[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

Monochloroamine with Organolithium and Zinc Compounds

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The reactions of monochloroamine and other haloamines with organometallic compounds, particularly Grignard reagents, have been studied in this Laboratory.[1] In only one case which has been reported previously have organometallic compounds other than Grignard reagents been used.[2] In that work alkylchloroamines were found to form amines with zinc alkyls in petroleum ether solution in yields approximately twice as large as those formed with the corresponding Grignard reagents. Since monochloroamine has thus far given the best yields of amines with Grignard reagents, it was of interest to determine whether the yields of primary amines from this compound could be increased materially by the use of zinc alkyls. By reference to Table I it will be observed that no increases were obtained.

Nitrogen trichloride[3] has been shown to form relatively small yields of primary and secondary amines with Grignard reagents. The reaction of this compound with zinc alkyls has now been carried out and the results are given in Table I for comparison. The percentage yields of amines are not significantly different from those with Grignard reagents. There was no definite evidence of the formation of tertiary amines. Some nitrogen gas was evolved during the reaction.

TABLE I

PERCENTAGE YIELDS OF AMINES AND AMMONIA FROM ZINC ALKYLS WITH MONOCHLOROAMINE AND NITROGEN TRICHLORIDE

Organometallic compound	Reactant	Yield RNH_2, %	Yield R_2NH, %	Yield NH_3, %
$(C_2H_5)_2Zn$	NH_2Cl	46		47
$(n\text{-}C_3H_7)_2Zn$	NH_2Cl	57		41
C_2H_5MgCl	NH_2Cl	57		39
$n\text{-}C_3H_7MgCl$	NH_2Cl	58		37
$(C_2H_5)_2Zn$	NCl_3	17	8	38
$(n\text{-}C_3H_7)_2Zn$	NCl_3	8	5	27
C_2H_5MgCl	NCl_3	29	6	22
$n\text{-}C_4H_9MgCl$	NCl_3	37	5	15

Within recent years methods for the preparation of organolithium compounds have been improved[4] and since the direct replacement of lithium in such a compound by the amino group might be of some value, the reaction of monochloroamine with several organolithium compounds was included in this study.

The reactions were carried out under three sets of conditions. In the first set (A) equimolecular quantities were used, the monochloroamine solution being added to the organolithium compound at 0°. In the second series (B) three moles of organolithium compound was used for each mole of monochloroamine. The same order of addition was followed and the temperature was again approximately 0°. In the third set (C) the reaction temperature was about $-50°$, the organolithium compound was added to the monochloroamine solution, three moles of lithium compound to each of chloroamine again being used. The results are given in Table II. For comparison the yields from some corresponding Grignard reagents are included.

TABLE II

PERCENTAGE YIELDS OF AMINES AND AMMONIA FROM MONOCHLOROAMINE AND ORGANOLITHIUM COMPOUNDS

Organometallic compound	A Yield, % RNH_2	A Yield, % NH_3	B Yield, % RNH_2	B Yield, % NH_3	C Yield, % RNH_2	C Yield, % NH_3
C_6H_5Li	3	48	10	42	33	37
$n\text{-}C_4H_9Li$	7	54	20	59	39	33
$p\text{-}CH_3C_6H_4Li$	5	48	16	24		
CH_3Li	4	90				
C_6H_5MgCl			27	68		
$n\text{-}C_4H_9MgCl$			59	39		

Experimental

Monochloroamine.—The method of preparation was essentially that described by Coleman and Forrester.[5] The ethereal solutions of monochloroamine were dried either with calcium chloride or by cooling in dry ice and acetone and filtering preferably without exposure to moist air. Samples for analysis were reduced with sodium bisulfite and the nitrogen and chlorine determined as previously described.

Zinc Alkyls.—Diethylzinc and di-*n*-propylzinc were prepared by Noller's[6] method from zinc alloy and alkyl iodides. After being distilled from the reaction mixtures the zinc alkyls were redistilled and collected in the flask in which the reaction with the haloamine was to be carried out. Petroleum ether (b. p. 90–100°) was placed in the receiver before the distillation.

Nitrogen Trichloride.—The preparation and analysis of nitrogen trichloride has been given in other papers.[3]

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(1) (a) Coleman and co-workers, THIS JOURNAL, **50**, 1193 (1928); (b) **51**, 567 (1929); (c) **55**, 3001 (1933); (d) **55**, 2075 (1933); (e) **56**, 965 (1934); (f) **58**, 27 (1936).

(2) Coleman, Anderson and Hermanson, *ibid.*, **56**, 1381 (1934).

(3) Coleman, Buchanan and Paxson, *ibid.*, **55**, 3669 (1933).

(4) Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

(5) Coleman and Forrester, *ibid.*, **58**, 27 (1936).

(6) Noller, *ibid.*, **51**, 594 (1929).

Reactions of Monochloroamine and Nitrogen Trichloride with Zinc Alkyls.—The cold solution of the monochloroamine or nitrogen trichloride was added slowly (thirty to forty-five minutes) with stirring to an excess of the petroleum ether solution of the zinc alkyl. The zinc alkyl solution previously had been cooled to −30° and was kept at that temperature during the reaction. The solution of monochloroamine or nitrogen trichloride was introduced through a vacuum jacketed delivery tube. Air pressure was used to force the cold solution of haloamine into the reaction flask from the graduated cylinder in which it was kept after preparation. In all cases a white precipitate was formed during the addition. The reaction mixture was allowed to stand overnight. It was then cooled with a freezing mixture and decomposed by adding water and dilute sulfuric acid. The two layers were separated and the ether layer was washed with dilute acid. The aqueous layers were combined, neutralized with sodium hydroxide, and steam distilled into dilute hydrochloric acid. About two liters or more of the distillate was collected and evaporated on the steam-bath. The residue was transferred to a weighed crystallizing dish and dried to constant weight. The possibility of loss of any reaction product in the ether layer that was discarded was tested several times by steam distillation and subsequent evaporation. The amount found present in the ether layer was negligible.

Separation of Amines.—After the crude reaction product was dried to constant weight the amines and ammonium chloride were separated by the use of *n*-butyl alcohol. The amines from the nitrogen trichloride reaction were further separated by a modification of Hinsberg's method as described by Coleman.[1c]

Phenyllithium and *p*-Tolyllithium.—These compounds were prepared in ether as described by Gilman, Zoellner and Selby.[4]

Reaction of Monochloroamine with Phenyllithium.—The reactions of monochloroamine with phenyllithium were carried out under three sets of conditions.

A. Under the first set of conditions equimolecular amounts of phenyllithium and monochloroamine were used. The reaction flask containing the phenyllithium was cooled with ice and water and the ether solution of monochloroamine was forced slowly into the flask through a closed system by means of dry nitrogen. The ether solution of monochloroamine was maintained at a temperature of about −50° with acetone and dry ice. The reaction mixture was stirred throughout the addition. The time of addition was approximately one hour. After allowing the mixture to stand for two hours, it was decomposed with water and acid and the products isolated as described for the reaction with zinc alkyls.

B. Under the second set of conditions three moles of phenyllithium was used for each mole of monochloroamine, the monochloroamine being added to the phenyllithium solution. The reaction flask was again cooled only with ice and water.

C. Under the third set of conditions the phenyllithium was added to the monochloroamine, both solutions being cooled to about −50°. Approximately three moles of phenyllithium was used for each mole of monochloroamine.

***n*-Butyllithium.**—In a 500-ml. flask connected to a condenser bearing a calcium chloride tube were placed 300 ml. of dry benzene and 4.59 g. of lithium in the form of wire. Nitrogen dried with concentrated sulfuric acid was passed through the flask. *n*-Butyl chloride (0.3 mole) was added and the reaction mixture heated at about 55° on a hot plate for sixteen hours. Slightly better yields were obtained if a number of glass beads were added and the mixture shaken occasionally during the reaction. At the end of sixteen hours the reaction mixture was cooled to room temperature and filtered through glass wool in an atmosphere of nitrogen into the flask to be used for the reaction with monochloroamine. Aliquot portions of the solution were taken for analysis. The yield was 70–75%.

In the reactions where it was necessary to cool the butyllithium considerably below zero, the benzene was diluted with anhydrous ether before filtering.

Monochloroamine with *n*-Butyllithium.—These reactions were carried out under three sets of conditions similar to those used with phenyllithium. In B and C the reaction temperatures were a little higher than in the reactions with phenyllithium on account of the presence of benzene in the *n*-butyllithium solution.

***p*-Tolyllithium with Monochloroamine.**—The reaction of monochloroamine with *p*-tolyllithium was carried out under two sets of conditions corresponding to A and B of the phenyllithium procedure.

Methyllithium.—This compound was prepared in ether using methyl iodide and lithium. A better method for the preparation of methyllithium was reported by Gilman, Zoellner, Selby and Boatner[7] shortly after the work with methyllithium had been completed. Since our interest was not primarily in the preparation of methyllithium, the work was not repeated.

Methyllithium with Monochloroamine.—The reaction was carried out under the conditions described for procedure (A) of the phenyllithium reaction.

In all of the reactions reported the products were identified by the preparation of derivatives.

Summary

1. Monochloroamine reacts with zinc alkyls and with alkyl and aryllithium compounds to form primary amines and ammonia.

2. With organolithium compounds the best yields of primary amines are formed when the solution of the organolithium compound is added to monochloroamine at relatively low temperatures.

3. Nitrogen trichloride reacts with zinc alkyls in petroleum ether to form primary amines, secondary amines, ammonia and nitrogen.

4. In general the percentage yields of amines from zinc alkyls and organolithium compounds are no greater than those from the corresponding Grignard reagents.

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[7] Gilman, Zoellner, Selby and Boatner, *Rec. trav. chim.*, **54**, 584 (1935).