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

THE FORMATION OF PRIMARY AMINES FROM GRIGNARD REAGENTS AND MONOCHLORO-AMINE. II

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In a recent[1] study of the reaction of monochloro-amine with Grignard reagents, it was found that primary amines and ammonia are formed according to the following reactions

$$RMgX + NH_2Cl = RNH_2 + MgXCl \quad (1)$$
$$RMgX + NH_2Cl = RCl + MgXNH_2 \quad (2)$$

The reagents used, with the exception of phenylmagnesium chloride, bromide and iodide, were prepared from primary halogen compounds.

Since some of the methods used for the preparation of primary amines cannot be used for amines in which the amino group is attached to a secondary or a tertiary carbon atom, the monochloro-amine reaction has been studied with Grignard reagents prepared from secondary and tertiary halogen compounds. The course of the reaction and the yields of amines and ammonia are much the same as with the primary reagents. The variation in yields with chlorides, bromides and iodides was again observed. The results obtained with the fifteen reagents thus far used are shown in Table I.

TABLE I

PERCENTAGE YIELDS OF AMINES AND AMMONIA FROM MONOCHLORO-AMINE AND GRIGNARD REAGENTS

	X = Cl		X = Br		X = I	
	% yields		% yields		% yields	
Reagents	RNH_2	NH_3	RNH_2	NH_3	RNH_2	NH_3
Iso-C_3H_7MgX	65.5	29.5	37.2	54.7	9.0	79.0
Sec.-C_4H_9MgX	70.0	20.0	51.1	38.9	15.8	74.13
Sec.-$C_5H_{11}MgX$[a]	71.7	19.0	31.6	61.9	13.7	79.13
Tert.-C_4H_9MgX	60.2	39.0	20.24	79.7	4.8	81.4
Tert.-$C_5H_{11}MgX$	66.2	30.9	14.25	79.2	2.0	80.2

[a] The secondary amyl halides used were the symmetrical compounds prepared from diethylcarbinol.

The monochloro-amine was prepared by a further slight modification of the method of Marckwald and Wille.[2] Instead of distilling the aqueous solution under diminished pressure the monochloro-amine was extracted directly with ether.

Since it was essential to have an excess of Grignard reagent present, the organomagnesium halide solutions were analyzed by titration with

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[1] Coleman and Hauser, THIS JOURNAL, **50**, 1193 (1928).

[2] Marckwald and Wille, *Ber.*, **56**, 1319 (1923).

acid as described by Gilman, Wilkinson, Fishel and Meyers[3] before adding the monochloro-amine.

The method of carrying out the reaction and isolating the products was very similar to that described by Coleman and Hauser.[1] The products obtained as the amine hydrochlorides and ammonium chloride were analyzed and derivatives prepared.

Work is being continued with other chloro-amines and with nitrogen trichloride with the thought of preparing secondary and tertiary amines. The work of Buylla[4] with iododiethylamine and Strecker[5] with nitrogen trichloride might indicate, however, that Reaction 2 predominates in these cases.

Experimental

Preparation of Monochloro-amine.—Two hundred cc. of cold sodium hypochlorite solution prepared as described by Marckwald and Wille[2] was added slowly with shaking to 200 cc. of 1 *N* ammonium hydroxide cooled to 0° or below. The monochloro-amine was extracted first with a 100-cc. portion of cold ether and then with three 50-cc. portions. The four extractions were combined and dried for a short time with calcium chloride. The yield of monochloro-amine by this method is somewhat less than that obtained by the distillation method described by Coleman and Hauser[1] using carbon dioxide snow around the receiver. The method is, however, much simpler and the yield is better than by the distillation method if the receiver is cooled with only ice and salt.

Analysis of the Monochloro-amine Solution.—The method used was that previously described[1] with a slight modification of procedure in the analysis for nitrogen. After adding the sample to the hydrochloric acid, the flask was stoppered and shaken vigorously for a short time. It was then opened and the chlorine and ether driven off by gentle warming. With the dilute solutions used the results were as satisfactory as those obtained by allowing the hydrochloric acid mixture to stand for several hours. For concentrated solutions of monochloro-amine the method used by Coleman and Craig[6] for concentrated solutions of nitrogen trichloride may be used.

Preparation of the Grignard Reagents.—The methods used in the preparation and analysis of the Grignard reagents were essentially those described by Gilman and his co-workers.[3,7]

Reaction of Monochloro-amine with Grignard Reagents

The reactions of monochloro-amine with the Grignard reagents were carried out as previously described.[1] After the excess Grignard reagent had been decomposed with water, however, the basic mixture was always brought into solution with acid before adding alkali and distilling with steam.

The purity of the hydrochloride was determined by analysis and the amines were identified by the preparation of derivatives. Mixed melting points were taken with known compounds when these were available.

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[3] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[4] Buylla, *Rev. real. acad. cien. Madrid*, 9, 635–653, 718–734 (1910).

[5] Strecker, *Ber.*, **43**, 1133 (1910).

[6] Coleman and Craig, THIS JOURNAL, **50**, 1816 (1928).

[7] Gilman and Meyers, *ibid.*, **45**, 159 (1923); Gilman and Zoellner, *ibid.*, **50**, 425 (1928).

Benzoyl-*tert.*-amylamine.—The benzoyl derivative was prepared from the amine hydrochloride by the Schotten-Baumann method. After recrystallization from ligroin the melting point was 93–94° (uncorr.).

Anal. Subs., 0.1982, 0.1617: 10.4, 8.49 cc. of 0.1 *N* HCl. Calcd. for $C_{12}H_{17}ON$: N, 7.33. Found: 7.34, 7.35.

Summary

The yields of amines and ammonia in the reaction of monochloro-amine with Grignard reagents prepared from secondary and tertiary halogen compounds are much the same as with reagents prepared from primary halogen compounds.

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FURTHER STUDIES OF SYRINGIC ACID AND ITS DERIVATIVES[1]

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In previous articles[3] from these Laboratories, we have described various derivatives of syringic acid and incidental compounds, and the present paper continues and supplements these earlier investigations.

The flow sheet represents the various products prepared in the course of the work and the origin of each.

The nitration of polyhydroxylated benzoic acids is complicated by the tendency of such compounds either to undergo complete decomposition, or to have the carboxyl displaced by the nitro group.[3a,4] These tendencies have been overcome by protecting the carboxyl group by esterification and the hydroxyls by alkylation or esterification.[3a,5] Bogert and Plaut[3a] obtained the dinitropyrogallol dimethyl ether by direct nitration of syringic acid. We have found similarly that when nitrosyringic acid is boiled with tin and hydrochloric acid, the product is the monaminopyrogallol dimethyl ether, but that the aminosyringic acid can be obtained by carrying out the reduction at 40–45° under suitable conditions.

Schiffer[6] encountered similar difficulties when he sought to reduce nitrotriethylgallic acid. We have also ascertained, in line with the above, that acetylsyringic acid can be nitrated easily, in acetic anhydride solution, to give the nitro-acetylsyringic acid without loss of carbon dioxide.

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[1] Presented in abstract before the Division of Organic Chemistry at the Swampscott Meeting of the American Chemical Society, September, 1928.

[2] DuPont Fellow at Columbia University, 1925–1927.

[3] (a) Bogert and Plaut, THIS JOURNAL, **37**, 2723 (1915); (b) Bogert and Ehrlich, *ibid.*, **41**, 798 (1919).

[4] (a) Harding, *J. Chem. Soc.*, **99**, 1585 (1911); (b) De Lange, *Rec. trav. chim.*, **45**, 19 (1926).

[5] (a) Hamburg, *Monatsh.*, **19**, 598 (1898); (b) Power and Shedden, *J. Chem. Soc.*, **81**, 73 (1902).

[6] Schiffer, *Ber.*, **25**, 727 (1892).