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

The Reaction of Nitrogen Trichloride with Grignard Reagents

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In a study of the reaction of boron trichloride and other chlorides with organomagnesium halides Strecker[1] tried the reaction of nitrogen trichloride with ethylmagnesium bromide and phenylmagnesium bromide and reported that only ammonium salts were formed. Le Fèvre[2] later obtained chlorobenzene but no amines from the reaction of phenylmagnesium bromide with nitrogen trichloride.

It has been shown in this Laboratory that monochloroamine[3] reacts with organomagnesium halides to form primary amines and ammonia. The similarity of nitrogen trichloride to monochloroamine suggested that it might also react with Grignard reagents to form amines.

The yields of amines obtained from Grignard reagents and monochloroamine vary greatly with the halogen present in the reagent, decreasing in the order, chlorine, bromine, iodine. It seemed probable, therefore, that if amines were formed in the nitrogen trichloride experiments mentioned they were formed in only small amounts and were overlooked in the relatively large amounts of ammonia. The results of the work here reported indicate that this was the case.

The reaction of nitrogen trichloride with Grignard reagents is similar to that of monochloroamine and was carried out in much the same manner. Primary amines, secondary amines, ammonia and nitrogen are the principal products. The reactions for the formation of the amines and ammonia may be represented by equations similar to those given for the reaction with monochloroamine. The results obtained with fifteen Grignard reagents are given in Table I. The percentage yields are based upon the nitrogen trichloride since the Grignard reagents were always used in excess.

The yields of primary amines are several times as large as the yields of secondary amines. This was to be expected in the light of the results of the reaction of alkyldichloroamines[4] with Grignard reagents in which the yields of secondary amines were never more than twenty-five per cent. In the products of only one reaction, that with benzylmagnesium chloride, was a tertiary amine definitely identified.

A variation in the yields of amines similar to that with monochloroamine with reagents prepared from chlorides, bromides, and iodides was observed in this work. It is probable that this variation is characteristic of the reaction of Grignard reagents with halogen derivatives of nitrogen com-

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(1) Strecker, *Ber.*, **43**, 1131 (1910).

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

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

(4) Coleman, *ibid.*, **55**, 3001 (1933).

TABLE I

PERCENTAGE YIELDS OF PRIMARY AND SECONDARY AMINES AND AMMONIA FROM NITROGEN TRICHLORIDE AND GRIGNARD REAGENTS

Reagent	X = Cl			X = Br			X = I		
	RNH_2	R_2NH	NH_3	RNH_2	R_2NH	NH_3	RNH_2	R_2NH	NH_3
C_2H_5MgX	29	6	22	16	2	30	3	1	26
n-C_4H_9MgX[a]	37	5	15	21	2	20	4	1	31
n-$C_5H_{11}MgX$	21	5	21						
i-C_3H_7MgX	23	2	23						
s-C_4H_9MgX	23	3	26	10	1	31	3	1	26
t-C_4H_9MgX	30	2	15						
C_6H_5MgX	4	1	38						
$C_6H_5CH_2MgX$[b]	32	7	8						
$C_6H_5CH_2CH_2MgX$	20	2	27						

[a] The nitrogen gas given off during the reaction with *n*-butylmagnesium chloride was determined and found to correspond to 37% of the nitrogen trichloride used.

[b] In this reaction a trace of tribenzylamine was formed.

pounds in which the halogen is attached directly to nitrogen. The yields of amines are, in general, considerably smaller than the yields from monochloroamine. The formation of large amounts of nitrogen observed in this work is not characteristic of the reaction with monochloroamine.

A number of methods for the analysis of nitrogen trichloride have been used by the different investigators who have worked with this compound. Some have used more than one method. Noyes,[5] for example, has compared the hydrochloric acid method for nitrogen with the sodium sulfite method and reports that the former gives slightly higher results. There has been, however, no systematic comparison of several methods for both nitrogen and chlorine to determine their relative accuracy.

Both for the purpose of determining the best method for use in this work and because the same or very similar methods are used in the analysis of many halogen derivatives of nitrogen compounds in which halogen is attached directly to nitrogen, such a comparison has been made, the results of which are given in the experimental part.

Experimental

Preparation of Nitrogen Trichloride.—The solutions of nitrogen trichloride were prepared by a slight modification of the method previously described.[6] For the reactions with Grignard reagents ether was used as the solvent. For the comparison of methods of analysis carbon tetrachloride was the solvent. With ether as the solvent it was necessary on account of its volatility and solubility to add a little larger volume than that desired in the final solution. The reaction flask was also fitted with a reflux condenser. The tube through which the chlorine was introduced extended just to the interface between the aqueous and ethereal layers. A normal solution of ammonium nitrate was the source of nitrogen. Chlorine was either prepared as needed from sodium dichromate and hydrochloric acid or drawn from a cylinder.

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(5) Noyes, THIS JOURNAL, **42**, 2173 (1920).

(6) Coleman with Noyes, *ibid.*, **43**, 2211 (1921); Coleman and Howells, *ibid.*, **45**, 3084 (1923).

Reaction of Nitrogen Trichloride with Grignard Reagents.—Ethereal solutions of nitrogen trichloride containing about 0.10 mole in 300 cc. of solution were added slowly to the Grignard reagents containing about 0.40 mole in 400 cc. of solution. The reaction was very similar to that of monochloroamine or the alkylchloroamines with Grignard reagents. The procedure followed in carrying out the reaction and separating the products was the same as that used with alkylchloroamines.[4]

Comparison of Methods of Analysis of Nitrogen Trichloride.—In this comparison five methods were studied. The sodium sulfite method of Bray and Dowell[7] was followed very closely. The slightly modified[8] hydrochloric acid method of Noyes[8] was used for nitrogen together with the determination of chlorine in the same sample by passing the liberated chlorine into potassium iodide solution. The sulfur dioxide method of Chapin,[9] slightly modified, was used for both nitrogen and chlorine. Assuming that sodium bisulfite might combine the advantages of both sodium sulfite and sulfur dioxide, a method using this reagent was included. The method in which nitrogen trichloride is added directly to potassium iodide solution was tried but was found to give results so variable that they were not included.

In Table II are shown the results of a typical series of analyses in triplicate for nitrogen and chlorine by each of the four methods.

TABLE II

ANALYSIS OF A SOLUTION OF NITROGEN TRICHLORIDE BY FOUR METHODS

Results are expressed in milligram atoms per cubic centimeter of solution

Reagents	Nitrogen, mg. atoms	Chlorine, mg. atoms	Ratio Cl/N	Reagents	Nitrogen, mg. atoms	Chlorine, mg. atoms	Ratio Cl/N
HCl and KI	0.413	1.260	3.05	SO_2	0.418	1.259	3.02
	.415	1.264	3.04		.420	1.257	3.00
	.410	1.258	3.06		.417	1.262	3.00
Na_2SO_3	.404	1.261	3.09	$NaHSO_3$	.417	1.260	3.02
	.405	1.263	3.11		.417	1.265	3.03
	.406	1.263	3.09		.417	1.258	3.01

The fact that the chlorine to nitrogen ratio is not exactly three in each case is not necessarily significant. Solutions prepared as described sometimes have, shortly after preparation, a chlorine to nitrogen ratio which is slightly less than three. This usually increases due to slow decomposition and loss of nitrogen.

It is evident that all four methods are fairly satisfactory. The values for chlorine are practically the same throughout. The values for nitrogen by the sodium sulfite method are slightly lower than those obtained by the other three methods.

Summary

Nitrogen trichloride reacts with Grignard reagents to form primary amines, secondary amines, ammonia and nitrogen. In at least one reaction, that with benzylmagnesium chloride, a trace of a tertiary amine is formed.

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(7) Bray and Dowell, THIS JOURNAL, **39**, 896 (1917).

(8) Coleman and Craig, *ibid.*, **50**, 1816 (1928); Noyes, *ibid.*, **42**, 2173 (1920); Noyes, *ibid.*, **50**, 2902 (1928).

(9) Chapin, *ibid.*, **51**, 2112 (1929).

The yields of primary amines are several times as large as the yields of secondary amines. The total yield of amines in any reaction is however less than the yield of primary amine in the reaction of monochloroamine with the same reagent.

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The Course of Addition of Sodium Enol Alkylmalonic Esters to Phenyl Isothiocyanate

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It has been shown that sodium enol malonic ester adds readily to phenyl isothiocyanate to give the sodium enolate of the monothioanilide of methane tricarboxylic ester.[1] Ruhemann[2] found that on treating this sodium enolate with benzyl chloride, a thiobenzyl ether was obtained, and he considered that this fact supported the original formulation of the addition reaction in which Na- and -CH(COOEt)$_2$ were written as addendum components. According to this view of the reaction mechanism, Ruhemann expected that the sodium enolates of monoalkyl malonic esters would also add to phenyl isothiocyanate, but he found that benzylmalonic ester was recovered unchanged from the reaction between sodium enol benzylmalonate and phenyl isothiocyanate in alcoholic solution, the phenyl isothiocyanate being converted completely into the enolate of phenyl thiourethan by the addition of sodium ethoxide.

Worrall[3] states that by the action of sodium enol α-ethylacetoacetic ester on phenyl isothiocyanate he obtained an addition product, but he did not prove the composition of this compound.

Phenyl isocyanate readily combines with enolates such as sodium enol malonic ester, but addition of sodium enol alkylmalonic esters to phenyl isocyanate does not take place, and the phenyl isocyanate is polymerized under the conditions of the reaction.[4] Phenyl isothiocyanate does not polymerize under the conditions of these reactions and for this reason its action toward compounds of sodium enol alkyl malonic ester type was examined. Moreover, since the monothioanilide of methane tricarboxylic ester gives a stable thio ether, the possibility of alkyl group migration might be expected to exhibit itself in this reaction.

In alcohol-free ether, sodium enol malonate adds to phenyl isothiocyanate to give the theoretical yield of the sodium enolate of the monothioanilide of methane tricarboxylic ester. This sodium derivative with methyl iodide gives a thiomethyl ether, but this result of alkylation is no

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[1] Michael, *J. prakt. Chem.*, **35**, 450 (1887).

[2] Ruhemann, *J. Chem. Soc.*, **93**, 621 (1908).

[3] Worrall, THIS JOURNAL, **40**, 415 (1918).

[4] Michael, *Ber.*, **38**, 22 (1905).