[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF LYONS, FRANCE, AND THE STATE UNIVERSITY OF IOWA]

The Reaction of Alkylchloroamines with Grignard Reagents

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Monochloroamine[2] has been shown to react with Grignard reagents to form primary amines. The present work was undertaken with the thought that this reaction might be extended to the alkylchloroamines and thus serve as a method for the preparation of secondary and tertiary amines.

Tcherniak[3] in a study of the structure of ethyldichloroamine reported the formation of a small quantity of triethylamine in the reaction of this compound with diethylzinc. Buylla,[4] however, did not obtain triethylamine in the reaction of diethyliodoamine with ethylmagnesium bromide, and Le Fèvre[5] states that no tertiary amines were formed in the reactions of dimethylchloroamine, diethylchloroamine and 1-chloropiperidine with phenylmagnesium bromide.

The alkylmonochloroamines can be prepared in ethereal solution in excellent yields from the corresponding amines and sodium hypochlorite by a modification of the method used by Berg.[6] The alkyldichloroamines were prepared by him from the amines and bleaching powder according to the method of Tcherniak.[7] These can however be prepared by the sodium hypochlorite method in very good yields.

Since with monochloroamine the best yields of amines were obtained with organomagnesium chlorides, reagents prepared from chlorides only were used in the present work. Of all the reagents studied with monochloroamine benzylmagnesium chloride forms the highest yield of amine, about 90% of the theoretical. This reagent was therefore used more frequently than others.

The reaction was studied with the three types of alkylchloroamines, $RNCl_2$, R_2NCl and $RNHCl$. Chloroamines of the first type $RNCl_2$, from which tertiary amines might normally be expected, form both secondary and tertiary amines. With chloroamines of the type R_2NCl only small yields of tertiary amines are formed. Variation in the temperature at which the reaction is carried out has very little effect on the percentage yield. With all three types a considerable proportion of the chloroamine is reduced and obtained as the corresponding amine upon hydrolysis of the reaction mixture.

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(1) Fellow of the John Simon Guggenheim Memorial Foundation.

(2) Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928); Coleman and Yager, *ibid.*, **51**, 567 (1929).

(3) Tcherniak, *Bull. soc. chim.*, [2] **25**, 166 (1876).

(4) Buylla, *Rev. real. acad. cien.* (Madrid), **9**, 635,718 (1910).

(5) Le Fèvre, *J. Chem. Soc.*, 1745 (1932).

(6) Berg, *Ann. chim.*, [7] **3**, 315 (1894).

(7) Tcherniak, *Bull. soc. chim.*, [2] **25**, 166 (1876).

The results with the three types of chloroamines and several Grignard reagents are given in Tables I, II and III.

In most reactions the entire amount of chloroamine used was not represented in the products isolated. Traces of neutral nitrogen compounds were found but not in sufficient quantity to account for the balance of the chloroamine.

TABLE I

PERCENTAGE YIELDS OF PRIMARY, SECONDARY AND TERTIARY AMINES FROM ALKYLDICHLOROAMINES AND GRIGNARD REAGENTS

	$C_2H_5NCl_2$			CH_3NCl_2		
Reagents	RNH_2	R_2NH	R_3N	RNH_2	R_2NH	R_3N
n-C_3H_7MgCl	52	12	8			
n-C_4H_9MgCl	36	11	9	43	22	5
n-$C_5H_{11}MgCl$	34	12	8			
$C_6H_5CH_2MgCl$	28	19	6	43	25	3

TABLE II

PERCENTAGE YIELDS OF SECONDARY AND TERTIARY AMINES FROM DIALKYLCHLOROAMINES AND GRIGNARD REAGENTS

		$C_6H_5CH_2MgCl$		n-C_4H_9MgCl	
Chloroamines	Temp. of reaction, °C.	R_2NH	R_3N	R_2NH	R_3N
$(CH_3)_2NCl$	5	95	5		
$(C_2H_5)_2NCl$	−10	90	5		
$(C_2H_5)_2NCl$	5	89	5		
$(C_2H_5)_2NCl$	40	83	5		
$(C_2H_5)_2NCl$	70	76	7		
$(n$-$C_3H_7)_2NCl$	5	78	5		
$(n$-$C_4H_9)_2NCl$	5			85	4

TABLE III

PERCENTAGE YIELDS OF PRIMARY AND SECONDARY AMINES FROM MONOALKYLMONOCHLOROAMINES AND GRIGNARD REAGENTS

	$C_6H_5CH_2MgCl$		n-C_4H_9MgCl	
Chloroamines	RNH_2	R_2NH	RNH_2	R_2NH
CH_3NHCl	70	14	72	14
C_2H_5NHCl	75	12		
C_2H_5NHCl[a]	..	16		

[a] In this solution the chlorine to nitrogen ratio was 1.3 indicating the presence of some ethyldichloroamine.

The mixtures of amines were separated by a modification of Hinsberg's[8] method and by fractional distillation when that was practicable. The results obtained by the two methods were in close agreement.

The percentage yields are calculated on the basis of the chloroamines. The Grignard reagents were always used in excess.

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He also wishes to express his appreciation to Professor Victor Grignard,

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(8) Hinsberg, *Ber.*, **38**, 906 (1905).

in whose laboratory the major portion of this work was carried out, for his kindness and for the many suggestions made during the course of the work.

Experimental

Preparation of Alkylchloroamines.—A solution of sodium hypochlorite containing about one mole per liter was prepared by passing chlorine into a cold solution of sodium hydroxide until the precipitate of yellow oxide formed by adding a little mercuric chloride just dissolved. The concentration of the solution was determined by titration.

Dialkylmonochloroamines.—The method used is illustrated by the preparation of diethylchloroamine. A cold solution of 21.9 g. (0.2) mole of diethylamine hydrochloride in about 80 cc. of water was added slowly (3–5 min.) to 240 cc. of a cold solution of sodium hypochlorite containing 0.25 mole. Before the addition 200 cc. of ether and about 20 g. of ice were added to the hypochlorite solution which was surrounded by ice water. During the addition the mixture was stirred. After thorough mixing the two layers were separated and the aqueous layer extracted twice with 100-cc. portions of ether. The ethereal solutions were combined and washed with 25 cc. of cold 8% sulfuric acid, then with 25 cc. of 5% sodium hydroxide, dried with calcium chloride and filtered. The calcium chloride was washed with a little anhydrous ether. The final volume of the ethereal solution was 396 cc. Analysis for nitrogen showed it to contain 0.188 mole of diethylchloroamine, which is 94% of the theoretical yield. Analysis for chlorine indicated a slight excess. The chlorine to nitrogen ratio was 1.04. The yield obtained in this preparation is typical of the other dialkylchloroamines prepared.

Alkyldichloroamines.—The procedure used was essentially the same as that described for diethylchloroamine. About 2.2 moles of sodium hypochlorite was used for each mole of amine. The ethereal solution was washed with 30% sulfuric acid and 5% sodium hydroxide. The yield was usually between 80 and 90%, and the chlorine:nitrogen ratio approximately 2.0.

Monoalkylmonochloroamines.—In order to obtain products in which the chlorine:nitrogen ratio was approximately 1.0 it was necessary to use the amine in 10 to 15% excess. The solution of the amine hydrochloride was made slightly alkaline to litmus by adding dilute sodium hydroxide. The sodium hypochlorite solution was also made slightly alkaline to mercuric chloride. The usual procedure for mixing and extraction with ether was followed. The ethereal solution was dried with calcium chloride. The yield was usually between 80 and 85%.

Chloroamines of this type cannot be washed with acid on account of the decomposition caused.[9] It is possible therefore that there is present in the solution a little of the corresponding amine together with about an equal quantity of the dichloroamine.

Analysis of the Chloroamine Solutions.—The usual method of analysis was practically the same as that described for monochloroamine.[2] In the analysis for chlorine the ether was separated from the sodium sulfite solution by gentle warming. In several cases the sodium ethylate method described by Berg[9] was also used. The results obtained by the two methods were in close agreement.

Preparation of the Grignard Reagents.—The methods used in the preparation and analysis of the Grignard reagents were essentially those given by Gilman and his co-workers.[10]

Reaction of Alkylchloroamines with Grignard Reagents.—All reactions with the exception of three of those with dialkylchloroamines were carried out at about 5°. The cold ethereal solution of the chloroamine was added slowly (45-60 min.) through a

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(9) Berg, *Ann. chim.*, [7] **3**, 315 (1894).

(10) Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923); Gilman and Meyers, *ibid.*, **45**, 159 (1923); Gilman and Zoellner, *ibid.*, **50**, 425 (1928).

separatory funnel to the Grignard reagent which was stirred continuously. A precipitate formed at once which became quite heavy near the end of the reaction.

For the hydrolysis of the reaction mixture the flask was surrounded with ice water and about 50 cc. of water and a slight excess of dilute sulfuric acid were slowly added while the mixture was stirred. When the magnesium hydroxide and any unchanged magnesium had dissolved the two layers were separated and the ethereal layer washed with a little dilute acid. This was added to the first aqueous layer and the solution transferred to a 2-liter flask. Excess sodium hydroxide was added and the mixture steam distilled into dilute hydrochloric acid. From two to four liters were collected depending on the character of the amines distilled. The distillate was evaporated to dryness on a steam-bath and dried to constant weight in a vacuum desiccator. In those cases in which the acid salts of the amines produced in the reaction might be difficultly soluble in water the reaction mixture after hydrolysis was distilled with steam without separating the ethereal layer.

The alkaline residues in the flask after steam distillation were tested for the presence of amines difficultly volatile with steam. The ethereal layers were tested for neutral nitrogen compounds. Traces of these were sometimes found but not in sufficient quantity to identify.

Separation of the Amine Mixtures.—Several methods for separating the mixtures of amines in the reaction products were tried. The one finally adopted was a modification of Hinsberg's[11] method using benzenesulfonyl chloride. The separation of the sulfonyl derivatives of the primary and secondary aliphatic amines on the basis of the solubility of the former in sodium or potassium hydroxide solution was not satisfactory on account of hydrolysis of the salt. This was particularly true when ether was used for extraction of the sulfonyl derivative of the secondary amine. The separation was therefore carried out by adding pieces of metallic sodium to an anhydrous ethereal solution of the two derivatives.

This method when applied to known mixtures of primary, secondary and tertiary amines did not give 100% recovery of the amines used, although the results were consistent for amines of the same general type. When applied to unknown mixtures therefore several separations were first made with mixtures as nearly like the unknown as possible and the average results used as correction factors for the separation of the unknown mixtures. On analysis the percentages of nitrogen of several of the products obtained by this method of separation were found to be in fairly close agreement with the theoretical values.

In addition to the separations by the benzenesulfonyl chloride method the products were separated by fractional distillation of the amines whenever the relative boiling points were such as to make this practicable. Some physical constants of the amines isolated are given in Table IV.

TABLE IV

PHYSICAL PROPERTIES OF AMINES

	B. p. (corr.), °C.[a]	n_D^{20}
Ethyl-*n*-amylamine	134–136° (745 mm.)	1.4135
Methylbenzylamine	77.5–78° (17 mm.)	1.5236
Dimethylbenzylamine	98–99° (24 mm.)	1.5157
Ethylbenzylamine	88.5–89° (18 mm.)	1.5134
Diethylbenzylamine	96–98° (17 mm.)	1.4995
Di-*n*-propylbenzylamine	120–122° (17 mm.)	1.4910

[a] The boiling points at atmospheric pressure of all but ethyl-*n*-amylamine have been previously reported.

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(11) Hinsberg, *Ber.*, **38**, 906 (1905).

Summary

Alkyldichloroamines react with Grignard reagents to form primary, secondary and tertiary amines.

Dialkylchloroamines form secondary and tertiary amines with Grignard reagents, and monoalkylmonochloroamines form primary and secondary amines.

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The Relative Stability of Penta-arylethanes. II.[1] Reactions of Penta-arylethanes

BY W. E. BACHMANN

The remarkable properties of Gomberg's hexaphenylethane have shown clearly that substitution of phenyl groups for the hydrogen atoms of ethane weakens the ethane carbon–carbon bond; with complete substitution, rupture of the bond occurs at room temperature and free radicals are formed. Of the polyarylethanes containing less than six aryl groups pentaphenylethane has been found to have a weak union between the ethane carbon atoms. Pentaphenylethane is stable at room temperature but undergoes decomposition at 180° as was first observed by Gomberg and Cone,[2] the discoverers of the compound, and this decomposition has been shown to consist of a rupture of the ethane carbon–carbon bond.[3] We have now investigated a number of penta-arylethanes in order to ascertain the effect of introducing into the penta-arylethane molecule those groups that have been found to exert a great influence in promoting dissociation of hexa-arylethanes. It was surmised that penta-arylethanes containing naphthyl, biphenyl and anisyl groups would be nearer in properties to the hexa-arylethanes than is pentaphenylethane itself.

Recently[1] we described a method of preparing penta-arylethanes of any desired structure. We found that in the region of the melting point all of the penta-arylethanes that were prepared suffered decomposition and were oxidized by the oxygen of the air. A number of methods have now been employed in order to obtain a comparison of the relative stabilities of the ethane carbon–carbon bonds.

Formation of Color.—Gomberg and Cone[2] observed the development of a yellow color when solid pentaphenylethane was heated. Schlenk and Herzenstein[3] noticed a similar color on heating a solution of pentaphenylethane in ethyl benzoate and they attributed the color to the forma-

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[1] Bachmann, THIS JOURNAL, **55**, 2135 (1933).

[2] Gomberg and Cone, *Ber.*, **39**, 1466 (1906).

[3] Tschitschibabin, *ibid.*, **40**, 367 (1907); Schlenk and Herzenstein, *ibid.*, **43**, 3542 (1910).