fillings and contact times. No butane was found in any instance although especial search was made for it because its presence has been inferred by other investigators. With a contact time of one second, the gas produced carried 10.3% ethylene; 15.5 seconds, 5.0%; eighty seconds, 0.5 per cent; with longer contact time, none at all. Hydrogen cyanide was always present at 890–900°, but only traces of ammonium cyanide or acetonitrile were noted except in a run made with a contact time of one second. In this particular run the saturated hydrocarbon content was also unusually high. Cyanogen is not a product of the pyrolysis.

Benzylamine was unchanged on being heated for several hours at 275–300° in a sealed tube. It was, furthermore, almost unchanged at 535° with a contact time of fifty-four seconds.

Benzylamine decomposed in 160 seconds at 630° to give benzonitrile, benzene, toluene, saturated hydrocarbons, hydrogen, hydrogen cyanide and traces of secondary amine. A mechanism for the reaction has been proposed.

p-Toluenesulfonebenzylamide and *p*-toluenesulfonedibenzylamide have been synthesized and characterized.

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RESEARCHES ON CHLORIMINES. II. SOME NEGATIVELY SUBSTITUTED AROMATIC ALD-CHLORIMINES

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A recent communication[2] from this Laboratory has described the preparation and properties of *o*-chlorobenzalchlorimine and anisalchlorimine. It has been shown that the latter compound undergoes spontaneous decomposition more rapidly than does the former, according to the general equation $RCH{=}NCl = RCN + HCl$. This difference in rate of decomposition of these compounds suggests that the nature of a substituent group in an aromatic ald-chlorimine may be an important factor in its stability.

In the present investigation a number of aromatic ald-chlorimines have been prepared with the purpose of studying the effect of the presence of substituent groups on the stability of these compounds as well as extending the list of readily available ald-chlorimines to be used in subse-

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[1] This paper is in part constructed from portions of a thesis presented by A. Gillaspie 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 Hauser, This Journal, 52, 2050 (1930). It should be mentioned that Raschig seems to have condensed anisaldehyde with monochloramine but no details are given; Raschig, "Schwefel und Stickstoff-Studien," 1924, p. 80.

quent work. Excellent yields of certain chlorimines have been obtained within a few minutes by reaction of aldehydes in ethereal solution with monochloramine in cold aqueous solution. A comparison of the temperatures at which the purified chlorimines decomposed when heated gradually, and of the rates of decomposition at 30°, showed that certain ones were more stable than others, but since the decompositions are apparently catalyzed by impurities and reproducible results were not obtained in several cases, only a general classification of these compounds seems warranted at this time. In general, anisal-, *o*-methoxybenzal-, piperonal- and *o*-nitrobenzal-chlorimines comprise a relatively unstable class as compared with *o*-chloro-, *p*-chloro-, *p*-bromo- and 2-chloro-5-nitro-benzal-chlorimines.

Experimental

Preparation of Ald-chlorimines from Solid Aldehydes.—Although several ald-chlorimines have been prepared by using alcohol as solvent, they were generally best prepared when solid aldehydes were used by vigorously shaking an ether solution of the aldehyde with a cold aqueous solution of monochloramine. By this method all of the aldehydes studied, with the exception of one, were rapidly converted into the corresponding chlorimines in 80–90% yields. The exception was *p*-dimethylaminobenzaldehyde which, when allowed to react with monochloramine by the method described below, was recovered in great part unchanged. However, when alcohol was used as solvent a small amount of dark colored material, which appeared to consist of some unstable chlorimine, was obtained. This was not further studied in this investigation.

The following method was adopted for the preparation of the chlorimines from solid aldehydes. An ether solution[3] of the aldehyde was vigorously shaken with three times the calculated amount of freshly prepared cold alkaline monochloramine[4] solution (1 *N*) containing crushed ice. A milky mixture or emulsion was formed almost immediately, and usually within a minute or two a precipitate was produced. After shaking for several minutes or until the solid material had coagulated sufficiently, the product was filtered and washed thoroughly with cold water. A yield of more than 85% of crude chlorimine was usually obtained.

Recrystallization and Analysis.—The chlorimines were best recrystallized from either 95% alcohol or acetone in the following manner. The sample was dissolved at room temperature (18–24°), the solution filtered and cold water added to the mixture until the precipitate which formed at first just redissolved on shaking. On standing in a cool place the product crystallized out. It was immediately filtered, dried on a porous plate and analyzed for active chlorine. The method of analysis previously described[2] has been modified as follows. A sample of chlorimine weighing 0.15–0.20 g. is dissolved in approximately 50 cc. of 95% alcohol, cooled and 10 cc. of 10% potassium iodide solution added. The cooled solution is then acidified with 0.5 cc. of concentrated hydrochloric acid and standard sodium thiosulfate solution immediately run in until the color of the solution has become light yellow. Starch indicator is next added, and then sufficient water to produce the characteristic blue color, after which the titration with thiosulfate is completed. In cases where the sample is sparingly soluble in 95% alcohol,

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[3] The best results were obtained when 5–7 cc. of ether per 100 cc. of aqueous monochloramine solution was used.

[4] See Hauser, THIS JOURNAL, **52,** 1108 (1930).

the analysis may be conveniently carried out in acetone solution or equally well in a mixture of the two solvents.

General Properties.—All of the chlorimines studied were obtained as crystalline compounds which underwent spontaneous decomposition yielding, as primary products, hydrogen chloride and the corresponding nitrile. When heated rapidly on a platinum foil or in a capillary tube they decomposed with a "puff" evolving a cloud of hydrogen chloride. The melting points and the decomposition temperatures of the chlorimines were determined, as soon as the compounds were dry, in the following manner. A capillary tube containing the sample was immersed in a bath which was 5–10° below the melting point of the substance, and the temperature raised at the rate of 1° in five to eight seconds. When the temperature of the bath was raised above the melting point of the substance at about this rate, some of the compounds decomposed rather vigorously while in other cases the first evidence of decomposition was the appearance of a cloudiness and then a precipitate. Sometimes the melted compound frothed and rose in the tube before precipitating.

Attempts to isolate stereoisomers from products which had been melted and then solidified again, were unsuccessful. Fractional crystallization of crude chlorimines from alcohol or from hydrocarbon solvents yielded no isomers.

Piperonalchlorimine, obtained as white crystals from alcohol, melted at 68–69° and precipitated at 72–77°. Sometimes the compound did not melt completely before precipitation began. On further heating more decomposition with discoloration resulted.

Anal. Calcd. for $CH_2O_2C_6H_3CH{=}NCl$: Cl, 19.33; N, 7.63. Found: Cl, 19.25, 19.20; N, 7.88.

A sample (0.3 g.) was immersed in a bath at 70–74° until it melted and precipitated. It was then cooled and pressed on a plate, after which it melted at 58–65°. When mixed with some pure chlorimine the melting point was 63–67°. Recrystallization of the material yielded pure chlorimine, m. p. 68–69°. When 0.5 g. of chlorimine was immersed in a bath at 80°, it "puffed" vigorously, evolving hydrogen chloride, and nitrile was isolated from the residue. The nitrile was also isolated from a sample which had been allowed to decompose in a desiccator containing sodium hydroxide. A small amount of another substance, insoluble in ether, apparently the imine hydrochloride, was also obtained. A sample of chlorimine left on a plate for two hours at room temperature (25–27°) melted at 66–69° and decomposed more readily than a freshly prepared product.

o-**Nitrobenzalchlorimine**, obtained as pale yellow crystals from alcohol, melted at 74–75° and frothed at 84–85°. Since the crude chlorimine soon darkens in color if allowed to remain in contact with the alkaline monochloramine solution, the product should be filtered as soon as it has coagulated.

Anal. Calcd. for $NO_2C_6H_4CH{=}NCl$: Cl, 19.22. Found: Cl, 19.00.

m-**Nitrobenzalchlorimine** melted at 79–80° and precipitated again at 81–83°. Sometimes the compound did not melt completely, but merely softened and then began to solidify. Its crystals are white when pure, but usually they were slightly colored even after two crystallizations from alcohol.

Anal. Calcd. for $NO_2C_6H_4CH{=}NCl$: Cl, 19.22. Found: Cl, 19.15, 19.10.

In one case the crude chlorimine after drying on a plate was dissolved in a small amount of benzene and filtered. When treated with about 4 volumes of ligroin a small quantity of light tan crystals was produced and filtered off. When the filtrate was cooled, white crystals were obtained. In a similar manner two crops of crystals were obtained from the crude chlorimine by using chloroform and ligroin. A third fraction was also obtained from the latter solvents by allowing them to evaporate spontaneously, until only a trace of the solvent remained. The crystals were then washed with a small amount of ligroin. The melting points of the various fractions ranged from 74 to 79°. By the mixed melting point method it was shown that all of the fractions were identical. A crude preparation of the chlorimine was also fractionally crystallized from alcohol and mixed melting points were taken with the crystals obtained from the other solvents mentioned above. All of the crystals were identical.

When a sample of this chlorimine which had been allowed to decompose in a desiccator over sodium hydroxide was treated with ether, practically all of the material dissolved. The nitrile was isolated, but no appreciable amount of the imine hydrochloride was found.

This chlorimine was compared with its ortho isomer as follows. When samples of *m*- and *o*-chlorimines in capillary tubes were immersed together in a bath at 80°, and heated, they both melted. At 83–85° the meta compound solidified, and at 95° the ortho compound frothed and decomposed. When the two chlorimines were immersed at 117°, both melted, and after a few seconds the meta "puffed;" after a few more seconds the ortho compound did likewise.

p-Chlorobenzalchlorimine, obtained as small white needles from alcohol or acetone, melted at 79–80°, became slightly cloudy at 95° and boiled up and solidified at 115–120°. Several preparations of this chlorimine heated in the same manner gave the following average results: became slightly cloudy at 90–95°, frothed or boiled up and precipitated at 100–127°.

Anal. Calcd. for $ClC_6H_4CH{=}NCl$: Cl, 20.39; N, 8.05. Found: Cl, 20.33, 20.10; N, 8.00, 8.19.

When the chlorimine was recrystallized from warm petroleum ether, needles were obtained which melted at 78–79°, and precipitated at 95°. Some colorless rectangular needles 7–12 mm. long, obtained by the partial spontaneous evaporation of a chloroform–ligroin or benzene–ligroin solution at room temperature, melted at 79–80°, became slightly cloudy at 90–95°, and continued to decompose with increasing temperature until at 122° the compound boiled up and solidified.

Crude preparations of this chlorimine were fractionally crystallized from chloroform and ligroin and from alcohol and water. The first fractions comprised a small proportion of the material used. The last fraction from the alcohol was obtained by the addition of excess water as long as a precipitate was formed. By the mixed melting point method it was shown that all the fractions were identical.

p-Bromobenzalchlorimine, obtained as white crystals, melted at 87–88°, became slightly cloudy at 90–95° and precipitated at 95–103°. At 120° more decomposition occurred. The chlorimine melted when immersed in a bath at 100–105°, and then a precipitate formed which partly dissolved when agitated for several minutes. It was evident that the chlorimine slowly decomposed with the gradual evolution of hydrogen chloride.

Anal. Calcd. for $BrC_6H_4CH{=}NCl$: Cl, 16.24; N, 6.41. Found: Cl, 16.23; N, 6.67.

2-Chloro-5-nitrobenzalchlorimine melted at 85–86°, frothed at 110°, and underwent more decomposition at 115°. Its crystals are white when pure.

Anal. Calcd. for $ClNO_2C_6H_3CH{=}NCl$: Cl, 16.20. Found: Cl, 16.25.

o-Methoxybenzalchlorimine, melted at 35–36° and frothed at 83–85°. After standing for several hours on a porous plate at 18–20°, it "puffed" mildly at 75°. This chlorimine precipitates with difficulty when the aldehyde is shaken with a solution of monochloramine according to the method[2] recently described for the preparation of anisalchlorimine. Two unsuccessful attempts were made before it was finally obtained as a white precipitate.

Anal. Calcd. for $CH_3OC_6H_4CH{=}NCl$: Cl, 20.92. Found: Cl, 20.70.

o-Chlorobenzalchlorimine has been obtained as a precipitate from Eastman's *o*-chlorobenzaldehyde (m. p. 8–9°) and monochloramine within three to five minutes when prepared according to the method[2] recently described, and within six to eight minutes when ether was used according to the method outlined in the present paper.

When this compound was heated gradually in a capillary tube. decomposition began at 110–118°. After this chlorimine had decomposed on standing in a desiccator over sodium hydroxide at 30°, the nitrile was isolated from the products. The material insoluble in ether or benzene consisted partly of ammonium chloride and of some unidentified substance.

Anisalchlorimine was prepared according to the method[2] recently described. When a sample was heated in a capillary tube it decomposed with a puff at 60–70°. One preparation of the crude chlorimine was fractionally crystallized from alcohol and water. Four fractions of about equal amounts were obtained. After drying it was shown by the mixed melting point method that all of the fractions were identical.

Stability of Chlorimines.—It has already been reported that anisalchlorimine is much less stable than *o*-chlorobenzalchlorimine. While working with the chlorimines described in this investigation, it soon became evident that certain ones were much more unstable than others. A qualitative classification of these compounds according to their stabilities was arrived at from a consideration of the temperatures at which the chlorimines decomposed when heated gradually in capillary tubes, and from a consideration of the length of time which they could be kept at room temperature without undergoing appreciable decomposition. Although anisalchlorimine appeared to be the least stable of any of the compounds described here, this compound along with *o*-methoxybenzal-, piperonal- and *o*-nitrobenzal-chlorimines, formed a class which was far more unstable than *o*-chloro-, *p*-chloro-, or *p*-bromo- and 2-chloro-5-nitrobenzalchlorimines. From a consideration of the temperature at which *m*-nitrobenzalchlorimine began to decompose, this compound should be classed with the unstable chlorimines. However, several preparations of the *m*-nitro compound were kept at room temperatures (18–24°) for several days without appreciable decomposition.

In an attempt to obtain a quantitative measure of the relative stabilities of these compounds, their velocity of decomposition was determined at 30°. After the chlorimines were purified by recrystallization from alcohol, and dried on a porous plate at room temperature (18–24°), weighed samples in small vials were placed in a desiccator which contained solid sodium hydroxide and kept in an air-bath at 30°. At suitable intervals the samples were analyzed for active chlorine. The data obtained are recorded graphically in Fig. 1.

It is evident from Fig. 1 that the qualitative classification of these compounds mentioned above is in general supported by these curves. While the rates of decomposition of the relatively unstable chlorimines checked fairly well, reproducible results were not obtained for some of the other compounds.

The product used in the determination of Curve 4 was prepared when the room temperature was about 20° and, after drying, an initial analysis of the compound was in close agreement with the theoretical. However, when the work was repeated the room temperature was about 30°, and although the compound was recrystallized several times from alcohol, analyses, after drying, gave low results, which indicated that some decomposition had occurred during the process of drying. This product decomposed at a much more rapid rate at 30° than that represented by Curve 4. After sixty-four hours the chlorimine was 20%, and after 110 hours, 47% decomposed. Similar results were obtained when crude *m*-nitrobenzalchlorimine was recrystallized from slightly warm chloroform and ligroin. These observations indicate that, in some cases at least, the rates of decomposition are catalyzed by the impurities present. A preliminary experiment showed that the rate of decomposition of *m*-nitrobenzalchlorimine was accelerated by a nitrile and retarded by an aldehyde.

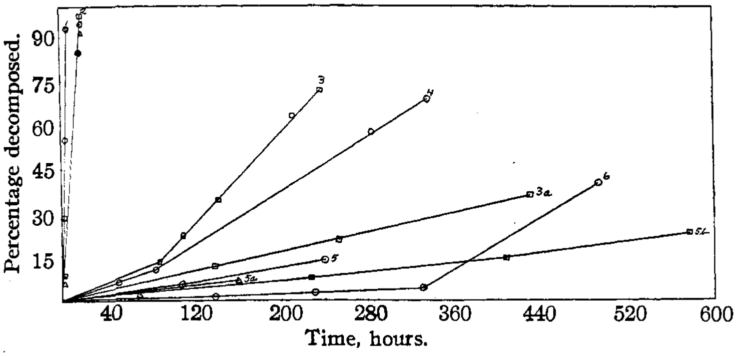

Fig. 1.—Rates of decomposition of ald-chlorimines at 30°. Curve 1, anisal- at 20–22°; *o*-methoxybenzal- gave approximately the same curve at 30°. Curve 2, points ○ and △, piperonal-; points □ and ⊗, *o*-nitrobenzal-. Curves 3 and 3a, *o*-chlorobenzal- (liq. at 30°). Curve 4, *m*-nitrobenzal-. Curves 5, 5a and 5b, *p*-chlorobenzal-. Curve 6, *p*-bromobenzal-.

Summary

A number of new aromatic ald-chlorimines have been prepared and their stabilities studied. In general, anisal-, *o*-methoxybenzal-, piperonal- and *o*-nitrobenzalchlorimines comprise a group which are distinctly less stable than *o*-chloro-, *p*-chloro-, *p*-bromo- and 2-chloro-5-nitrobenzalchlorimines.

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