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CHEMISTRY

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AMMONOLYSIS OF 1,1-DI-(CHLOROPHENYL)ETHANE

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The replacement of a halide bound to an aromatic nucleus by an amino group was first carried out by Ullmann (^1). In the ammonolysis of chlorobenzene in the presence of finely divided metallic copper, aniline was obtained by this author. Subsequently, a number of patents proposed methods for obtaining aniline from chlorobenzene by ammonolysis of chlorobenzene with a concentrated aqueous ammonia solution in the presence of copper salts. N. N. Vorozhtsov and co-workers (^2) studied in detail the reaction of ammonolysis of chlorobenzene with an aqueous ammonia solution; as a result, reaction conditions were found under which the yield of aniline was 90% of the theoretical. L. N. Nikolenko and K. K. Babievskii (^3) investigated the ammonolysis of *p*-chlorododecylbenzene with a 30% aqueous ammonia solution at 250°. Under these conditions, the authors obtained *p*-dodecylaniline in a yield of 80.2% of the theoretical.

The ammonolysis of dinuclear aromatic dihalogen derivatives in which the halogen atoms are located in different benzene nuclei has not been described in the literature, although it is of substantial interest as a new method for obtaining aromatic diamines.

The well-known method described in the literature for obtaining such compounds consists of three stages:

1. Synthesis of 1,1-diphenylalkanes

$$\mathrm{Ph{-}CH(R){-}Ph}$$

by condensation of benzene with aldehydes (dihaloalkanes, acetylene).

2. Nitration of diphenylalkanes and preparation of dinitrodiphenylalkanes

$$\mathrm{O_2N{-}C_6H_4{-}CH(R){-}C_6H_4{-}NO_2}$$

3. Reduction of dinitrodiphenylalkanes.

$$H_2N-C_6H_4-CH(R)-C_6H_4-NH_2$$

The synthesis of 1,1-di-(aminophenyl)ethane by this method is described in work (~4). In the present work a new method is proposed for obtaining this diamine, consisting in the reaction of ammonolysis of the aromatic dinuclear dihalogen derivative 1,1-di-(chlorophenyl)ethane. We investigated the influence of various factors on the yield and composition of the ammonolysis products and found the optimum conditions for obtaining 1,1-di-(aminophenyl)ethane. The reaction was carried out in a rotating autoclave with a capacity of 250 ml, heated by an electric furnace. The temperature inside the autoclave was regulated by a laboratory autotransformer and measured by means of a chromel–alumel thermocouple. The rotation speed of the autoclave was kept constant in all experiments. The 1,1-di-(chlorophenyl)ethane taken for the reaction was obtained

by condensation of chlorobenzene with acetylene and had the following constants: b.p. 173-174°/8 mm Hg; n_D^{20} 1.5914; d_4^{20} 1.2117; MR 70.057, calcd. 69.387. The data available in the literature on the constants of this product [5]: n_D^{18} 1.5318; d_4^{18} 1.0943.

A mixture of 1,1-di-(chlorophenyl)ethane, an aqueous solution of ammonia, and a catalyst (CuCl or Cu_2O) was placed in an autoclave. The autoclave was heated to 220-250°. Upon reaching the necessary temperature, the reaction time was counted. The pressure in the autoclave varied, depending on the temperature and ammonia concentration, within the range 75–160 atm.

After the end of the reaction, the contents of the autoclave were treated with ether; the ether solution was washed with water, dried with sodium sulfate, and distilled. The reaction products were distilled in a Claisen flask under reduced pressure, giving two fractions: an insignificant amount of a fraction up to 206°/2 mm Hg, a diamine fraction 206-211°/2 mm Hg, and a small (0.5–1 g) residue in the distillation flask. Preliminary experiments were carried out at 220-240° in the presence of cuprous chloride and using 24% ammonia; the reaction time varied from 2 to 6 h. However, in all experiments the starting product was obtained essentially unchanged. In subsequent experiments, ammonia of higher concentration (30–34%) was used, which led to a considerable increase in the rate of ammonolysis. The results of the experiments presented in Table 1 make it possible to draw a number of conclusions concerning the influence on the rate of ammonolysis of temperature, amount of catalyst, and reaction time.

Fig. 1. Effect of temperature on the yield of 1,1-di-(aminophenyl)ethane

Table 1

Results of ammonolysis* of 1,1-di-(chlorophenyl)ethane

No. of experiment	Dichlorodiphenylethane, g	Dichlorodiphenylethane, g-mol	Catalyst, compound	Catalyst, g	Catalyst, g-mol	Temp., °C	Pressure, atm	Time, h	Yield of diamine fraction, g	Yield of diamine fraction, %**
1	10	0.04	CuCl	3	0.33	240	115	6	2.0	24.0
2	10	0.04	CuCl	10	0.10	250	140	6	3.0	35.5
3	10	0.04	CuCl	10	0.10	260	160	10	1.7	20.1
4	20	0.08	Cu_2O	10	0.10	250	150	8	11.2	66.7
5	10	0.04	CuCl	10	0.10	250	150	6	5.1	60.0
6	10	0.04	CuCl	10	0.10	220	100	6	3.4	40.3
7	10	0.04	CuCl	10	0.10	240	125	6	4.4	52.2
8	10	0.04	CuCl	10	0.10	250	140	3	4.0	47.5
9	10	0.04	CuCl	10	0.10	250	140	9	5.1	60
10	20	0.08	Cu_2O	5	0.05	250	150	6	9.6	57
11	20	0.08	Cu_2O	15	0.15	250	150	6	11.4	68

* Ammonia concentration: expt. 1, 30%; in the remaining experiments, 33%. Amount of ammonia in all experiments, 170–180 ml.
** Yield as percent of theoretical, calculated on the 1,1-di-(chlorophenyl)ethane taken for the reaction.

As shown in Fig. 1, the rate of ammonolysis depends strongly on temperature, reaching a maximum value at 250°. However, even at this temperature the formation of a small amount of low-boiling substances was observed, which indicated partial decomposition of the reaction products; therefore carrying out the reaction at temperatures above 260° is inadvisable.

At lower temperatures (220–230°), along with a decrease in the yield of diamine, the formation of a considerable amount of resinous products occurred in the form of a residue in the distillation flask. These resins possessed

with basic properties and were apparently polycondensation products.

Figure 2 presents the dependence of the diamine yield on the duration of the reaction. When the reaction time is increased from 3 to 6 hours, the yield of diamine increases from 47.5 to 60%. A further increase in the reaction time has practically no effect on the yield. The effect of the amount of catalyst on the rate of ammonolysis was studied in the presence of cuprous oxide. Since, according to the literature data (^{2}), the optimum amount of catalyst in the ammonolysis of monohalogen derivatives is 0.2 mole per 1 mole of the halogen derivative, in our experiments we doubled this amount. Better results are obtained when 0.8–0.9 mole of catalyst per 1 mole of dichloride is used (Fig. 3). A further increase in the molar ratio catalyst : dichloride has practically no effect on increasing

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

the yield of diamine.

Fig. 2. Effect of the reaction duration on the yield of 1,1-di-(aminophenyl)ethane

The diaminodiphenylethane fraction was a solid transparent mass of pale-yellow color, readily soluble in organic solvents and in mineral acids.

Analyses performed on the diamine fraction make it possible to identify it as 1,1-di-(aminophenyl)ethane.

Molecular weight (by Beckmann): found 208, $C_{14}H_{16}N_2$ calculated 212.
Active hydrogen was determined by the Chugaev–Tserevitinov method using anisole as solvent: found H 1.86%, calculated 1.88%.

Found, %: C 79.13; 79.33; H 7.61; 7.61; N 13.10; 13.33
Calculated, %: C 79.27; H 7.54; N 13.20

Preparation of the hydrochloride salt. The diamine fraction was dissolved in dilute hydrochloric acid; the solution was boiled with activated charcoal and, after filtration, neutralized with ammonia. The diamine was extracted with ether. When dry pure hydrogen chloride was passed through the ethereal solution, the diamine hydrochloride precipitated; it dissolved in water, and its solution was again boiled with activated charcoal, filtered, and evaporated. Crystals of the hydrochloride precipitated, with m.p. 210°. Literature data for the hydrochloride of 1,1-di-(4-aminophenyl)ethane give 209° (^{6}).

Fig. 3. Effect of the amount of catalyst on the yield of 1,1-di-(aminophenyl)ethane

The hydrochloric acid solution of the diamine was subjected to diazotization (^{7}). The diazonium salt coupled with β-naphthol, giving an orange dye. Attempts to decompose the diazonium salt in order to obtain the corresponding diphenol—1,1-di-(oxyphenyl)ethane—were unsuccessful. It should be noted that, despite thorough purification of 1,1-bis-(aminophenyl)ethane, repeated attempts to convert it from the glassy to the crystalline state were unsuccessful. This is evidently explained by the fact that the diamine obtained by us, like the starting dichloride (^{5}), is a difficultly separable mixture of n, n'- and o, n'-isomers. Probably the o, n'-isomer, which has a markedly unsymmetrical structure and shows a tendency to remain in the glassy state, prevents crystallization of the n, n'-isomer. The tendency of compounds having an unsymmetrical structure to remain in the glassy state is reported in (^{8}). The authors have shown that 4-amino-4-nitro-2,2-dihalogenodiphenyls are not capable crystallize, although thorough purification and the results of analysis are a convincing guarantee that they were dealing with products of a high degree of purity.

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Note: Figure translations are in progress. See original paper for figures.