

chlorine atoms attached to the doubly bound carbon atoms also decrease the rate of addition. Where two or three double bonds are conjugated with each other, one bond adds ozone rapidly while the others add only slowly. In the case of *cis-trans* isomers where the rate of addition is de-

creased by other groups, the *trans* is found to add more rapidly than the *cis* form. The procedure should prove valuable in the investigation of unsaturated compounds of unknown structure.

STANFORD UNIVERSITY, CALIF.

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

## A Study of Possible Rearrangement Reactions of Monochloroamine and Certain Grignard Reagents

BY GEORGE H. COLEMAN AND ROBERT A. FORRESTER

It has been observed that in the reaction of formaldehyde with benzylmagnesium chloride *o*-tolylcarbinol<sup>1</sup> is formed instead of benzylcarbinol as expected. Other compounds<sup>2</sup> such as benzaldehyde, ethyl formate, and ethyl chloro-carbonate have also been found to react abnormally with this reagent. Rearrangement occurs in varying amounts, usually forming the *o*-tolyl products. Numerous other reactants, however, such as carbon dioxide, acetone, many acetals and esters, produce the normal product with benzylmagnesium chloride. Thus the nature of the reactant has an important influence on the possibility of rearrangement.

Certain other Grignard reagents such as  $\alpha$ -naphthylmethylmagnesium chloride and cinnamylmagnesium chloride<sup>3</sup> react abnormally with some compounds. The former may produce a compound having methyl in the alpha-position and the other group in the beta-position, similar to the *o*-tolyl product from benzylmagnesium chloride. Cinnamyl chloride may undergo rearrangement in the formation of the Grignard reagent itself, subsequently reacting normally with the reactant used.<sup>4</sup>

(1) Tiffeneau and Delange, *Compt. rend.*, **137**, 573 (1903).

(2) Austin and Johnson, *THIS JOURNAL*, **54**, 647 (1932).

(3) (a) Gilman and Kirby, *ibid.*, **51**, 3475 (1929); (b) Gilman and Harris, *ibid.*, **53**, 3541 (1931).

(4) To quote from Gilman and Harris "In general, it appears that  $\alpha$ -phenylallyl types,  $C_6H_5CHCH=CH_2$ , are formed from the cin-

namyl chloride Grignard reagent and all reactants, or in any event, from a greater variety of reactants than give rise to the nuclear substitutions observed with benzylmagnesium chloride types. This is hardly incontrovertible evidence in all cases for an  $\alpha$ -phenylallylmagnesium chloride structure,  $C_6H_5CHCH=CH_2$ . We might

have initially a cinnamylmagnesium chloride,  $C_6H_5CH=CHCH_2MgCl$ , some of whose reaction products might, under the experimental conditions, rearrange to  $\alpha$ -phenylallyl derivatives."

Monochloroamine has been used<sup>5,6</sup> with various Grignard reagents to produce the corresponding primary amines. The normal product obtained from benzylmagnesium chloride would be benzylamine. If rearrangement had occurred as outlined, the product would be *o*-toluidine. Likewise  $\alpha$ -naphthylmethylamine would be the normal product from  $\alpha$ -naphthylmethylmagnesium chloride but a rearrangement would form  $\alpha$ -methyl- $\beta$ -naphthylamine. Cinnamylmagnesium chloride if it has the  $\alpha$ -phenylallyl structure would normally form  $\alpha$ -phenylallylamine. If cinnamyl chloride forms a normal Grignard reagent, cinnamylamine would be obtained as a normal product in the reaction with monochloroamine.

In the present work a study has been made of the reaction of monochloroamine with the three Grignard reagents mentioned for the purpose of determining whether rearrangement occurs, and if so to what extent.

With benzylmagnesium chloride and  $\alpha$ -naphthylmethylmagnesium chloride, benzylamine and  $\alpha$ -naphthylmethylamine are formed, respectively. No indication of the formation of the rearrangement products, *o*-toluidine and  $\alpha$ -methyl- $\beta$ -naphthylamine was obtained and it was shown that if present at all they were present to the extent of less than 1% in the reaction products. From cinnamylmagnesium chloride and monochloroamine the only amine obtained was cinnamylamine. The structure was confirmed by reduction to  $\gamma$ -phenyl-*n*-propylamine.

### Experimental

**Preparation of Monochloroamine.**—The method used by Coleman and Hauser<sup>5</sup> was modified slightly to increase

(5) Coleman and Hauser, *THIS JOURNAL*, **50**, 1193 (1928).

(6) Coleman and Yager, *ibid.*, **51**, 567 (1929).

the yield to 0.15–0.20 mole. Instead of using 200 cc. each of molar solutions of ammonia and sodium hypochlorite, 400 cc. of each was used. Approximately 100 cc. of water was distilled over with the monochloroamine, and was collected as ice in a wide-necked Florence flask containing 250 cc. of ether and surrounded with a cooling bath of solid carbon dioxide and acetone.

**Reaction of Monochloroamine with Benzylmagnesium Chloride.**—Benzylmagnesium chloride was prepared in the usual manner. After the addition of monochloroamine the reaction mixture was decomposed with water and the product steam distilled into dilute hydrochloric acid. The solution of the hydrochlorides was evaporated to partial crystallization only since *o*-toluidine hydrochloride loses weight when heated in the dry form.

A known mixture of benzylamine hydrochloride and *o*-toluidine hydrochloride was separated by treating a dry ethereal solution of the free bases with carbon dioxide. After the separation both compounds were again converted to the hydrochlorides. Ninety-six per cent. of the benzylamine and 75% of the *o*-toluidine were recovered.

Following the same procedure with the product obtained in the reaction of 0.096 mole of monochloroamine and an excess of the Grignard reagent, it was possible to recover 12.58 g. of benzylamine hydrochloride and a residue weighing 0.11 g. This residue could not be identified as *o*-toluidine. The 12.58 g. of benzylamine hydrochloride represents a yield of 92% based on the monochloroamine.

**Reaction of Monochloroamine with  $\alpha$ -Naphthylmethylmagnesium Chloride.**—The Grignard reagent was obtained in 75% yields by the method of Gilman and Kirby.<sup>7</sup> After the addition of monochloroamine to the Grignard reagent, the reaction mixture was decomposed and the product distilled into dilute hydrochloric acid. The solution was evaporated to dryness, since the hydrochlorides of the two possible products do not lose weight when heated on a water-bath.

A known mixture of  $\alpha$ -naphthylmethylamine hydrochloride and  $\alpha$ -methyl- $\beta$ -naphthylamine hydrochloride was separated by the carbon dioxide method as described for benzylamine and *o*-toluidine. Ninety-five per cent. of the  $\alpha$ -naphthylmethylamine and 90% of the  $\alpha$ -methyl- $\beta$ -naphthylamine were recovered. It was possible to detect the presence of 10 mg. of  $\alpha$ -methyl- $\beta$ -naphthylamine hydrochloride in 4.0 g. of  $\alpha$ -naphthylmethylamine hydrochloride by this method of separation followed by diazotization of the  $\alpha$ -methyl- $\beta$ -naphthylamine residue and coupling with  $\beta$ -naphthol.

Using this method of separation on the product from the reaction of 0.053 mole of monochloroamine with an excess of  $\alpha$ -naphthylmethylmagnesium chloride, 4.93 g. of  $\alpha$ -

naphthylmethylamine hydrochloride (47% yield) and a residue of 0.017 g. were obtained. This residue did not show the characteristic diazotization and coupling test for  $\alpha$ -methyl- $\beta$ -naphthylamine.

**Reaction of Monochloroamine with Cinnamylmagnesium Chloride.**—Cinnamylmagnesium chloride was prepared in 50% yields by the method of Gilman and Harris.<sup>7</sup> Inasmuch as their experiments with carbon dioxide showed that rearrangement of the product occurred on heating, these experiments were carried out at a temperature of  $-20^\circ$ . After addition of the monochloroamine and decomposition by water and hydrochloric acid the solution was made alkaline and extracted with 250 cc. of ether. The water was removed from the ether by cooling to  $-50^\circ$ , and the amine hydrochloride was precipitated by the addition of a dilute ethereal solution of hydrogen chloride. The weight of amine hydrochloride obtained by the use of 0.050 mole of monochloroamine and an excess of the Grignard reagent was 1.2 g. This is a 14% yield.

**Identification of the Amine.**—The benzoyl derivative of the product was prepared and after recrystallization melted at  $94-95^\circ$  (uncorr.). Cinnamylamine was prepared by the Gabriel synthesis<sup>8</sup> and the benzoyl derivative made. This also melted at  $94-95^\circ$  (uncorr.). A mixed melting point showed no depression.

The structure of the product was further proved by reduction with sodium amalgam. The benzoyl derivative of the resulting amine melted after recrystallization at  $58-59^\circ$  (uncorr.) and showed no depression in melting point when mixed with an authentic sample of benzoyl- $\gamma$ -phenyl-*n*-propylamine.

### Summary

1. Monochloroamine reacts with benzylmagnesium chloride to produce benzylamine in 92% yield. If *o*-toluidine is formed in this reaction it is present to the extent of less than 1%.
2. Monochloroamine reacts with  $\alpha$ -naphthylmethylmagnesium chloride to produce  $\alpha$ -naphthylmethylamine in 47% yield. If  $\alpha$ -methyl- $\beta$ -naphthylamine is formed in this reaction it is present to the extent of less than 1%.
3. Monochloroamine reacts with cinnamylmagnesium chloride to produce cinnamylamine in 14% yield.

IOWA CITY, IOWA

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(7) Gilman and Harris, *Rec. trav. chim.*, **50**, 1052 (1931).

(8) Posner, *Ber.*, **26**, 1856 (1893).