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Reactions of Aromatic Compounds in Molten Salts. I. Dimerization of Aromatic Amines in a Molten Mixture of $AlCl_3$-NaCl-KCl

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Aromatic amines underwent dimerization in a molten salt consisting of a mixture of $AlCl_3$-NaCl-KCl. The reaction is an oxidative cationic polymerization but, in contrast with the reactions of the ordinary aromatic compounds which gave the corresponding polyaryls, in the cases of aromatic amines the reaction was regiospecific and stopped at the stage of biaryl to yield benzidine derivatives.

The coupling of aromatic nuclei using Lewis or protonic acids as a catalyst is called a Scholl reaction,[1] and is applicable to the preparation of derivatives of polyaryl;[2-4] however, this reaction is not useful for the synthesis of ordinary biaryl derivatives because of their low yields.

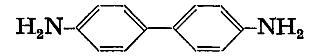
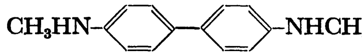
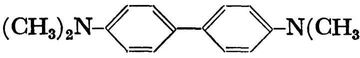
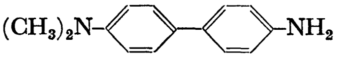
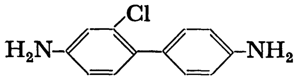
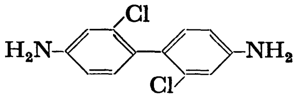
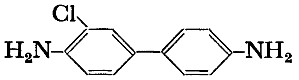
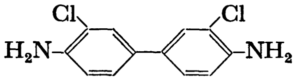
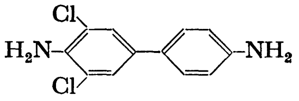
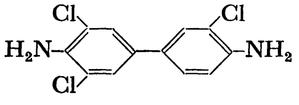
When aromatic amines were heated in a molten salt consisting of a mixture of $AlCl_3$-NaCl-KCl, derivatives of *p,p'*-diaminobiaryl were found to be obtained as a major product. This paper reports the reactions of aromatic amines in molten salts to give benzidine derivatives.

Experimental

All the melting points are uncorrected. NMR spectra were recorded on a Varian A-60D spectrometer. Mass spectra were recorded on a JEOL-JMS-07 mass spectrometer. Elemental analyses were performed in the Micro-analytical Center of Gunma University. The structural assignments of the reaction products were done by means of their NMR, MS spectra, and elemental analyses and by a mixed-melting-point test with an authentic sample.

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

TABLE 1. BENZIDINE DERIVATIVES

No.	Compound	Mp (°C) (Lit,)	Solvent for recrystalization	Anal. (%), Found (Calcd) C	H	N	Cl
1		123—125 (125—126)[a]	C_6H_6	—	—	—	—
2		92—93 (74—76)[b]	EtOH-H_2O	—	—	—	—
3		192—193 (193.5)[c]	EtOH	—	—	—	—
4		144—145	EtOH	78.67 (79.21	7.60 7.60	13.35 13.20)	—
5		102—103	C_6H_{12}	66.04 (65.91	5.15 5.07	12.87 12.81	16.2 16.21)
6		162—163 (163)[d]	C_6H_{12}	—	—	—	—
7		105—107	C_6H_{12}	66.23 (65.91	5.08 5.07	12.94 12.81	16.3 16.21)
8		131—132 (132—133)[e]	CCl_4	—	—	—	—
9		109—110	C_6H_{12}	56.52 (56.94	4.03 3.98	10.88 11.07	27.5 28.01)
10		168—169	C_6H_{12}	50.41 (50.12	3.17 3.15	9.69 9.74	37.0 36.98)

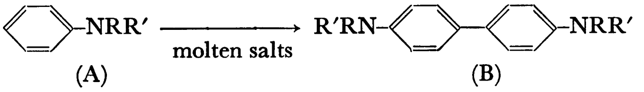
a) R. J. W. Le Fèvre and E. E. Turner, *Chem. Zentr.*, **98, II,** 818 (1927). b) R. Willstätter and L. Kalb, *Ber.*, **37**, 3773 (1904). c) R. Willstätter and L. Kalb, *Ber.*, **37**, 3766 (1904). d) G. Schultz, *Ber.*, **17**, 465 (1884). e) P. Cohn, *Ber.*, **33**, 3552 (1900).

A typical example of the reaction is shown below: 5 ml of aniline (0.0549 mol) was added into a molten mixture of $AlCl_3$–NaCl–KCl (0.60: 0.20: 0.20 mol) under stirring and then the reaction mixture was stirred under blowing of O_2 (or N_2) (20—30 ml/min). The mixture was then poured into a mixture of 500 ml of 0.1M HCl and 100 g of ice. After a small amount of the insoluble matter had been filtered off, the filtrate was made alkaline and the unreacted aniline was removed by steam distillation. The reaction products which remained in the residue were extracted with benzene, separated by column chromatography [silica gel, benzene–acetone (10: 1 v/v)], and recrystallized (Table 1).

Results and Discussion

Formation of Benzidines. When aniline and some *N*-alkylanilines were heated at 150 °C in a mixture of $AlCl_3$–NaCl–KCl (0.6: 0.2: 0.2 mol), the corresponding benzidine derivatives were obtained as the major products. Table 1 lists the benzidine derivatives thus obtained in this work. The yields increased very much in the presence of O_2, but above 250 °C dealkylation of *N*-alkylanilines occurred. Table 2 lists the yields of benzidine derivatives in the presence of O_2. When a mixture of two kinds of amines (in a molar ratio 1: 1) was heated in the molten salt, the unsymmetric derivative of *p,p'*-diaminobiaryl was obtained along with the symmetric ones.

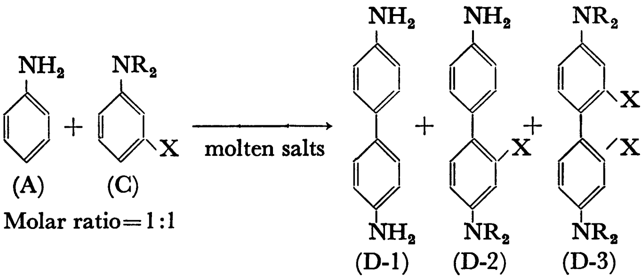
Table 2. Yields of benzidine derivatives in the reaction of anilines in molten salts ($AlCl_3$:NaCl:KCl=3:1:1)[a] at 150 °C in the presence of O_2



(A) R	(A) R'	Condition Atmosph.	Condition Time (h)	Condition Conv. (%)	(B) Yield (%)
R	H[b]	O_2	10	46	78
H	CH_3[c]	O_2	10	67	67
CH_3	CH_3[d]	O_2	10	57	65

a) $AlCl_3$:0.60 mol, NaCl:0.20 mol, and KCl:0.20 mol were used. b) 0.0549 mol, c) 0.0462 mol, d) 0.0394 mol of amines were used, respectively.

Table 3. Formation of benzidine derivatives in the reaction of amine mixture ($AlCl_3$: NaCl:KCl=3:1:1) at 150 °C[a]



(C)	R	X	Condition Atmosph.	Condition Time (h)	products (%) (D-1)	products (%) (D-2)	products (%) (D-3)
(C-1)	CH_3	H	O_2	10	26	28	5
(C-2)	H	Cl	O_2	10	28	8	2

a) 5 ml (0.0549 mol) of aniline was used. $AlCl_3$: 0.60 mol, NaCl: 0.20 mol, and KCl: 0.20 mol were used.

Effects of Lewis Acid. The dimerization of aromatic amines was affected very much by the Lewis acids used: in the reaction of aniline, $AlBr_3$ was found to be as effective as $AlCl_3$, but in the case of $ZnCl_2$, no benzidine derivative was found in the reaction mixture. On the other hand, $SnCl_4$ was ineffective at 100 °C; most of the starting material was recovered even after heating for a long time.

Table 4. Effect of molten salt composition on product yields in the reaction of aniline[a]

Composition (mol)	Condition Atmosph.	Condition Temp (°C)	Condition Time (h)	Product Conv. (%)	Product Yield (%)	Product Coke (g)
$AlCl_3$:NaCl:KCl (0.6:0.2:0.2)	O_2	200	5	66	79	—
$AlBr_3$:NaCl:KCl (0.6:0.2:0.2)	O_2	150	5	62	78	—
$ZnCl_2$:NaCl:KCl (0.6:0.2:0.2)	O_2 O_2	200 240	100 40	30 100	trace —	0.9 5.2
$SnCl_4$[b] (0.5)	O_2	100	20	$\simeq 0$	—	—

a) Substrate: aniline, 0.0549 mol. b) This system is not a molten salt, but cited here for comparison. In this case, anilinium salt was insoluble in $SnCl_4$ at 100 °C.

These Lewis acids are known to form complexes with aromatic amines. In our experiment, the complexation was much more exothermic in the mixture of $AlBr_3$–NaCl–KCl (0.6: 0.2: 0.2 mol) or of $AlCl_3$–NaCl–KCl (0.6: 0.2: 0.2 mol) than in the mixture of $ZnCl_2$–NaCl–KCl (0.6: 0.2: 0.2 mol).[5] Table 4 clearly shows that the above-described heat of complexation is parallel to the yields for the dimerization, and also comparable to the relative acid-strengths of $AlBr_3$, $AlCl_3$, and $ZnCl_2$ toward 2-methyl-4-nitroaniline in diethyl ether *ca.* 2: 1: *ca.* 0.01.[6] These results suggest that the complexation ability of the Lewis acids with amines plays an important role in the dimerization.

Formation of Chlorinated Benzidines. When aromatic amines were heated in the molten salts in the presence

Table 5. Effect of atmosphere on the yields of chlorinated benzidines in the reaction of benzidine hydrochloride in molten salt ($AlCl_3$: NaCl:KCl=3:1:1) at 150 °C[a]

Condition		
Atmosph.	N_2	O_2
Temp (°C)	150	150
Time (h)	10	10
% Conv.	$\simeq 0$	60
Yield (%)		
3-Chlorobenzidine	trace	72
3,3'-Dichlorobenzidine	—	16
3,5-Dichlorobenzidine	—	4
3,3',5-Trichlorobenzidine	—	trace

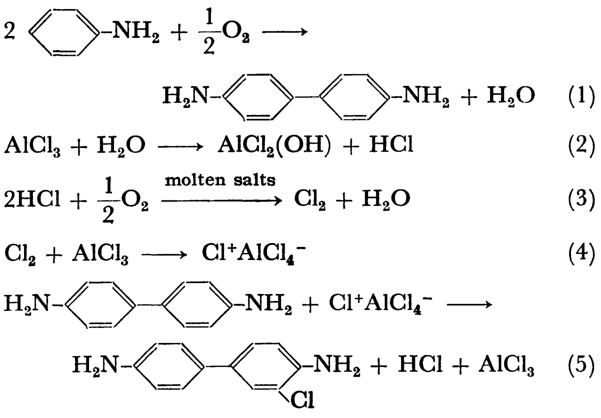
a) $AlCl_3$: 0.60 mol, NaCl: 0.20 mol, and KCl: 0.20 mol were used. 0.0182 mol of benzidine hydrochloride was used.

of O_2, a small amount of chlorinated benzidines was obtained; their amounts increased with the reaction time. However, the formation of chlorinated benzidines was not observed in the absence of O_2; in the presence of O_2, the gas mixture evolved in the reaction vessel turned KI-starch test paper into blue, indicating the presence of Cl_2 which would react with amines to yield the chlorinated benzidines. Thus, when benzidine hydrochloride was heated in the molten salt, various chlorinated benzidines were obtained (Table 5). In the presence of aniline hydrochloride, chlorinated products were formed more rapidly and in high yields; thus, the formation of chlorinated products is assumed to proceed by the sequence shown in Scheme 1.

TABLE 6. EFFECT OF HYDROGEN CHLORIDE ON THE FORMATION OF CHLORINATED BENZIDINE IN MOLTEN SALT ($AlCl_3$:NaCl:KCl=3:1:1) AT 150 °C[a]

Substrate	Aniline[b]	Aniline hydrochloride[c]
Condition		
Atmosph.	O_2	O_2
Temp (°C)	150	150
Time (h)	10	20
% Conv.	85	95
Yield (%)		
Benzidine	87	38
3-Chlorobenzidine	trace	37
3,3′-Dichlorobenzidine	—	10
3,5-Dichlorobenzidine	—	4
3,3′,5-Trichlorobenzidine	—	trace

a) $AlCl_3$: 0.60 mol, NaCl: 0.20 mol, and KCl: 0.20 mol were used. b) 0.0549 mol. c) 0.0182 mol.



$$AlCl_3 + H_2O \longrightarrow AlCl_2(OH) + HCl \qquad (2)$$

$$2HCl + \frac{1}{2}O_2 \xrightarrow{\text{molten salts}} Cl_2 + H_2O \qquad (3)$$

$$Cl_2 + AlCl_3 \longrightarrow Cl^+AlCl_4^- \qquad (4)$$

Scheme 1. Process for the formation of chlorinated benzidines.

Effects of Composition of Molten Salt. Although $AlCl_3$ is known to form the 1:1 complex with NaCl or KCl in a molten salt and only the remaining $AlCl_3$ has any catalytic activity,[7] benzidine was also formed even in the molten salt of a molar ratio $[AlCl_3/(NaCl+KCl)]$ less than unity, suggesting that aniline took $AlCl_3$ away from the complex. When the molar ratio of aniline to free $AlCl_3$ was 1:4 or 1:2 in the molten salt of $AlCl_3$: NaCl: KCl (0.6: 0.2: 0.2 mol) at 200 °C in a stream of N_2, the reaction mixture remained completely clear. On the other hand, as the molar ratio became 1:1 or larger, the mixture increasingly became more turbid. These facts indicate that the $AlCl_3$–aniline, $AlCl_3$–NaCl, and $AlCl_3$–KCl complexes are practically soluble in a molten salt and that the free NaCl and KCl, formed when aniline takes $AlCl_3$ from the $AlCl_3$–NaCl or $AlCl_3$–KCl complex, are insoluble in a molten salt,[8–10] supporting the above-

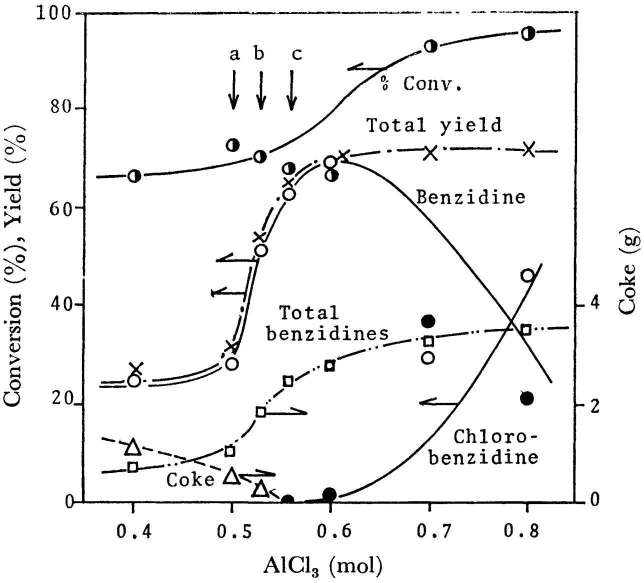


Fig. 1. Effect of molten salt composition on the product yields (reaction temp 200 °C, reaction time 5 h, substrate; aniline 0.0549 mol).

a) Aniline: free AlC_3l=1: 0.
b) Aniline: free $AlCl_3$=1: 1.
c) Aniline: free $AlCl_3$=1: 2.
◑: Conversion(%). ×: Total yield(%).
○: Benzidine(%). □: Total Benzidines(g).
△: Coke(g). ●: Chlorobenzidine(%).

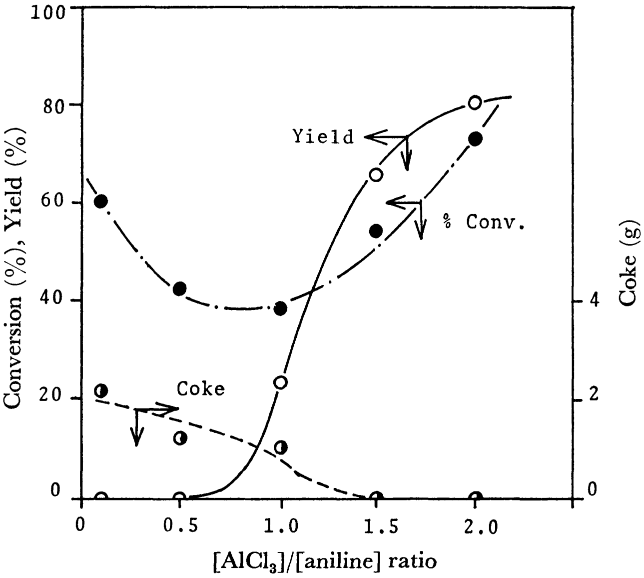


Fig. 2. Effect of $[AlCl_3]$/[aniline] ratio on the product yields (reaction temp 150 °C, reaction time 20 h, substrate; aniline 0.0549 mol).

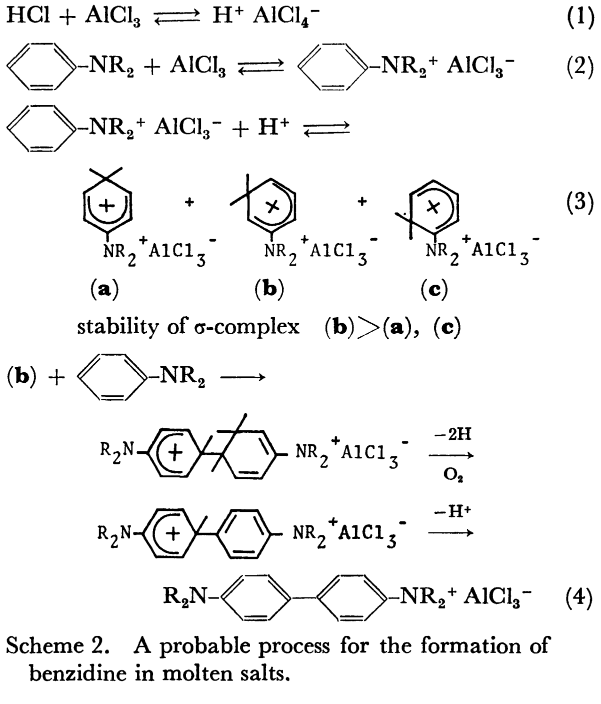
—○—: yield (%).
–·●·–: Conversion (%).
—◑—: Coke (g).

described suggestion. Of course, the yield of benzidine increased with an increase in the ratio of $AlCl_3/(NaCl+KCl)$; in the region of ratio between 1—2 the increase in yield was most remarkable.

Reactions of Aniline with $AlCl_3$ in the Absence of NaCl and KCl. In the reaction of aniline with $AlCl_3$ in the absence of KCl and NaCl, a large amount of black tarry matter was obtained, and the yield of benzidine increased with an increase in the amount of $AlCl_3$. These results suggest that $AlCl_3$ complexed aniline at the site of amino group preferentially, arguing from a consideration of the similar spectral change on addition of $AlCl_3$ or HCl to aniline, and that more than one equivalent amount of $AlCl_3$ is necessary for the dimerization of aniline.

When aniline was heated with aniline hydrochloride in the absence of $AlCl_3$, no benzidine was formed, and no corresponding derivative of benzidine was similarly observed when dimethylaniline was heated with *N*,*N*-dimethyl-*N*-ethylanilinium iodide. Therefore, it may be obvious that the activation by quaternization of an amino group is not sufficient to dimerize an aromatic amine, in spite of the strong electron-withdrawing power of the $-\overset{+}{N}R_3$ group.[11]

From these results, a probable process for the formation of benzidine from aniline in the molten salt is shown in Scheme 2:



Scheme 2. A probable process for the formation of benzidine in molten salts.

1) Formation of $H^+AlCl_4^-$ from $AlCl_3$ and HCl, which would be formed from $AlCl_3$ and trace amounts of water in the molten salt.

2) Formation of a complex from aniline and $AlCl_3$. Although an equilibrium of the complex formation should lie far to the right, a slight amount of free aniline would be present in the reaction mixture, judging from the fact that all the chlorinated benzidine derivatives obtained in the reactions should be derived from free amines; all of them have halogen atoms at *ortho* or/and *para* positions to the amino group.

3) Formation of a σ-complex by the reaction of the aniline–$AlCl_3$ complex with $H^+AlCl_4^-$. In this reaction, the formation of three kinds of σ-complexes may be possible and from the adjacent charge rule the complex (**b**) should be the most stable and probable one among them; a similar σ-complex was observed by Olah *et al.*[11] However, the σ-complex formation would take place only with difficulty because of the positive character of the aniline–$AlCl_3$ complex. Thus, even though the concentration of the complex (**b**) is very low, **b** would be very electrophilic and a true reactive species in this reaction.

4) Formation of protonated dihydrobenzidine by a combination of the complex (**b**) with aniline, which would be present in a slight amount in the reaction mixture; this combination of two aromatic nuclei would be the key step in the benzidine formation from aniline in the molten salt.

5) Formation of a complex consisting of benzidine and $AlCl_3$ from protonated dihydrobenzidine by dehydrogenation and deprotonation. Monosubstituted benzenes such as halo-[3] and alkyl-benzenes[4] reacted with Lewis acids to give the derivatives of polyphenylene. However, the reaction of aromatic amines was very regiospecific and stopped at the stage of dimerization to yield *p*,*p*′-diaminobiaryls. The difference in the reaction between amine and other aromatic compounds would be attributed to the amino group which complexes $AlCl_3$ preferentially. Then the coordinated amine would react with $H^+AlCl_4^-$ to give the σ-complex of *meta* type (**b**), which would attack a free amine at the *ortho* or *para* position to the amino group, with the *para* attack predominating because of the steric hindrance in the *ortho* attack.

As to the reaction site of the free amine component, it may be reasonable to consider as follows: in the ordinary electrophilic substitution of aromatic compounds having an *o*- and *p*-directive group, the *para* attack proceeds more readily than the *ortho* attack even in the absence of steric hindrance. The positive charge of the reagent (**b**) spreads over three *o*- and *p*-positions to the sp^3 carbon in the ring, and consequently the electrophilic reactivities of *para* and *ortho* carbon atoms would be very low. Therefore, this reaction should be very selective, as in the cases of azo-coupling reactions of diazonium salts with aromatic amines; thus, in the present cases, the reactions took place almost exclusively at the *o*-position to the sp^3 carbon.

It may also be possible to form a similar benzidine–$AlCl_3$ complex (of the molar ratio of 1 : 1 or 1 : 2) to that from aniline. However, protonation of the 1 : 2 complex to yield a reactive species (**d**), corresponding to **b** in structure, would be much harder by two $-\overset{+}{N}<$ groups than in the case of an aniline complex.[11] The concentration of a 1 : 1 complex should be very low in the presence of an excess of $AlCl_3$. Moreover, protonation would occur at the free amino group to give a complex similar to the 1 : 2 complex. After all, protonation is considered to be very difficult in the case of the benzidine–$AlCl_3$ complex (1 : 1 or 1 : 2), and, therefore, there is little possibility that a corresponding reactive species to **b** reacts with aniline to produce a trimer.

On the other hand, the concentration of free benzidine would be very low in the presence of an excess of $AlCl_3$ compared with the case of aniline, and, moreover, the attack of **b** on the *ortho* position to the amino group of benzidine is considered to be very difficult because of the steric hindrance. Thus, **b** should react with aniline preferentially even in the presence of benzidine. Therefore, the possibilities of giving a trimer [reaction product of **b** with benzidine or reaction product of **d** with aniline] or tetramer [reaction product of **d** with benzidine] should be very low. This interpretation is consistent with the fact that the reaction of aromatic amines stopped at the stage of dimerization.

These speculations may be supported by the fact that *m*-phenylenediamine did not undergo dimerization and most of it was recovered in the molten salt; in the presence of an excess of $AlCl_3$, *m*-phenylenediamine would complex 2 mol of $AlCl_3$ to form a 1 : 2 complex, whose protonation to yield a σ-complex would occur with great difficulty. Even if a σ-complex is formed, little biphenyl would be formed, because *m*-phenylenediamine would not be present as a free base in the presence of an excess of $AlCl_3$.

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5) On the addition of 5 ml (0.0549 mol) of aniline into the stirred molten mixtures of $AlBr_3$-NaCl-KCl (0.6: 0.2: 0.2 mol, 150 °C), $AlCl_3$-NaCl-KCl (0.6: 0.2: 0.2 mol, 150 °C), and $ZnCl_2$-NaCl-KCl (0.6: 0.2: 0.2 mol, 200 °C), the temperature of the reaction mixture rose by 30—35, 20—25, and 5—7 °C, respectively.

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