NOTES

Reaction of Dichlorocarbene and Primary Amines—Preparation of Aromatic Isocyanides

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It has been established that dichlorocarbene is formed by the reaction of haloform and bases, such as potassium *t*-butoxide[1], sodium hydroxide[2] and alkyl lithium[3], and the existence of carbene has been confirmed by Doering[1] with the formation of an adduct of carbene to cyclohexene. These facts might suggest that the so-called carbylamine reaction is a reaction involving dichlorocarbene as an intermediate, as has been suggested by Hine[4].

In order to confirm this speculation the present authors have studied the reaction using sodium *t*-butoxide in place of potassium or sodium hydroxide. To a hexane solution (or toluene-hexane solution) of an aromatic primary amine and sodium *t*-butoxide was added chloroform drop by drop at 0~5°C. The reaction took place immediately. After the addition of chloroform was over, the reaction mixture was left to stand at 0°C for thirty minutes, and then at 25°C for thirty minutes. The isocyanide was fractionated in the atmosphere of nitrogen or separated by the formation of silver complex compound[5].

$$ArNH_2 + CHCl_3 + 3(CH_3)_3CONa \longrightarrow ArNC + 3NaCl + 3(CH_3)_3COH$$

The results obtained are summarized in the following table.

As shown in the table, it is recognized that the reaction takes place also in the system of chloroform and *t*-butoxide, which has been recognized as a typical system to produce dichlorocarbene, and that the yield of isocyanides is increased according to increase of the concentration of chloroform (compare Expt. 3 with Expts. 4 and 5). Moreover, the yield of isocyanides in this case was much higher than that in the cases of sodium hydroxide.

TABLE I. YIELD OF ISOCYANIDES FROM PRIMARY AMINES

Primary amine, 0.2 mol. Chloroform, 0.2 mol.
Sodium *t*-butoxide, 0.6 mol.
Reaction time, 5 hr.

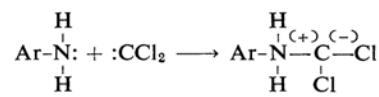
Expt. No.	Primary amine	Isocyanide	(yield)
1	Aniline	Phenyl isocyanide	(73%)
2	*o*-Toluidine	*o*-Tolyl isocyanide	(71%)
3	*p*-Toluidine[a]	*p*-Tolyl isocyanide	(72%)
4	*p*-Toluidine	*p*-Tolyl isocyanide	(86%)
5	*p*-Toluidine[b]	*p*-Tolyl isocyanide	(98%)
6	*o*-Chloraniline	*o*-Chlorophenyl isocyanide	(93%)
7	*p*-Chloraniline	*p*-Chlorophenyl isocyanide	(94%)

a) 0.1 mol. of chloroform was added.
b) 0.4 mol. of chloroform was added.

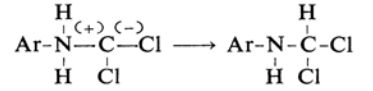
The results mentioned above indicate that the carbylamine reaction is a reaction involving dichlorocarbene as an intermediate.

We would like to suggest the following reaction mechanism for this reaction.

$$CHCl_3 + t\text{-}BuO^- \longrightarrow t\text{-}BuOH + Cl^- + :CCl_2 \quad (1)$$



(2)



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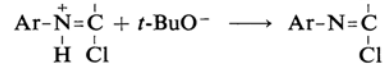

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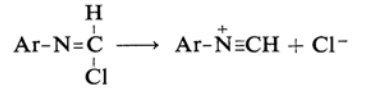

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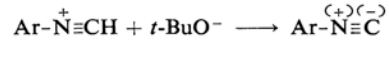

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4) J. Hine, ibid., **72**, 2438 (1950).
5) D. L. Hammick et al., *J. Chem. Soc.*, **1930**, 1876.