

3. These results indicate that the directive effect of the monosulfon-amido and disulfonamido groups in the benzene ring is predominantly ortho-para.

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THE PREPARATION OF CERTAIN KETO-CHLORIMINES BY THE ACTION OF CHLORINE ON COMPOUNDS OF THE TYPE
 $R'R''C=NMgX^1$

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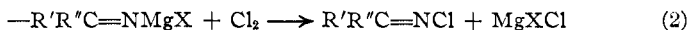
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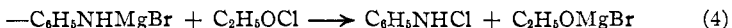
In connection with a study of ald-chlorimines² we were desirous of obtaining certain keto-chlorimines in order to make a comparative study of these compounds. Several keto-chlorimines previously have been prepared by Peterson³ by a method which involves several steps. Thus, benzophenone was converted into benzophenone dichloride, which in turn was converted, by means of urethan, into the imine hydrochloride. The latter was treated with hypochlorous acid, yielding the chlorimine according to equation (1).



In the hope of developing a shorter method for the preparation of certain keto-chlorimines, it seemed worth while to attempt the chlorination of nitrogen-magnesium compounds of the type $R'R''C=NMgX$,⁴ which may readily be obtained from Grignard reagents and nitriles,⁵ by means of chlorine (2), and of alkyl hypochlorites (3).



Since Durand and Naves⁶ have shown previously that ethyl hypochlorite reacts with the nitrogen-magnesium compound obtained from aniline and ethylmagnesium bromide to yield presumably a chloramine (4), it might



¹ This paper is in part constructed from portions of a thesis presented by G. J. Haus in partial fulfilment of the requirements for the degree of Master of Arts in the Graduate School of Arts and Sciences, Duke University.

² Hauser and Gillaspie, *THIS JOURNAL*, **52**, 4158, 4517 (1930).

³ Peterson, *Am. Chem. J.*, **46**, 325 (1911).

⁴ Since compounds of the type $R'R''C=NMgX$ might be considered as salts of imines ($R'R''C=NH$) and $MgX(OH)$, chlorine might be expected to react with the nitrogen-magnesium linkage under certain conditions. Doubtless other reactions also occur. A discussion of these reactions is withheld pending further investigation.

⁵ Blaise, *Compt. rend.*, **132**, 40 (1901).

⁶ Durand and Naves, *Bull. soc. chim.*, **37**, 717 (1925).

be expected that under certain conditions a chlorimine could be prepared according to equation (3). In this work *tert.*-butyl and *tert.*-amyl hypochlorites have been used since these are far more stable than either primary or secondary hypochlorites.⁷

It has been found that when diphenylmethylene-iminemagnesium bromide, obtained from phenylmagnesium bromide and benzonitrile, is treated with an equivalent quantity of chlorine or tertiary alkyl hypochlorite, an orange-red color develops and, after filtering and removing the ether, a red product is obtained which apparently contains about 60% of benzophenone chloramine as calculated from its active chlorine content. The pure chlorimine has not yet been isolated but its presence is further indicated by the fact that when the crude product in ether or benzene solution is treated with dry hydrogen chloride, a precipitate is obtained, which, presumably, is benzophenone-imine hydrochloride,⁸ since benzophenone is obtained on hydrolysis.

The action of chlorine on the nitrogen-magnesium compound obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*-chlorobenzophenone chlorimine, which has a melting point of 104°, agreeing with that of the higher melting stereoisomer obtained by Peterson.³ None of the lower melting stereoisomer has been found.

The action of chlorine on the nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile yields *p,p'*-dichlorobenzophenone chlorimine.

Further work is in progress.

Experimental

Preparation of Tert.-Butyl and Tert.-Amyl Hypochlorites.—These hypochlorites were prepared by the method of Chattaway and Brackenberg.⁷ The tertiary alcohol (1 mol) was added to a strong solution of sodium hydroxide (2 mols) and the resulting mixture diluted with water until a clear, homogeneous solution was obtained. After transferring to a brown bottle, the solution was cooled in an ice-bath and chlorine passed in as long as it was freely absorbed. The alkyl hypochlorite collected on the surface as a yellow oil and, after separating, was dried quickly with three successive portions of calcium chloride by shaking with the latter for a few seconds and then pouring the hypochlorite onto fresh calcium chloride, keeping the substance cold throughout the procedure. Eastman's *tert.*-butyl and *tert.*-amyl alcohols were used in this work. It was found that practical *tert.*-butyl alcohol gave a hypochlorite which decomposed within a short time.

Preparation of Nitrogen-Magnesium Compounds of the Type R'R''C=NMgX.—These compounds were prepared by Blaise's method.⁵ The calculated amount of nitrile dissolved in ether was added to an ether solution of a Grignard reagent and the mixture warmed to complete the reaction. In our first experiments the amount of nitrile used

⁷ Chattaway and Brackenberg, *J. Chem. Soc.*, **123**, 3000 (1923).

⁸ Peterson has converted this imine hydrochloride into the chlorimine by means of hypochlorous acid (see eq. (1)).

was calculated by assuming a 75% yield of the Grignard reagent, but generally the reagent was analyzed by the acid titration method,⁹ and the calculated amount of nitrile added, assuming that the substances react mole for mole. Sufficient Grignard reagent was always prepared so that one-eighth to one-quarter mole quantities of the nitrile were required in the preparation of the nitrogen-magnesium compound. The latter, which partially precipitated from the ether solution (volume about 150 to 300 cc.), was generally chlorinated as a suspension in this solvent, avoiding excess chlorine. In a few cases when the ether was first evaporated and benzene added, practically the same results were obtained.

Reaction of Tert.-alkyl Hypochlorites and of Chlorine with the Compound (C₆H₅)₂C=NMgBr.—To a suspension in ether of the nitrogen-magnesium compound, obtained from phenylmagnesium bromide and benzonitrile, was added slowly with shaking an equivalent¹⁰ amount of cold ether solution of *tert.*-butyl or amyl hypochlorite, cooling the reaction mixture in an ice-bath throughout the procedure. An orange-red color developed. After shaking vigorously for several minutes¹¹ the mixture was rapidly filtered with suction and the ether solution allowed to evaporate or distilled from a water-bath. A red oily residue with only a slight odor was obtained which was found to contain 10 to 11% of active chlorine. Calculated from its active chlorine content¹² the product contained more than 60% of benzophenone chlorimine. Yields were generally about 50% of crude product or about 30% of the chlorimine calculated from the benzonitrile used.

Similar results were obtained when the nitrogen-magnesium compound suspended in ether or benzene was treated with an equivalent of chlorine instead of the hypochlorite as described above. No hydrogen chloride was observed. After filtering rapidly the solvent was evaporated under vacuum by drawing the air through a calcium chloride drying tower. It had been found that when the red ether solution of the crude chlorimine was shaken with cold dilute sodium hydroxide, a yellow emulsion was produced which finally separated into two yellow layers. When the ether layer was dried and evaporated a lighter colored oily residue was obtained which contained about 10% of active chlorine; when the alkaline layer was acidified a few drops of red oil separated, which is being further studied.

Attempts thus far to obtain the pure chlorimine¹³ by recrystallization of the crude products, obtained by both methods described above, have been unsuccessful. Oils which contained a slightly higher percentage of active chlorine and small quantities of crystals which contained no active chlorine were obtained.

A portion of the crude chlorimine (5 g.) in ether (100 cc.) was shaken with dilute sulfuric acid, then washed with water, shaken with dilute potassium hydroxide and again washed with water. After drying by shaking with calcium chloride in the cold, the

⁹ Gilman, Wilkinson, Fishel and Meyers, *THIS JOURNAL*, **45**, 150 (1923); Gilman, Zoelner and Dickey, *ibid.*, **51**, 1577 (1929).

¹⁰ The amount of hypochlorite used was equivalent to the amount of benzonitrile employed in the preparation of the nitrogen-magnesium compound.

¹¹ In several cases when the reaction mixture was allowed to stand at room temperature for several hours before filtering, practically the same results were obtained.

¹² The analysis for active chlorine was carried out by dissolving a sample in acetic acid, adding potassium iodide, and titrating with sodium thiosulfate, or by the method recently used for ald-chlorimines.²

¹³ Benzophenone chlorimine (m. p. 37°) has been prepared by Peterson.³ Since we were especially desirous of obtaining the chloro substituted chlorimines described in this paper, no further attempt has been made to isolate benzophenone chlorimine.

ethereal solution was saturated with dry hydrogen chloride. A precipitate was obtained which when warmed with water yielded benzophenone. When repeated without extracting with acid and alkali, similar results were obtained. When the acid extract, which had been separated from the ether solution of the crude chlorimine described above, was made alkaline, a trace of an organic solid was obtained, and when the alkaline extract was acidified, a small amount of red oil was obtained.

Preparation of *p*-Chlorobenzophenone Chlorimine.—To a suspension in ether of the nitrogen-magnesium compound, obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile, was added slowly with shaking the calculated amount of chlorine, keeping the mixture cold throughout the procedure. An orange-red color developed, being the darkest when approximately the calculated amount of chlorine had been added. After shaking vigorously, the mixture was filtered rapidly with suction and the ether solution either evaporated directly or first extracted with dilute sodium hydroxide, dried rapidly with calcium chloride, and then evaporated using a drying tower as described above. If the extraction with alkali is carried out carefully by shaking just sufficiently to remove the red color and yet not produce a heavy emulsion, the crude chlorimine obtained by the evaporation of the ether is generally a purer product having a lighter color, but the yield is smaller. The yield of chlorimine calculated from the nitrile used in the preparation of the nitrogen-magnesium compound was about 32% as calculated from the active chlorine content of the crude product. Two recrystallizations from ligroin or chloroform yielded white crystals melting at 104°, agreeing with the melting point of the higher melting stereoisomer obtained by Peterson.³ Analysis for active chlorine gave the following result.

Anal. Calcd. for $\text{ClC}_6\text{H}_4\text{-C}_6\text{H}_5\text{C}\equiv\text{NCl}$: Cl, 14.18. Found: Cl, 14.13.

An attempt was made to isolate a stereoisomer by following the procedure by which Peterson³ isolated an isomer melting at 56°, but when a chloroform-ligroin solution of the product, from which a portion of the higher melting isomer had been separated, was cooled to -12°, more of the same isomer was obtained, and even after evaporating almost all of the solvent the substance obtained melted above 100°. None of the lower melting isomer was found. Since the precipitate obtained by filtering the ethereal reaction mixture yielded *p*-chlorobenzophenone when treated with acid, it appeared as if some of the suspension of the nitrogen-magnesium compound had not reacted with the chlorine, yet when a portion of this same precipitate was again suspended in ether or benzene and treated with more chlorine, only a small additional amount of product was obtained which contained active chlorine. When the preparation was carried out using sufficient ether to keep the nitrogen-magnesium compound in solution, about the same yield of chlorimine was obtained.

Preparation of *p,p'*-Dichlorobenzophenone Chlorimine.—The nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile was treated with chlorine as described in the preparation of *p*-chlorobenzophenone chlorimine. An orange color developed which, after filtering, was not entirely removed from the ether solution of the chlorimine by shaking carefully with dilute sodium hydroxide. When the ether was evaporated a red residue was obtained. When the latter was treated with hot ligroin, most of the red material dissolved, leaving a slightly colored crystalline solid, and when the ligroin solution was cooled, more of the slightly colored crystalline solid was obtained. After recrystallization from hot ligroin an analysis showed that the substance contained 11.86% of active chlorine; the theoretical amount, calculated for *p*-dichlorobenzophenone chlorimine, is 12.47% active chlorine. The yield was about 35–40% calculated from the nitrile used for the preparation of the nitrogen-magnesium compound. Further recrystallization from ligroin yielded white prisms, melting at 74° and containing 12.05, 12.06% active chlorine.

Summary

1. Certain keto-chlorimines have been prepared by the action of chlorine on nitrogen-magnesium compounds of the type $R'R''C=NMgX$, which may readily be obtained from Grignard reagents and nitriles.

2. The action of chlorine on the nitrogen-magnesium compound obtained from phenylmagnesium bromide and *p*-chlorobenzonitrile yields *p*-chlorobenzophenone chlorimine, m. p. 104° . No stereoisomer has been isolated.

3. The action of chlorine on the nitrogen-magnesium compound obtained from *p*-chlorophenylmagnesium bromide and *p*-chlorobenzonitrile yields *p,p'*-dichlorobenzophenone chlorimine, m. p. 74° .

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[CONTRIBUTION FROM THOMAS AND HOCHWALT LABORATORIES, INC.]

POLYMERIZATION OF DIOLEFINS WITH OLEFINS. I. ISOPRENE AND PENTENE-2

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When anhydrous aluminum chloride is placed with pure isoprene in which there is no appreciable amount of olefin present, and the mixture shaken, there is no temperature rise or any other obvious chemical reaction even when a considerable portion of anhydrous aluminum chloride has been added. Upon prolonged standing slow polymerization takes place, producing mainly the insoluble polymer described below. If to this mixture a small amount of olefin, such as pentene-2 or trimethylethylene, is added and the mixture shaken, an obvious reaction starts immediately which becomes violent if much of the olefin has been added, and unless the mixture is cooled the products will soon boil away. This interesting reaction, some phases of which were also observed and discussed by Aschan,¹ has led to the following investigation.

If an equimolar mixture of isoprene and pentene-2 or trimethylethylene is diluted with an inert hydrocarbon solvent and the mixture cooled with constant stirring, there can be added portion-wise small amounts of anhydrous aluminum chloride. After several hours a point is reached where there is no more evolution of heat. From the reaction mixture there is obtained, after decomposition of the aluminum chloride complex, two organic polymers, one soluble, the other insoluble in hydrocarbon solvents.

Soluble Polymer.—This polymer ranges from a viscous oil to a hard resin, depending upon the proportions of the olefin and diolefin employed and the subsequent treatment to which the product is subjected. The

¹ Aschan, *Chem. Abstracts*, **14**, 3823 (1916); *Ofversigi Finska Vetenskaps Soc.*, **58**, 42 (1916).