ORGANIC REACTIONS
IN LOW MELTING CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT
Mixtures of 1, 3-dialkylimidazolium chlorides and aluminum chloride are liquid considerably below room temperature, and they promote certain organic reactions. Acidic mixtures of 1-methyl-3-ethylimidazolium chloride and AlCl3 act both as a solvent and a catalyst for alkylation and acylation of aromatic compounds. The rate of reaction may be controlled by changing the Lewis acidity of the melt and the temperature. The melts that were used permit reactions at sub-zero temperatures. Spectroscopic experiments showed the identity of the catalytic species in the melt and the reactive intermediate.

INTRODUCTION
The behavior of organic compounds in chloroaluminate molten salts has been studied by several groups in the last decade. Early work involved the relatively high temperature (approximately 175°C) NaCl-AlCl3 molten salts, but problems with solubility, thermal stability and volatility were experienced. Later, low temperature melts comprised of 1-alkylpyridinium chloride and aluminum chloride were used to study the electrochemistry of a variety of organics at or near room temperature. As a rule, these electrochemical reactions took advantage of the ability of the AlCl3-rich melts to stabilize positive oxidation states of aromatic compounds (1). Numerous types of organic reactions employing chloroaluminate melts have been reviewed by Jones and Osteryoung (2). Surprisingly, reactions in the new low temperature melts have not been as extensively studied as those in the high temperature NaCl-AlCl3 melts.

Recently, we have been studying the structure, physical properties and chemistry of chloroaluminate melts consisting of mixtures of 1,3-dialkylimidazolium chloride and aluminum chloride (3). These mixtures are liquid at room temperature and some compositions melt substantially below room temperature. In addition, they demonstrate a much wider range of Lewis acidity than the NaCl-AlCl3 mixtures. The binary mixture of 1-methyl-3-ethylimidazolium chloride and AlCl3 ("MeEtIm melt") has a particularly favorable combination of physical properties and ease of preparation. We noted that the
MeEtImCl-AlCl₃ mixtures dissolved a wide variety of organic compounds and stabilized organic radical actions. We report here that the low melting MeEtImCl-AlCl₃ molten salts can act as catalyst and/or solvent for classic Friedel-Crafts alkylation and acylation of aromatic compounds.

**EXPERIMENTAL**

All melts were prepared as reported previously (3). In a glove box the appropriate amount of melt and aromatic compound were added to an "airless-ware" reaction flask (Kontes), usually 50 mL, equipped with a magnetic stirring bar. All further operations were done outside the glove box, using a dry nitrogen flow to exclude moisture. The reaction mixtures were usually cooled to 0°C in an ice/water bath. The organic chloride was added to the aromatic/melt mixture by pipet and the reaction was allowed to proceed for the appropriate time, after which the reaction was quenched by pouring over ice. The mixture was made alkaline with a concentrated NaOH solution until all precipitate was dissolved. The mixture was extracted with diethyl ether, dried over magnesium sulfate and analyzed by GC/MS.

**RESULTS AND DISCUSSION**

The venerable Friedel-Crafts electrophilic alkylation and acylation reactions are normally run in an inert solvent and catalyzed by suspended or dissolved AlCl₃. In this report we describe the reactivity and extent of these simple reactions employing the unusual MeEtImCl-AlCl₃ catalyst and solvent system. Since an acidic species is required to catalyze the reactions, compositions of the MeEtIm melt where AlCl₃ was in excess over the MeEtImCl was the most effective catalyst. We usually express the melt composition as apparent AlCl₃ mole fraction, N, realizing that free AlCl₃ does not exist in the melt. An N = 0.67 melt is prepared by adding 2 moles of AlCl₃ to 1 mole of MeEtImCl and is acidic. Likewise an N = 0.50 melt is prepared by combining 1 mole of each, and is neutral. N ≤ 0.5 implies a basic melt. A combination of the two solids produces a liquid that has the unique dual character of catalyst and solvent for Friedel-Crafts reactions.

A series of alkylating agents was investigated. Primary and secondary alkyl halides were added to mixtures of melt and benzene under anhydrous conditions. Alkylated benzenes were observed after reactions with methyl chloride, ethyl chloride, n-propyl chloride, n-butyl chloride, cyclohexyl chloride and benzyl chloride. Gaseous HCl was evolved during all of the alkylation reactions. In addition to mono-alkylation products, poly-alkylated benzenes were present in the reaction products. For example, excess ethyl chloride reacted with benzene to produce the following ethylbenzenes: mono-(12%),

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di-(11%), tri-(33%), tetra-(24%), penta (17%) and hexa-(2%). Methyl chloride produced an interesting array of products (Table 1). Note that the odd substitutions are virtually absent under the reaction conditions described. We have no explanation for this and we could not find any reports of similar phenomena in the literature.

Polyalkylation can be accounted for by considering the enhanced activity of the alkylated product. An excess of aromatic substrate would minimize polyalkylation. Thus, a ten fold excess of benzene over n-propyl chloride, in the presence of the 0.67 melt, produced predominately mono-propylbenzene (95%) with only 5% poly-propylated products. The mono-propylbenzene consisted of 70% iso-propylbenzene and 30% n-propylbenzene. The presence of iso-propylbenzene gives evidence of rearrangement of the primary carbonium ion to the more favorable secondary carbonium ion prior to ring substitution. The predominance of the rearranged product is an indication that the carbonium ion is formed, since reactions where ionization does not take place (i.e. where a "polarized covalent complex" is formed) show primarily the unrearranged product (4). Rearrangement of n-butyl carbonium ion to secondary butyl carbonium ion also occurs in alkylation reactions with n-butyl chloride. Rearrangements such as these are common in classic Friedel-Crafts electrophilic aromatic alkylation reactions. Spontaneous formation of carbonium ions in 1-(1-butyl)pyridinium chloride-AlCl₃ melt has been reported (5), so we believe that the alkylation proceeds by way of the completely dissociated carbonium ions in the reactions described here.

Comprehensive positional isomerization studies of the polyalkylated benzenes have not been done in the melt to detect intramolecular rearrangements. Under usual Friedel-Crafts conditions intermolecular migrations among polyalkylated benzenes can also occur, especially in the presence of excess catalyst, to produce a non-thermodynamically controlled product distribution (6). The intermolecular migration usually occurs following protonation of the polyalkylbenzene at the carbon bearing an alkyl group with subsequent dissociation of the carbonium ion. The same process should not be possible in the aprotic MeEtIm melts. An equimolar mixture of benzene and hexamethylbenzene in an acidic MeEtIm melt (N = 0.67) resulted in no toluene, xylenes, mesitylenes, etc., thus there is no dissociation of the methyl substituents, probably due to lack of H⁺ in the medium. Koch et al. (7) observed that Friedel-Crafts transalkylations could be initiated electrochemically in ethylpyridinium bromide/AlCl₃ melts, which are chemically similar to the MeEtIm melt described here.

The versatility of the MeEtImCl-AlCl₃ melt in Friedel-Crafts reactions was demonstrated by attempting the alkylation reaction with different aromatic compounds. Table 2 lists the compounds and the alkylated products. The reactions showed the expected behavior towards activated and deactivated aromatic substrates, with no reaction occurring with nitrobenzene.
The classic nature of Friedel-Crafts electrophilic aromatic substitution reactions in chloroaluminate melts was further demonstrated through relative reactivity measurements. In competitive propylation, toluene was found to be 1.9 times more reactive than benzene, and chlorobenzene was approximately 0.55 times as reactive as benzene. The relative rates suggest that a highly reactive electrophile is produced during the reaction. Such reactive attack by electrophiles is relatively non-selective for aromatic compounds that are activated or deactivated by substituents, therefore, relative rates are usually within the same order of magnitude.

Friedel-Crafts acylation of aromatic compounds with MeEtImCl molten salts proceeds with relative ease. Acylation proved simpler than alkylation because the first substitution product deactivates the aromatic nucleus towards further ring substitution. As a result, mono-substitution is observed with essentially no poly-substitution when benzene and acetyl chloride are reacted in acidic MeEtIm melt. A competitive rate experiment similar to that described for alkylation was done and the expected order of reactivity for benzene, toluene and chlorobenzene was observed. The relative rates were 1, 37, and 0.015 respectively. Note that the substituents are exerting more kinetic control in the case of acylation.

The simplest of the acylation reactions, i.e., MeEtImCl-AlCl3 catalyzed reaction of acetyl chloride with benzene to produce acetophenone was studied in detail. The rate at which acetophenone was produced was dependent on the composition (hence Lewis acidity) of the melt. In the melts described here, Lewis acidity is determined by the proportions of AlCl3 to MeEtImCl used to prepare the melt, and is expressed as the quantity N (vide infra). In chloroaluminate melts, the Lewis acidity is known for any given composition. Melts of greater Lewis acidity demonstrated greater catalytic activity than those of weaker acidity or neutral and basic melts. A series of experiments using constant weights of reactants and melt but variable melt composition demonstrated the expected dependency. Figure 1 shows the initial rate of acetylation of benzene plotted vs N. The reactions were run at 0°C, and progress monitored by GC/MS analysis of aliquots. No substitution occurred in melts where $N \leq 0.5$, and the initial rates or reactions were found to increase as the acidity of the melt increased. These observations are almost certainly due to the increasing concentration of the actual catalytic species in the melt. The concentration of Al$_2$Cl$_7^-$ in the melts also is plotted in Figure 1, and the dependence of [Al$_2$Cl$_7^-$] on N suggests that Al$_2$Cl$_7^-$ may be the catalyst responsible for promoting the reaction.

We examined the reaction between the melt and acetyl chloride by nuclear magnetic resonance (NMR) spectroscopy in order to learn some details about the nature of the catalyst in the melt and the electrophile that is produced from the acetyl chloride. Observation of the proton NMR resonance of the methyl group in the acetyl chloride (or
its reaction product) was useful, since it was a singlet well separated from the proton resonances of the imidazolium ions in the melts. Figure 2 shows the dependence on the acetyl proton chemical shift on the relative concentrations of acetyl chloride \([\text{CH}_3\text{COCl}]\) and \(\text{Al}_2\text{Cl}_7^-\) in the mixture. At low concentrations of acetyl chloride, the acetyl resonance was shifted downfield, and did not change much with increasing concentration. At high \([\text{CH}_3\text{COCl}]\), the resonance moved upfield with increasing relative concentration. The threshold that delineated these two types of behavior was where \([\text{CH}_3\text{COCl}]\) was equal to the \([\text{Al}_2\text{Cl}_7^-]\) in the mixture (zero on the plot in Figure 2). This is very suggestive of a stoichiometric reaction between the \(\text{CH}_3\text{COCl}\) and \(\text{Al}_2\text{Cl}_7^-\), which is probably the actual catalyst in the melt. This is a very useful fact, because we can now easily select the reactivity of the medium toward Friedel-Crafts substitution by adjusting the \(N\) of the melt used. The product of the reaction between \(\text{CH}_3\text{COCl}\) and \(\text{Al}_2\text{Cl}_7^-\) is still an open question. The simplest case would be complete transfer of the chloride in acetyl chloride to produce the acetyl cation (1-oxo-ethylium):

\[
\text{CH}_3\text{COCI} + \text{Al}_2\text{Cl}_7^- \rightarrow \text{CH}_3\text{CO}^+ + 2\text{AlCl}_4^-
\]

Alternatively, a reactive complex of \(\text{CH}_3\text{COCl}^* \cdot \text{Al}_2\text{Cl}_7^-\) might be the species formed. The \(^1\text{H} NMR\) chemical shift of \(\text{CH}_3\text{CO}^+\) has been measured (8), but in an entirely different solvent and with a different reference. Olah reported that \(\text{CH}_3\text{CO}^+\) was shifted 1.9 ppm downfield from its parent \(\text{CH}_3\text{COF}\). We see a 1.0 ppm downfield shift from the parent \(\text{CH}_3\text{COCl}\), which we cannot interpret unambiguously as the completely dissociated \(\text{CH}_3\text{CO}^+\). \(^{13}\text{C} NMR\) measurements are being done to clarify the matter.

From the results of the experiments described above we suggest the reaction scheme outlined in Figure 3. Note that \(\text{Al}_2\text{Cl}_7^-\) is regenerated and that the observed products (acetophenone and HCl are accounted for). We have written the reactive electrophile as \(\text{CH}_3\text{CO}^+\); but it may not be completely dissociated, as discussed above.

We have not yet established the full scope of Friedel-Crafts reactions in the \(\text{MeEtImCl}\cdot\text{AlCl}_3\) molten salts. At this point we know that alkylations and acylations are promoted by the melt, the reactions are homogeneous, and the work-up is relatively simple. The melt is easily prepared in two steps from commercially available materials, so it may be a generally useful reagent and solvent.

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### TABLE 1
**ALKYLATION OF BENZENE**

| Alkylation Agent (R-Cl) | N of Melt | Mole Ratio R-Cl:Benzene: Melt | % Alkylated Products | Mono- | Di- | Tri- | Tetra- | Penta- | Hexa- |
|-------------------------|-----------|-------------------------------|----------------------|-------|----|-----|-------|-------|------|
| R=methyl<sup>a</sup>    | 0.67      | xs:1:1                        | 1.5                  | 58.5  | 1.5| 26.8| 1.4   | 10.2  |
| R=ethyl<sup>a</sup>     | 0.67      | xs:1:1                        | 11.5                 | 10.8  | 33.4| 24.4| --    | 1.5   |
| R=n-propyl<sup>b</sup>  | 0.60      | 1.25:1.25:1                   | 24.8                 | 19.9  | 55.3| --  | --    | --    |
| R=cyclo-hexyl           | 0.60      | 10:10:1                       | 35.0                 | 30.0  | 34.4| --  | --    | --    |
| R=benzyl<sup>c</sup>    | 0.60      | 0.78:1.17:1                   | 50.0                 | 34.5  | 15.6| --  | --    | --    |

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* a. Run at reflux temperature of alkyl chloride
* b. Room Temperature, dry box conditions, exothermic with evolution of gas
* c. Tar formation, small amount of alkylated product isolated
# TABLE 2

## PROPYLLATION OF AROMATIC COMPOUNDS

| Aromatic       | N of Melt | PrCl:Aromatic:Melt | Product            |
|----------------|-----------|--------------------|--------------------|
| Benzene        | 0.67      | 10:1:1             | 95% Mono-, 5% Poly-|
| Toluene        | 0.67      | 10:1:1             | 73% Mono-, 27% Poly-|
| Chlorobenzene  | 0.67      | 10:1:1             | 96% Mono-, 4% Poly |
| Nitrobenzene   | 0.67      | 10:1:1             | no reaction        |

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*Reactions run at 0° C for 10 min.*
Fig. 1. Acetylation of Benzene

Fig. 2. H NMR of Acetyl Chloride in Melt

Fig. 3. Friedel-Crafts Acylation Mechanism