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PRELIMINARY COMMUNICATION

The reaction of dichlorocarbene with secondary amines

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THE intermediacy of dichlorocarbene in the formation of isocyanides from primary amines in the presence of aqueous base and chloroform was first suggested by Nef[1] and later by Hine.[2] We wish to report that secondary amines react to give the derived formamide under conditions which have been demonstrated[3] to involve dichlorocarbene as an intermediate. When chloroform is added to a stirred mixture of the amine, benzene; and potassium *tert.*-butylate maintained at 5°, an exothermic reaction takes place to give, after work up, the corresponding amide. Thus, diethylamine, dimethylamine, diphenylamine and piperidine react to give diethylformamide, dimethylformamide, diphenylformamide, and N-formylpiperidine, respectively. The amides were identified by comparing the infrared absorption spectra with those of the authentic materials. Yields varied from less than 1–31 per cent. The poorer yields were obtained in earlier experiments and may be improved by more recent refinements in experimental technique.

We believe that this reaction proceeds by an attack of dichlorocarbene on the amine with the expected dichloromethylamine intermediate proceeding to the observed amide product under the conditions of the reaction and work up. It seems unlikely that the reaction involves a displacement on chloroform by the dialkylamide anion since chloroform would not be expected to exist very long in the medium used. When aqueous sodium formate and the amine are placed together under the reaction conditions no amide is formed. Thus the trivial explanation, involving prior basic hydrolysis of chloroform to the formic acid salt, followed by reaction with the amine to give the amide, is ruled out.

Smith[4] recently reported the formation of a small amount of 3-diethylaminopropylformamide in the attempted preparation of the isocyanide from 3-diethylaminopropylamine by treatment with chloroform and base. He suggests an attack of dichlorocarbene on the amine to give the structure $R\text{-}NH\text{-}CHCl_2$ which then hydrolyzed to give the observed product.

We have also found that the tertiary amine, benzyldimethylamine, reacts under the conditions described above to give a small yield of dimethylphenylacetamide, m.p. 39–40°, mixed m.p. with authentic dimethylphenylacetamide, 39–40°. The infrared spectrum of the product was identical to that of authentic dimethylphenylacetamide. We believe that this product arises through a Stevens rearrangement of the nitrogen ylid formed by the addition of dichlorocarbene to the amine. Migration of a benzyl group in such a manner, followed by hydrolysis, could explain the observed product. The reaction also produced dibenzyl, identified by m.p., infrared spectrum, nuclear magnetic resonance spectrum; and other, as yet unidentified products.

Stevens and Bamford[5] have shown that when diazofluorene is irradiated in the presence of benzyldimethylamine a considerable quantity of 9-benzyl-9-dimethylaminofluorene is produced. These authors explain the product by postulating a migration of the benzyl group in the nitrogen ylid intermediate formed from the addition of the carbene to the amine.

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