanol or ethanol. Possibly the cyano radical is hydrogen bonded, making the formation of the isonitrile impossible. $\cdot C{\equiv}N \cdots H{-}OR$
The distribution of cyclohexyl cyanide, 3-cyanocyclohexene, and 3,3'-bicyclohexenyl was common to all the solvents studied.

The details of this reaction will be reported in a forthcoming paper.

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* Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

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