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Reactions of Aromatic Compounds in Molten Salts. II. The Rearrangement of Phenylhydrazine to Give *o*-Phenylenediamine in a Molten Mixture of $AlCl_3$–NaCl–KCl

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Phenylhydrazine gave *o*-phenylenediamines as the major product upon heating in a molten mixture of $AlCl_3$–NaCl–KCl. In the molten mixture, some aromatic compounds gave the corresponding aromatic amines in good yields in the presence of phenylhydrazine, suggesting that the method provides a novel direct process for the preparation of aromatic amines.

Many derivatives of *N*-substituted aniline have been known to rearrange to give *C*-substituted anilines; as examples, Bamberger's phenylhydroxylamine²⁾ and phenylnitroamine rearrangement,³⁾ Chattaway's *N*,*N*-diacylaniline rearrangement,⁴⁾ Fischer-Hepp's rearrangement,⁵⁾ Hofmann-Martin's alkylaniline rearrangement,⁶⁾ and Reilly-Hickinbottom's *N*-alkylaniline rearrangement⁷⁾ can be cited.

On the other hand, phenylhydrazine is known to give *p*-phenylenediamine upon heating in the presence of hydrochloric acid; in this case, however, no detectable formation of *o*-phenylenediamine was observed.⁸⁾ Phenylhydrazine has also been known to decompose to give aniline, benzene, ammonia, and other products upon heating in the presence of Lewis acid,⁹⁾ metals¹⁰⁾ or phenylhydrazine hydrochloride.¹¹⁾ However, the reaction to give *o*-phenylenediamine has not been reported. We have now found that, in a molten mixture of $AlCl_3$–NaCl–KCl, phenylhydrazine gives *o*-phenylendiamine and that several aromatic compounds yield the corresponding amines in the presence of phenylhydrazine in the molten mixture.

Experimental

All the melting points are uncorrected. The structural assignment of the reaction products was done by means of their NMR, MS, IR, UV spectra, and elemental analyses and by a mixed-melting-point-test with an authentic sample.

Materials. The $AlCl_3$, NaCl, KCl, and other inorganic materials used were of a reagent grade. The organic materials used were purified by distillation or recrystallization, and their purities were checked by TLC or GLC before use.

A typical example of the reaction will now be described; 5 ml of phenylhydrazine (0.051 mol) was stirred, drop by drop, into a molten mixture of $AlCl_3$–NaCl–KCl in an atmosphere of prepurified nitrogen. After stirring at a given temperature for a given time, the reaction mixture was poured into a mixture of 500 ml of 0.1 M HCl and 100 g of ice. After a small amount of the insoluble matter had then been filtered off, the filtrate was made alkaline and the reaction products were extracted with diethyl ether. The solvent was removed by distillation; then the reaction products were separated and purified by column chromatography. The quantitative determinations of the reaction products were carried out by GLC (Column: Lubrol MO 15%/Cromsorb WAW, 4 mm × 1 m).

Results and Discussion

Formation of o*-Phenylenediamine.* When phenylhydrazine (0.05 mol) was heated at 100 °C in a mixture of $AlCl_3$–NaCl–KCl (0.60 : 0.23 : 0.17 mol), aniline and *o*-phenylenediamine were both obtained in about a 30% yield; however, no *p*-phenylenediamine was detected in the reaction mixture. The yield of *o*-phenylenediamine was affected very much by the Lewis acids used. When $ZnCl_2$ was used instead of $AlCl_3$, the yield of *o*-phenylenediamine decreased considerably. However, in the reaction of phenylhydrazine in a molten mixture of CuCl–NaCl–KCl (0.60 : 0.20 : 0.20 mol) at 200 °C, aniline was the sole major product; *o*-phenylenediamine was not detected at all in the reaction mixture. Similar results were also obtained in the reactions of

Table 1. Effects of molten salt composition on product yields in the reactions of phenylhydrazine

Composition (mol)	Condition		Conv. (%)	Products (%)			
	Temp (°C)	Time (h)		Aniline	*o*-Phenylene diamine	Chloro-aniline	Benzidine
$AlCl_3$: NaCl : KCl (0.60 : 0.23 : 0.17)	100	1	100	30	30	—	—
$ZnCl_2$: NaCl : KCl (0.60 : 0.20 : 0.20)	200	5	81	27	12	—	—
CuCl : NaCl : KCl (0.60 : 0.20 : 0.20)	200	0.5	100	45	—	—	—
$SnCl_4$$^{a)}$ (0.5)	100	1	80	33	—	—	—
$TiCl_4$$^{a)}$ (0.5)	120	2	91	52	—	—	—
PH·HCl$^{b_1)}$	100	2	100	15	3	10	32
PH·HCl$^{b_2)}$	100	2	100	14	2	8	33

5.0 ml (0.0508 mol) of $C_6H_5NHNH_2$ was used.

a) Phenylhydrazinium salt was insoluble in $SnCl_4$ or $TiCl_4$. b) A $AlCl_3$: NaCl : KCl mixture(=0.60 : 0.23 : 0.17) and 7.4 g (0.06 mol) of phenylhydrazine hydrochloride were used. b_1) Phenylhydrazine hydrochloride was added to a molten mixture of 100 °C. b_2) The temperature of a mixture of $AlCl_3$, NaCl, KCl, and phenylhydrazine hydrochloride was gradually raised to 100 °C.

phenylhydrazine in $SnCl_4$ and $TiCl_4$.

When phenylhydrazine hydrochloride was heated in a molten mixture of $AlCl_3$: NaCl : KCl (0.60 : 0.23 : 0.17 mol) at 100 °C, *o*-phenylenediamine was obtained only in low yields; on the contrary, benzidine became the major product in this case. These results are summarized in Table 1.

From the reaction products and their yields, *o*-phenylenediamine is assumed to be produced from the phenylhydrazine–$AlCl_3$ complex formed by the HCl–$AlCl_3$ exchange from phenylhydrazine hydrochloride. On the other hand, chloroanilines would result from the chlorination of aniline with the chlorine formed by the oxidation of hydrochloric acid by the air included in the voluminous phenylhydrazine hydrochloride powder; benzidine would be formed from the aniline produced by the decomposition of phenylhydrazine hydrochloride, as has been reported in the previous paper.[1)]

When phenylhydrazine was heated in a molten mixture of $AlCl_3$–NaCl–KCl (0.60 : 0.23 : 0.17 mol) at 120 °C, the yield of *o*-phenylenediamine varied depending upon the amount of the molten mixture employed, as is shown in Fig. 1. The results show that an excess of $AlCl_3$ is necessary for the formation of *o*-phenylenediamine in good yields.

Decomposition of Phenylhydrazine–$AlCl_3$ Complex. Phenylhydrazine is known to form a complex with $AlCl_3$ of a molar ratio of 2 : 1.[12)] Therefore, the thermal behavior of the complexes of phenylhydrazine with $AlCl_3$ were investigated in order to make clear the reaction of phenylhydrazine in the molten salt. The complexes were prepared by mixing phenylhydrazine with powdered $AlCl_3$ in benzene. When the ratio of $AlCl_3/PhNHNH_2$ is less than unity, the complex was obtained as a crystalline solid. In the range of ratios above unity, however, the complex obtained was a viscous molten mass from which the complete removal of benzene was very difficult. In some cases, the yield of aniline (based on the phenylhydrazine) was found to exceed 100% (the best yield was about 150%, in the case of a $AlCl_3/PhNHNH_2$ molar ratio of 3), suggesting that the residual benzene in the complex was aminated to give aniline. In these cases, the yields of *o*-phenylenediamine remained low.

On the other hand, in the reactions using the complexes prepared in petroleum ether the yield of *o*-phenylenediamine increased with an increase in the $AlCl_3/PhNHNH_2$ ratio until about 2 (the best yield was 30%); however, aniline was obtained only in low yields, as may be anticipated in the absence of benzene. From these results, it is obvious that the formation of *o*-phenylenediamine and the amination of benzene take place competitively.

When phenylhydrazine was heated with powdered $AlCl_3$ in benzene under reflux, the solubility of the resulting complex was found to vary depending upon the $AlCl_3/PhNHNH_2$ ratio. In the range of the ratios below 0.6, the complex was isolated as a white solid which was insoluble in the solvent. However, in the range of the ratios above 0.8, the resulting complex was soluble in the solvent to give a clear orange solution. These observations indicate that the composition of the complex varied with the change in the $AlCl_3/PhNHNH_2$.

Fig. 2 shows the results of the reactions of the phenylhydrazine–$AlCl_3$ complex in benzene. From Fig. 2, it is clear that the decomposition of phenylhydrazine takes place in the range of $AlCl_3/PhNHNH_2$ ratios above unity and that the yield of *o*-phenylenediamine increases with an increase in the ratio until 2, showing that stoichiometrically at least 1 mol of $AlCl_3$ to 1 mol of phenylhydrazine is necessary for the formation of *o*-phenylenediamine. In this case, the formation of aniline from benzene was also observed.

Decomposition of Phenylhydrazine–$AlCl_3$ Complex in Monosubstituted Benzene Derivatives. When phenylhydrazine was heated in a molten mixture of $AlCl_3$: NaCl : KCl in the presence of *p*-chloroaniline at 100 °C, no 4-chloro-*o*-phenylenediamine was detected (Table 2), indicating that the amination of aromatic amine did not take place under these reaction conditions. To get more insight into the amination in the molten mixture, the amination of several monosubstituted benzene derivatives was investigated. The results are shown in Table 3. Two noticeable points in

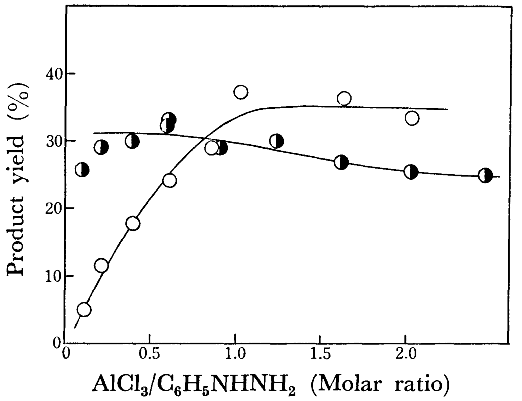


Fig. 1. Effect of amount of molten salt on product yield.
Molar ratio: $AlCl_3$: NaCl : KCl = 0.60 : 0.23 : 0.17.
Temperature: 120 °C, Time: 1 h.
◑: Aniline, ○: *o*-phenylenediamine.

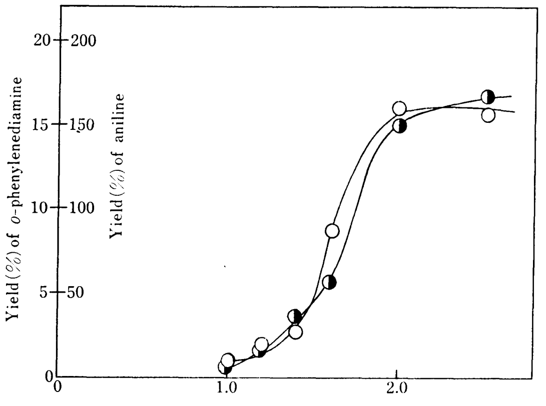


Fig. 2. Product yields in the decomposition of phenylhydrazine-$AlCl_3$ complex in refluxing benzene.
◑: Aniline, ○: *o*-phenylenediamine.

Table 2. Reaction of phenylhydrazine in molten salt in the presence of *p*-chloroaniline at 100 °C

Condition		Conv. (%)	Products (%)		
Temp (°C)	Time (h)		Aniline	*o*-Phenylene-diamine	Chloro-*o*-phenylene-diamine
100	1	100	24	37	—
100	1	100	21	46	—

$AlCl_3 : NaCl : KCl = 0.60 : 0.23 : 0.17$ mol.
0.051 mol of $C_6H_5NHNH_2$ and 0.051 mol of *p*-chloroaniline were used.

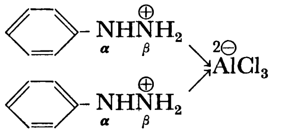
Table 3. Yields of monosubstituted anilines

X-Substituted benzene derivative	Conv. (%)	Aniline (%)	*o*-Phenylene-diamine (%)	X-substituted aniline derivative (%)		
				o-	*m*-	*p*-
X=-CH_3	100	77	11	45		
-H	100	150	16	—	—	—
-Cl	100	34	16	6	20	
-F	100	44	19	4	1	10

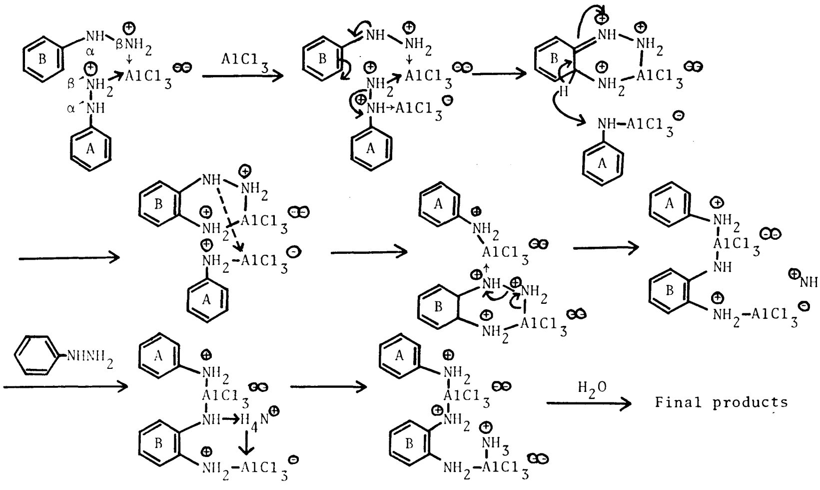
$AlCl_3 = 0.105$ mol; $C_6H_5NHNH_2 = 0.0518$ mol.
Benzene derivative, 30 ml; heated for 1 h under reflux.

Table 3 are that, even though all of these aromatic compounds were aminated, the total yield of toluidines was higher than those of chloro- and fluoroaniline, and that the amination took place at the ortho and para positions to the fluoro substituents. These results suggest that the reaction takes place by means of a mechanism of electrophilic substitution; the fact that the amination of chloroaniline did not take place may be understood to indicate that chloroaniline combines at first with $AlCl_3$ to form a inert complex towards an electrophile. Accordingly, the formation of *o*-phenylenediamine is not considered to result from the amination of aniline, but may be assumed to result from the rearrangement of the phenylhydrazine–$AlCl_3$ complex. This is because, if *o*-phenylenediamine were produced by the intermolecular amination of aniline by an electrophile such as NH_2^+, *p*-phenylenediamine should be produced at the same time.

When $AlCl_3$ was added to a solution of phenylhydrazine in dioxane, the UV spectrum of phenylhydrazine (λ_{max} 293 nm) showed a blue shift, and at the point of a $AlCl_3/PhNHNH_2$ ratio of 1/2,[12] the spectrum coincided in position with that of phenylhydrazine hydrochloride ($PhNHNH_2 : HCl = 1 : 1$, λ_{max} 272 nm). In phenylhydrazine, the *β*-amino group is more basic than the *α*-amino group; therefore, a 2:1 complex between phenylhydrazine and $AlCl_3$ may be expected to possess the skeleton described below:



The fact that 1 mol of $AlCl_3$ is necessary for each mole of phenylhydrazine for the formation of *o*-phenylenediamine, as is shown in Fig. 2, suggests that an additional attack by $AlCl_3$ upon the 2 : 1 complex is essential. Thus, the reaction of the phenylhydrazine–$AlCl_3$ com-



Scheme 1.

plex to give *o*-phenylenediamine in the molten salt may be reasonably explained by a process shown in Scheme 1.

1) The formation of a 2:1 complex from phenylhydrazine and $AlCl_3$.

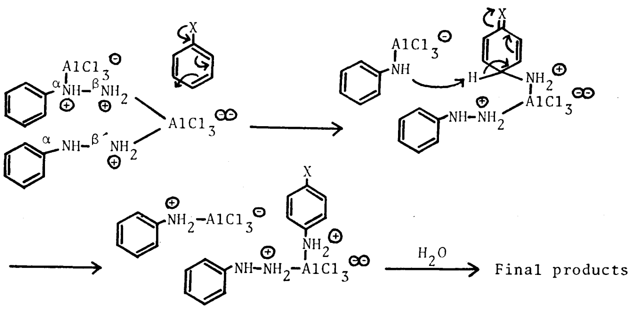
2) An additional attack by $AlCl_3$ upon one of the N_α atoms (N_α'), resulting in a new complex which has a N atom of a high electrophilicity as a result of the electrostatic repulsion between N_α' and N_β' atoms.

3) In the new complex, even though the electron-donating ability of the N_β atom is low, the electron density of the B phenyl group will be high at the ortho and para positions. Therefore, the electrophilic attack by N_β' upon the ortho carbon atom would take place without difficulty through the 6-membered transition state.

Step 3 would be the key step for the reaction; the following sequences of the reaction would proceed according to the process shown in Scheme 1, in which only the skeletons of the complexes are shown because the exact compositions of the complexes including the ligands are still uncertain. During the reaction, the nitrenium cation is assumed to be produced, even though its formation has not been confirmed; the nitrenium cation may react with phenylhydrazine to give the ammonium cation in a manner similar to that of the phenylnitrenium cation.[13] In fact, ammonia was detected during the course of the reaction.

The amination of aromatic compounds by the phenylhydrazine–$AlCl_3$ complex to give the corresponding derivatives of aniline would take place in a manner similar to that described above, as is shown in Scheme 2.

Several methods have been reported for the direct amination of aromatic compounds in the presence of Lewis acid: the aminations by hydroxylamine,[14] by hydrazoic acid,[15] and by *N*-chlorodialkylamine[16] may be cited. As to the amination by means of hydrazine, however, only the photochemical amination of cyclohexane has been reported.[17] Thus, the amination of aromatic compounds described above may provide a novel direct method for the preparation of aromatic amines; in addition, this method may be expected to develop into a general method of the amination of aromatic compounds using hydrazine and its derivatives in the presence of Lewis acid.



Scheme 2. Probable process for the amination benzene derivatives.

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