[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

The Addition of Primary and Secondary Amines to Ethylenimine in the Presence of Aluminum Chloride

BY GEORGE H. COLEMAN AND JOSEPH E. CALLEN[1]

Various difficulties have been encountered in the synthesis of certain mono- and *unsym*-di-N-substituted ethylenediamines. A summary of the work with the mono-substituted compounds is presented by Aspinall[2] in a paper describing an indirect method of alkylating ethylenediamine to yield mono-substitution products. Recently Linsker and Evans[3] have reported the direct alkylation of ethylenediamine to give good yields of monoalkylethylenediamines. However, this method is not applicable to the preparation of *unsym*-di-N-substituted ethylenediamines.

N,N-Dialkylethylenediamines have been prepared by the Gabriel synthesis using β-bromoethylphthalimide and a secondary amine,[4] by the amination of a β-bromoethyldialkylamine hydrobromide[5] and by the reduction of dialkylaminoacetonitriles.[6,7,8] All of these methods involve several steps and although the last method appears to be the best, low yields are reported in some cases and no appreciable yield of N-phenylethylenediamine was obtained in the attempted reduction of phenylaminoacetonitrile.[8]

The present paper deals with a general, one-step method for preparing both mono- and *unsym*-di-N-substituted ethylenediamines. The method involves the addition of primary and secondary amines to ethylenimine[9] under anhydrous conditions in the presence of a catalyst.[10] Aluminum chloride was the catalyst used in the work here reported. In a recent patent Wilson[11] describes a process for the addition of amines to ethylenimine in the presence of water. This method has some disadvantages in that the products are not always easily separated from the reaction mixture and that considerable quantities of polyamines are often formed. In the present work no appreciable amounts of polyamines were formed and the yields of the diamines were relatively high. The procedure used involved the addition of ethylenimine in the vapor state at somewhat elevated temperatures.

It was found that considerably higher temperatures were desirable for the addition of primary amines than for the addition of secondary amines to ethylenimine. Thus, benzene was used as the solvent when secondary amines were involved and the temperature of reaction was approximately 90°. With primary amines higher boiling solvents such as tetralin or diphenyl were used and reaction temperatures were about 180°. Under the conditions described the catalyzed reaction between ethylenimine and primary and secondary amines is rapid and exothermic. The yields for the compounds prepared ranged from 77 to 89%. Amines which have thus far been successfully added to ethylenimine by the method described are diethylamine,[8] dibutylamine,[8] N-methylaniline,[12] benzylamine[13] and aniline.[12] The boiling points of the products corresponded to those previously reported.

The method has the disadvantage that at least one mole of catalyst is required for each mole of ethylenimine which reacts. This fact indicates that it is the adduct between the aluminum chloride and primary or secondary amine which reacts with ethylenimine forming a new adduct which is stable under the conditions of the reaction and undergoes no further change. This is further evidenced by the fact that no triamines or tetramines were isolated from the reaction product. These compounds would be expected if the catalyst migrated from one amino group to another and the addition of ethylenimine was then random. For example, Wilson[11] found that in the addition of *n*-octylamine to ethylenimine in water solution there was formed 39% of N-*n*-octylethylenediamine, 17% of N-*n*-octyldiethylenetriamine and 25% of higher polyamines.

Work now in progress includes the use of catalysts other than aluminum chloride in the reaction and a study of the addition of ethylenimine to compounds other than amines.

Experimental

The following procedure is typical and was used with only minor modification for the preparation of each of the compounds listed. The selection of the inert solvent of the proper boiling point was determined in each case by the reaction temperature desired and by ease of separation from the final product. Benzene was used for secondary amines and tetralin or biphenyl for the primary amines.

N,N-Di-*n*-butylethylenediamine.—In a 500-ml. three-necked flask, equipped with a motor-driven stirrer, thermometer, reflux condenser and dropping funnel, was placed 89.8 g. (0.675 mole) of anhydrous aluminum chloride and 100 ml. of dry benzene. To this mixture was

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[1] From a dissertation submitted by Joseph E. Callen to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree, June, 1946.

[2] Aspinall, THIS JOURNAL, **63**, 852 (1941).

[3] Linsker and Evans, *ibid.*, **67**, 1581 (1945).

[4] Ristenpart, *Ber.*, **29**, 2526 (1896).

[5] Amundsen and Krantz, THIS JOURNAL, **63**, 305 (1941).

[6] Winans and Adkins, *ibid.*, **55**, 4167 (1933).

[7] *Chem. Zentr.*, **101**, II, 3083 (1930).

[8] Bloom, Breslow and Hauser, THIS JOURNAL, **67**, 539 (1945).

[9] The ethylenimine was prepared by the method of Wenker, *ibid.*, **57**, 2328 (1935). It is a relatively toxic compound; Danehy and Pflaum, *Ind. Eng. Chem.*, **30**, 778 (1938).

[10] Some preliminary work on this reaction was carried out in this Laboratory by Dr. R. L. Sundberg and by Zella A. Hicks.

[11] Wilson, U. S. Patent 2,318,729; *C. A.*, **37**, 5986^1 (1943).

[12] Munch and Schlichting, German Patent 561,156; *Chem. Zentr.*, **104**, II, 444 (1933).

[13] Van Alphen, *Rec. trav. chim.*, **54**, 595 (1935).

added slowly with stirring and cooling 116 g. (0.9 mole) of di-*n*-butylamine. When the addition was complete the reaction mixture was heated to 90° and the dropping funnel was replaced by a gas-inlet tube having a tip 0.5–1.0 mm. in diameter. To the gas-inlet tube was attached an ampoule containing 19.3 g. (0.45 mole) of ethylenimine.[9] The ampoule was immersed in a water-bath maintained at a temperature of 75–85°. At this temperature the ethylenimine was vaporized and bubbled into the stirred mixture at such a rate that the addition was complete in about thirty minutes. No external heating was necessary since the reaction was sufficiently exothermic to maintain reflux. When the addition of ethylenimine was complete the gas-inlet tube was replaced quickly with a rubber stopper to prevent sucking back of the reaction mixture. The mixture was stirred for an additional thirty minutes and was then transferred to a 3-liter three-necked flask equipped with reflux condenser and stirrer. The flask was immersed in an ice-bath and 500 g. of ice and water was added slowly through the condenser. To the almost solid mass which resulted there was added with stirring 300 g. of solid potassium hydroxide in small portions. When the mixture was cold the benzene layer was separated. The aqueous layer was extracted four times with 100-ml. portions of benzene. The combined benzene layers were dried over potassium hydroxide pellets, the solvent was distilled and the residue was distilled through a 12-in. helices-packed, partial take-off fractionating column.

Summary

1. The addition of primary and secondary amines to ethylenimine to form N-substituted ethylenediamines has been effected in anhydrous media using aluminum chloride as a catalyst.

2. Higher temperatures were required for the satisfactory addition of primary amines to ethylenimine than was the case for secondary amines.

3. Several types of primary and secondary amines were used.

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The Beckmann Rearrangement in the Preparation of Aldehydes[1]

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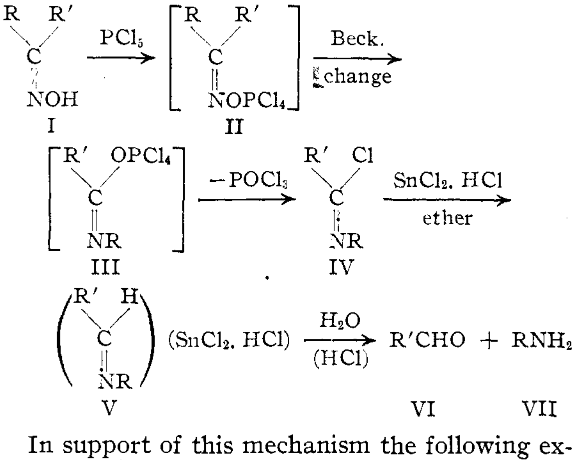
In this Laboratory we recently had occasion to prepare a considerable quantity of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde. This compound had previously been prepared from the anilide[2] of the corresponding acid by treatment with phosphorus pentachloride and reduction of the product with stannous chloride. The anilide was prepared from 9-benzoyl-1,2,3,4-tetrahydrophenanthrene oxime by means of the Beckmann rearrangement.

It seemed possible from a consideration of the probable mechanism of the reaction that the aldehyde could be prepared directly from the oxime. This assumption was based on the probability that in the Beckmann rearrangement of the oxime an imidyl chloride was formed which was identical with that formed from the anilide in the previous method. Experimental trial has shown that such a procedure is possible and that satisfactory yields of 1,2,3,4-tetrahydrophenanthrene-9-aldehyde can be obtained by treatment of the corresponding oxime with phosphorus pentachloride and reduction of the product.

In order to gain additional information concerning its general applicability, the method has been studied further and used in the preparation of two other aromatic aldehydes, benzaldehyde and *p*-chlorobenzaldehyde. The intermediate imidyl chlorides have been isolated in both cases and other evidence with respect to the mechanism obtained.

It is postulated that the reaction can be explained by the following mechanism. The ketoxime (I) reacts with phosphorus pentachloride to form an ester (II) which undergoes a Beckmann rearrangement to form an intermediate (III). An imidyl chloride (IV) is formed from this by the loss of phosphorus oxychloride. This imidyl chloride is reduced by stannous chloride and separates as the stannous chloride, hydrogen chloride double salt of a Schiff base (V) which upon hydrolysis forms the desired aldehyde (VI) and a primary amine (VII).



In support of this mechanism the following experimental facts are presented. Hydrochloric acid and phosphorus oxychloride are formed in the reaction. The imidyl chlorides formed from diphenyl ketoxime and from *syn*-*p*-chlorophenyl phenyl ketoxime were isolated and were shown to be identical with the imidyl chlorides obtained from the corresponding anilides. Samples of both of the isolated imidyl chlorides were converted to the corresponding aldehydes by the

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[1] From a dissertation submitted by R. E. Pyle to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1946.

[2] Bachmann and Cronyn, *J. Org. Chem.*, **8**, 456 (1943).