

A Novel Method for the Preparation of Carbodiimides from *N*-Haloamidine

By Eiichi HARUKI, Toshihiro INAIKE and Eiji IMOTO

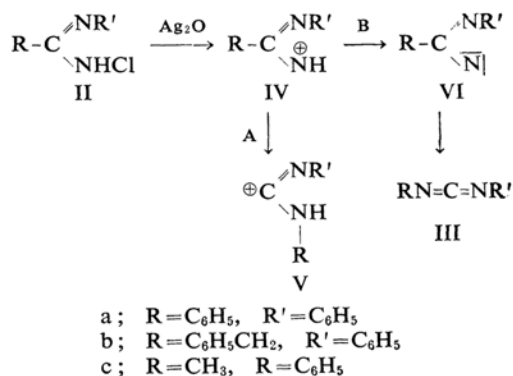
(Received August 2, 1965)

In a previous communication,¹⁾ we have shown that *N*-aryl-*N'*-haloamidines react with sodium ethoxide to form benzimidazole derivatives or 2-phenylnaphtho[1,2-d]imidazole depending on the structure of the haloamidines. In this communication we wish to report on the reaction of *N*-aryl-*N'*-haloamidines with silver oxide. The *N*-haloamidines were mixed with silver oxide in ligroin or benzene, and these mixtures were refluxed. This treatment caused a rearrangement, thus forming the carbodiimides.

To 2.3 g. of *N*-chloro-*N'*-phenylbenzamidine in 10 ml. of dry ligroin, 5.0 g. of silver oxide was added. The mixture was stirred under reflux for two hours, and then silver oxide and silver chloride were removed by filtration. After the solvent had been evaporated from the filtrate in vacuo, diphenylcarbodiimide b.p. 140–144°C/14 mmHg, was obtained in a 80% yield. Its infrared spectrum showed the characteristic carbodiimide absorption at 2150 cm⁻¹ and agreed completely with that of an authentic sample prepared by the method described in the literature.²⁾ Chemical evidence for structure III was given by the reaction with hydrochloric acid. When refluxed in dilute hydrochloric acid, diphenylcarbodiimide was converted quantitatively into *N,N'*-diphenylurea.

In a similar manner, *N*-phenylphenylacetamidine (Ib) and *N*-phenylacetoamidine (Ic) yielded *N*-benzyl-*N'*-phenylcarbodiimide (IIIb, 52% yield) and *N*-methyl-*N'*-phenylcarbodiimide (IIIc, 36% yield) respectively.

The mechanism of the described conversion of *N*-chloroamidines to carbodiimides may be supposed to be as follows:



Whether the rearrangement proceeds through route A or route B is not certain. However, it is sure that this reaction involves the migration of the R group to an electron-deficient nitrogen.

Department of Applied Chemistry
 Faculty of Engineering
 University of Osaka Prefecture
 Sakai, Osaka

1) E. Haruki, T. Inaike and E. Imoto, This Bulletin, 38, 1805 (1965).

2) P. Schlack and G. Keil, *Ann.*, 661, 164 (1963).