The Direct Introduction of Cyano and Ethoxycarbonyl Radicals into Cyclohexane by a Photochemical Reaction

By Tamotsu TOMINAGA, Yoshinobu ODAIRA and Shigeru TSUTSUMI

(Received February 28, 1964)

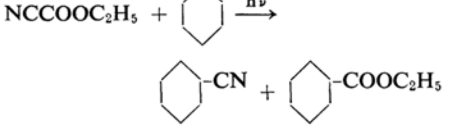
Since the cyanation of cyclohexane by a cyano radical generated photochemically from cyanogen chloride was first attempted by Müller,[1] increasing interest has, from the standpoint of organic synthesis, been shown in the study of the new direct method of introducing the important functional groups (such as cyano and alkoxycarbonyl) by radical reaction.

The present investigation was undertaken to examine the possibility of the direct and concurrent introduction of cyano and ethoxycarbonyl radicals into hydrocarbon by means of photochemical reaction.

For this purpose, ethyl cyanoformate was selected as a source of the above radicals. It has been shown by previous investigations[2,3] that the primary steps occurring in the photolyses of various alkyl esters are as follows:

$$\begin{aligned} \mathrm{RCOOR'} + h\nu &\rightarrow \mathrm{RCO\cdot} + \mathrm{\cdot OR'} \\ &\rightarrow \mathrm{R\cdot} + \mathrm{\cdot COOR'} \\ &\rightarrow \mathrm{RCOOH} + \mathrm{\cdot R''} \end{aligned}$$

Since the above steps may be applicable in the decomposition of ethyl cyanoformate in the presence of cyclohexane, both cyano and ethoxycarbonyl derivatives may be expected to be produced by recombinations between the cyano or ethoxycarbonyl radicals that were generated by the above processes and the cyclohexyl radical formed by hydrogen abstraction from cyclohexane.



The irradiation of a solution of ethyl cyanoformate (99 g.) in cyclohexane (252 g.) with a 600 W. high pressure mercury arc lamp was carried out under nitrogen for 48 hr. at room temperature. During the irradiation, the continuous evolution of gas was observed, and at the end of the reaction, 4000 ml. of gas, consisting of carbon dioxide, carbon monoxide and methane, in the ratio of 30 : 8 : 1 was collected and analyzed, by gas chromatography.

Moreover, the 0.56 g. of hydrogen cyanide produced was determined quantitatively as a cyanide ion by volumetric analysis using silver nitrate. The conversion percentage of the reaction was 38.4% and, as the liquid products a cyanide (1.8 g.) and an ester (3.5 g.) were obtained, accompanied by propionitrile (4.2 g.), ethanol (3.4 g.), ethylcyclohexane (2.5 g.) and bicyclohexyl (0.5 g.). The above cyanide and ester were identified as cyclohexyl cyanide and ethyl cyclohexanecarboxylate respectively by gas chromatographic and infrared analyses and by the mixed melting point tests using an authentic cyclohexanecarboxamide (m. p. 184~186°C) with the amides derived separately from the above compounds.

Although no quantitative interpretation of the results has been given because of the complexity due to the many different radicals generated in the primary steps, the direct introduction of cyano and ethoxycarbonyl radicals has been successful.

In this connection, it would be interesting to study the direct-introducing reaction of the α-keto ester radical, which should be more stable than the ester radical.

Department of Applied Chemistry
Osaka University
Miyakojima-ku, Osaka

---

1) E. Müller, *Chem. Ber.*, **96**, 670 (1963).
2) R. Brokowski et al., *J. Am. Chem. Soc.*, **83**, 1053 (1961).
3) M. Wijnen, ibid., **82**, 1847 (1960).