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DIALKYLIMIDAZOLIUM CHLORIDES

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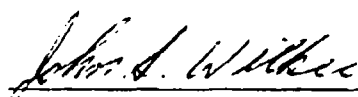
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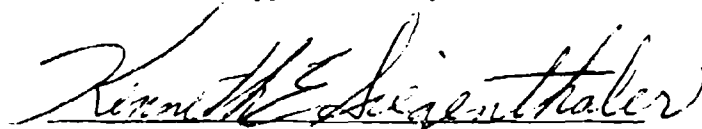
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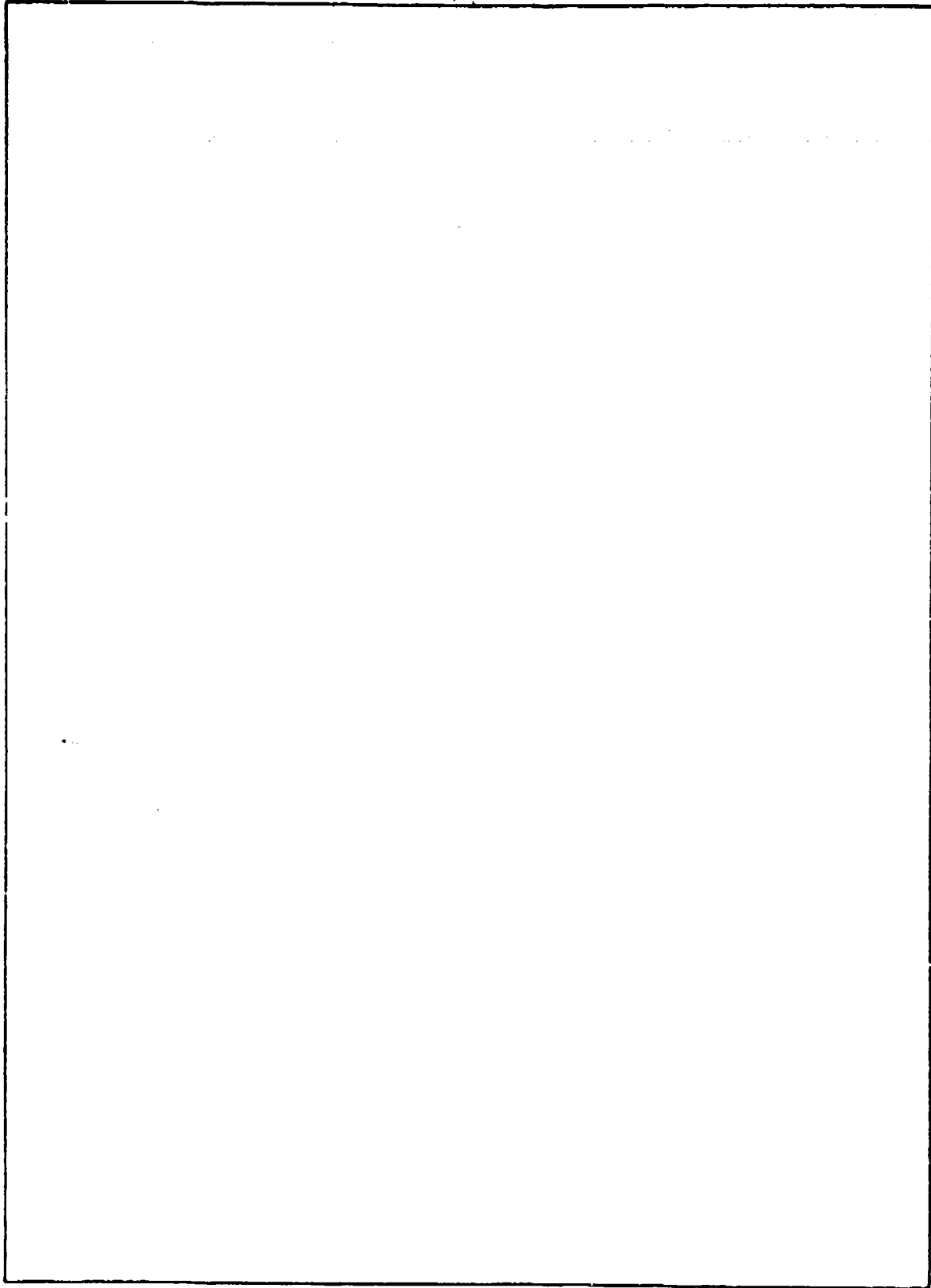
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DIALKYLIMIDAZOLIUM CHLORIDES

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JANUARY 1981

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ABSTRACT

The synthesis of a homologous series of 1-methyl-3-alkylimidazolium chlorides is described. NMR and IR spectra for these compounds are presented.

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PREFACE

This report describes the preparation of a series of heterocyclic chlorides that were used as the basis of some ambient temperature chloroaluminate molten salts. Details for the syntheses and the NMR and IR spectra are not normally published in journals, therefore they are documented here to establish a complete record of this phase of our research in chloroaluminate molten salts.

INTRODUCTION

Air Force requirements for high power density thermal batteries has generated considerable interest in low melting fused salt electrolytes. In this laboratory extensive research has been done on molten salt electrolytes composed of mixtures of alkali halides and aluminum chloride (1-3). These chloroaluminate mixtures melt at considerably lower temperatures than conventional fused salts, but batteries using them still must be maintained at about 200°C (4). For this reason we investigated some salts that are molten at ambient temperature, that is, approximately 30°C.

Mixtures of 1-alkylpyridinium halides and aluminum chloride have been shown to be molten at room temperature (5), and are useful as electrolytes in electrochemical cells (6,7). Furthermore, the alkylpyridinium chloroaluminates were shown to be suitable as battery electrolytes (8).

The major failing of the use of alkylpyridinium as the cation in chloroaluminate melts is that the cation can be reduced electrochemically or by active metals in the basic and neutral melts (9,10). Since aluminum itself will reduce the alkylpyridinium cations, the usefulness of the melts would be limited (in batteries) to cells having anodes less active than aluminum. The solution to this problem is to use a cation which is less easily reduced than alkylpyridinium.

Molecular orbital calculations using the MNDO method indicated that several classes of organic cations might be suitable (11,12). The alkylated imidazoles were attractive candidates for reduction resistant cations. The reduction potential was predicted to be about 0.8V lower than the alkylpyridinium cations and the similar size indicated that low melting chloroaluminate melts might be prepared.

In this report we describe the preparation and properties of a series of 1,3-dialkylimidazolium chlorides. The preparation of most of the simple 1,3-dialkylimidazolium iodides has been previously described and are referenced in Table 1. The chloride salts of the imidazolium cations have not been as extensively studied as the more easily prepared iodides. We describe the synthesis of a homologous series of dialkylimidazolium chlorides derived from 1-methylimidazole.

EXPERIMENTAL

The 1-methylimidazole was obtained from the Aldrich Chemical Co. and was vacuum distilled from BaO before use. The 1-chloropropane and 1-chlorobutane were obtained from the Aldrich Chemical Co. and were used without purification. The chloromethane and chloroethane were obtained from Linde Specialty Gases. NMR spectra were run on a Varian T-60 spectrometer. IR spectra were run on a Beckman IR-20 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories. Melting points are uncorrected.

1,3-Dimethylimidazolium chloride. 1-methylimidazole (62.3 g, 0.76 mol) was weighed in a 250 ml glass pressure vessel and chloromethane (100 ml, 1.40 mol) condensed into it using a dry ice condenser. The container was sealed and heated overnight (16 hrs) at 65°C with magnetic stirring. The pressure in the vessel was reduced by cooling in a dry ice/acetone bath and the top was removed. The excess chloromethane was allowed to boil off through a drying tube. The white solid crude product was recrystallized from acetonitrile. Isolated yield was 66.6 g (67%). Melting point 124.5-128°C. Elemental analysis, calculated for $C_5H_9N_2Cl \cdot 0.35H_2O$; 43.23% C, 7.04% H, 20.17% N, 25.53% Cl, 3.17% O. Observed: 42.82% C, 7.32% H, 20.13% N, 26.01% Cl, 3.72% O.

1-Methyl-3-ethylimidazolium chloride. 1-Methylimidazole (19.3 g, 0.235 mol) was weighed in a 250 ml glass pressure vessel and chloroethane (56.0 g, 0.867 mol) condensed into it using a dry ice condenser. The container was sealed and heated for two days at 75°C with magnetic stirring. The pressure in the vessel was reduced by cooling in a dry ice/acetone bath and the top was removed. The excess chloroethane was allowed to boil off through a drying tube. A slightly off white solid product was obtained that showed no starting material by NMR. Isolated yield was 34.38 g (99.8%). The product was recrystallized by dissolving in a minimum amount of acetonitrile and dropping it into cold ethyl acetate. Melting point 82-87°C. Elemental analysis; calculated for $C_6H_{11}N_2Cl \cdot 0.2H_2O$: 47.97% C, 7.65% H, 18.65% N, 23.60% Cl, 2.13% O. Observed: 48.18% C, 7.80% H, 18.66% N, 23.52% Cl, 1.84% O.

1-Methyl-3-propylimidazolium chloride. 1-Methylimidazole (10.1 g, 0.123 mol) and 1-chloropropane (12.7 g, 0.161 mol) were mixed in a 250 ml glass pressure vessel. The mixture was heated at 80°C for 20 hours with magnetic stirring. The reaction flask was allowed to cool to room temperature and the excess chloropropane was removed at reduced pressure. The slightly yellow oily product was diluted with about 10 ml of acetonitrile and cooled in the freezer. Crystallization was induced with a seed crystal and took several days. The seed crystals were obtained with much difficulty. Yield was 18.7 g (94.3%). Melting point 58-66°C. Elemental analysis; calculated for $C_7H_{13}N_2Cl \cdot 0.3H_2O$: 50.63% C, 8.26% H, 16.87% N, 21.35% Cl, 2.89% O. Observed: 50.70% C, 8.45% H, 17.08% N, 21.55% Cl, 2.22% O.

1-Methyl-3-butylimidazolium chloride. 1-Methylimidazole (60 ml, 0.752 mol) and 1-chlorobutane (87 ml, 0.828 mol) were refluxed without additional

solvent overnight with stirring. The reaction mixture was cooled to room temperature, the top liquid phase decanted and residual excess chlorobutane removed at reduced pressure. The slightly yellow oil was diluted in about 15 ml acetonitrile and crystallized in the freezer with the aid of a seed crystal. The original seed crystals were obtained with much difficulty. Melting point 65-69°C. Elemental analysis; calculated for $C_8H_{15}N_2Cl \cdot 0.1H_2O$: 54.45% C, 8.68% H, 15.87% N, 20.09% Cl, 0.91% O. Observed: 53.94% C, 8.90% H, 16.03% N, 20.52% Cl, 0.61% O.

1-Methyl-3-benzylimidazolium chloride. 1-Methylimidazole (5.0 ml, 63.1 mmol) and benzyl chloride (8.0 ml, 69.4 mmol) were stirred together without solvent for 2 hours at room temperature. The reaction mixture set into a hard glass which could not be crystallized despite many attempts.

RESULTS AND DISCUSSION

The iodide salts of the 1,3-alkylated imidazoles are readily prepared by quaternization of the nucleophilic nitrogen of N-substituted imidazoles with alkyl iodides (~~see references in Table 1~~). The simple procedures used are not entirely applicable to the chlorides because the corresponding chloroalkanes are not as active alkylating agents as iodoalkanes and some of the chloroalkanes are gases at atmospheric pressure. Organic iodide salts can be converted to chloride salts by treatment with methanolic HCl, followed by distillation of the methyl iodide produced in the reaction (20). Compounds I, II and III (the iodide salts) were prepared, then converted to the chlorides as described. Unfortunately, in all cases the products were oils that resisted all attempts at crystallization.

Direct alkylation by the appropriate chloroalkanes proved to be more successful. In some cases the product was obtained in high yield and was

quite pure, even without recrystallation. The procedure for reactions using chloromethane or chloroethane (both gases) consisted of heating the homogeneous mixture of 1-alkylimidazole and chloroalkane in a sealed vessel. Excess chloroalkane was removed by evaporation and the residue was almost pure product. NMR analysis of the residue showed nearly 100% conversion. In the case of liquid chloroalkanes, reactions were run by refluxing mixtures of the reactants, using excess chloroalkane as solvent. The formation of VIII was relatively slow under these conditions, but was much more rapid when run in a sealed tube at 80°C.

Proton NMR provides a convenient way to monitor the extent of reaction for all of the imidazolium salts, since there is no overlap of reactant and product resonances. ~~NMR~~ spectra of VI-X are shown in figures 1-5. In those compounds the C-2 proton resonance in the salt is shifted considerably downfield from the position in the neutral 1-methylimidazole, and it is exchangeable with D₂O.

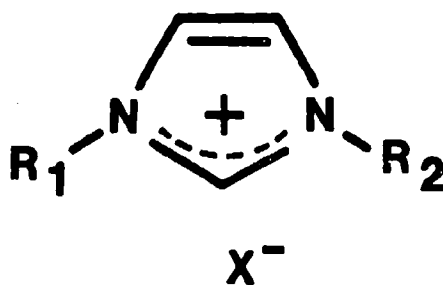
IR spectra of VI-X are shown in figures 6-9.

All of the salts are white solids except X, which is an oil. It may be that X is a true liquid as indicated in the literature (18), but all attempts to crystallize it at low temperature were unsuccessful. All of the salts are extremely hygroscopic, so work up procedures insured exclusion of atmospheric moisture. Elemental analyses invariably indicated the presence of water

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TABLE 1



Alkyimidazolium Salts

<u>Compound</u>	<u>R1</u>	<u>R3</u>	<u>X⁻</u>	<u>Melting Point (°C)</u>	<u>Reference</u>
I	Me	Me	I ⁻	88	12-17
II	Me	Et	I ⁻	80	17, 18
III	Me	Pr	I ⁻		19
IV	Me	Bu	I ⁻	liq.	17
V	Me	Bz	I ⁻	92	16, 17
VI	Me	Me	Cl ⁻	125	this work
VII	Me	Et	Cl ⁻	85	17, this work
VIII	Me	Pr	Cl ⁻	62	16, 19, this work
IX	Me	Bu	Cl ⁻	67	this work
X	Me	Bz	Cl ⁻	oil	17, this work

FIG. 1 -- NMR OF Me₂ImCl (COMPOUND VI)

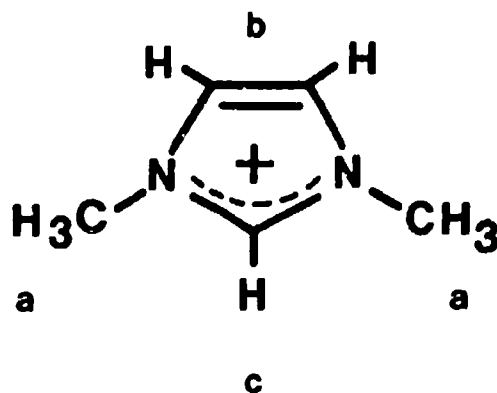
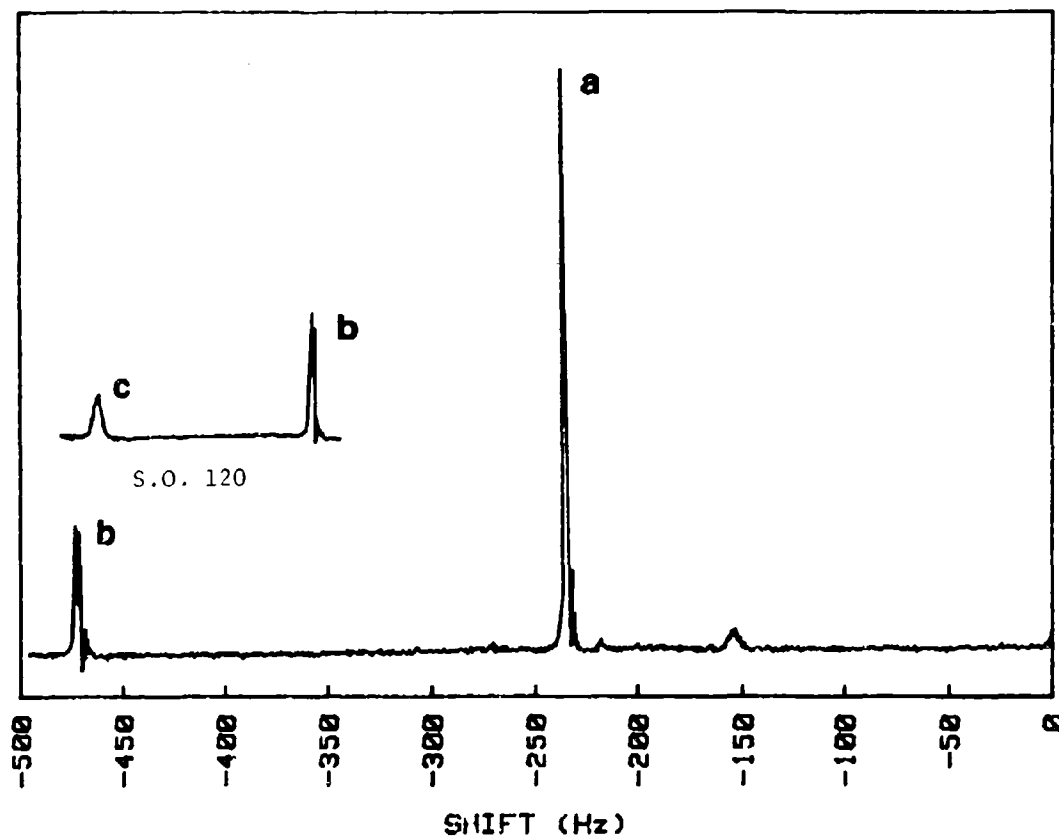


FIG. 2 -- NMR OF MeEtImCl (COMPOUND VII)

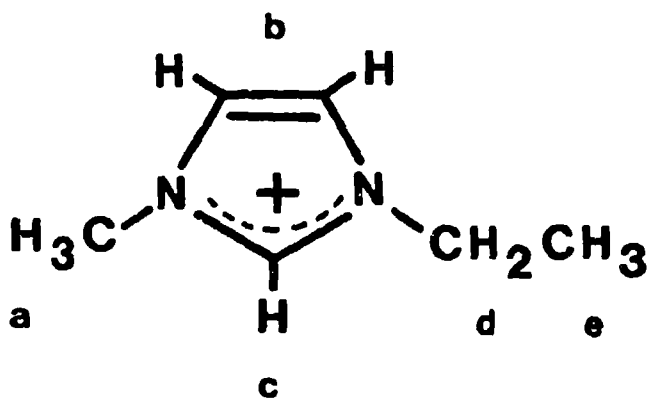
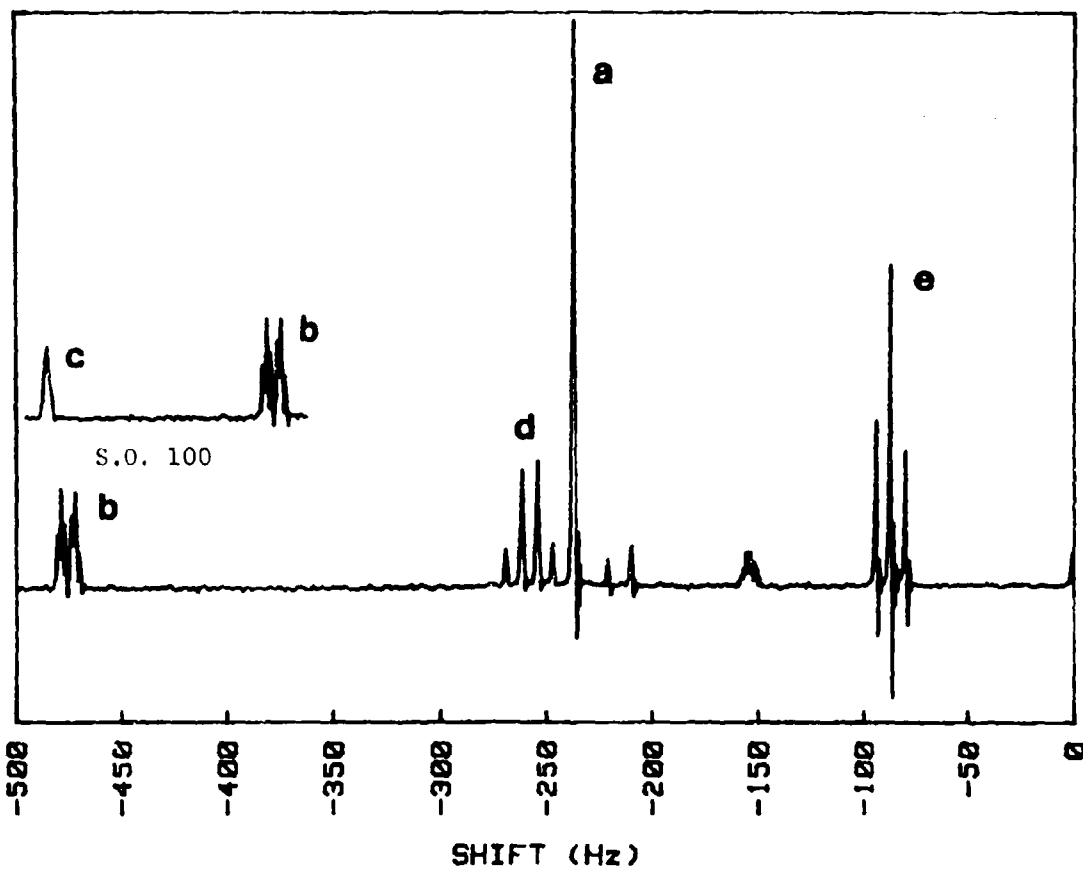


FIG. 3 -- NMR OF MePrImCl (COMPOUND VIII)

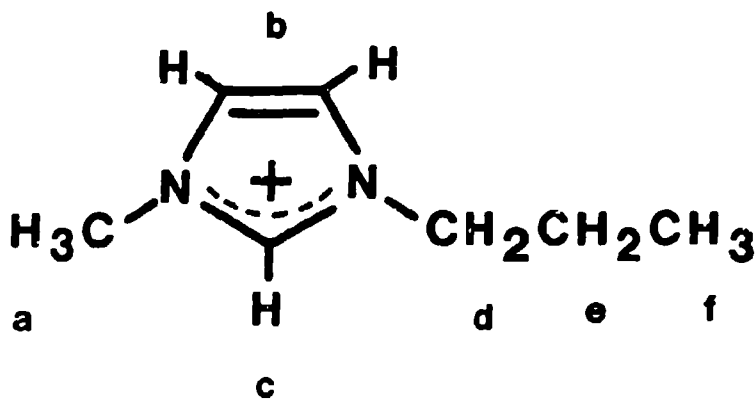
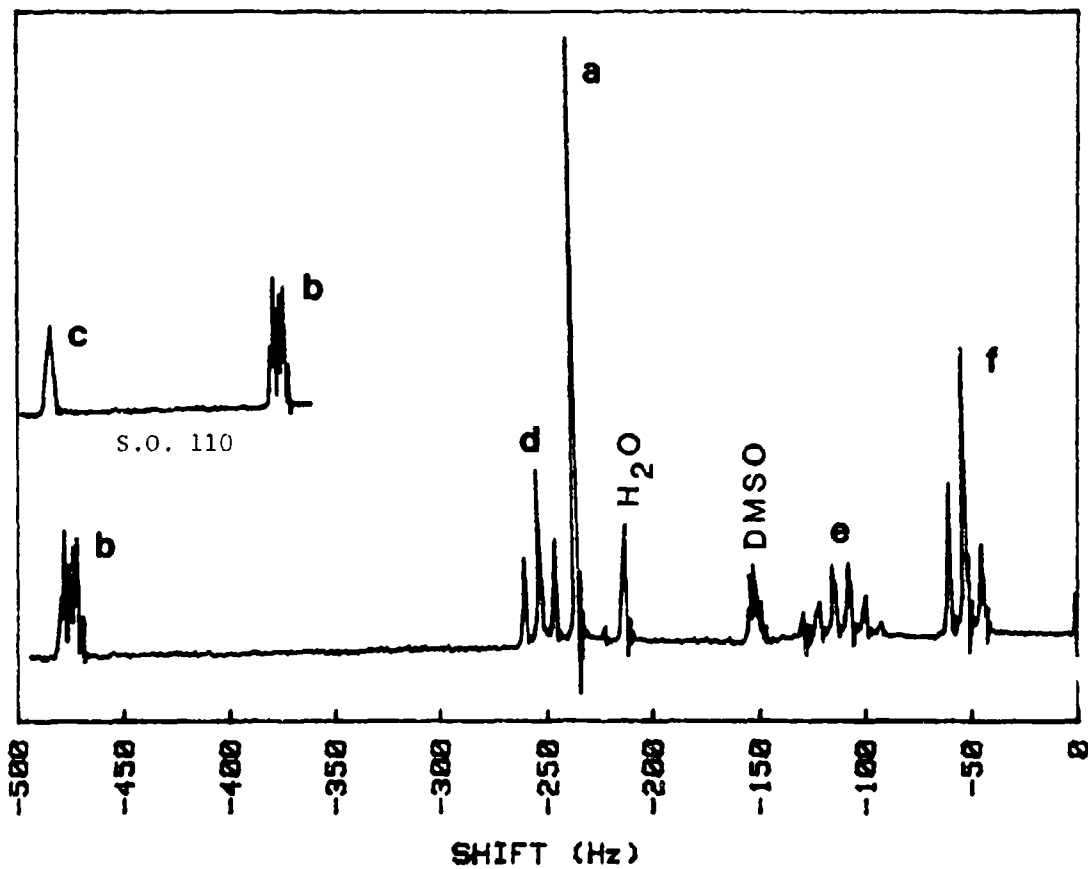


FIG. 4 -- NMR OF MeBuImCl (COMPOUND IX)

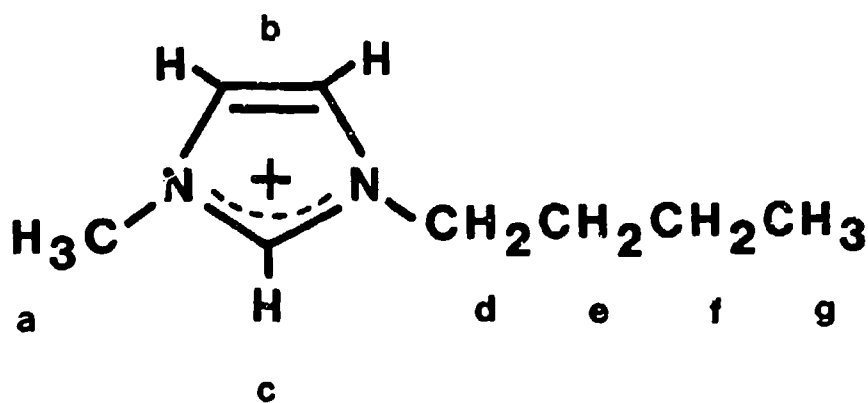
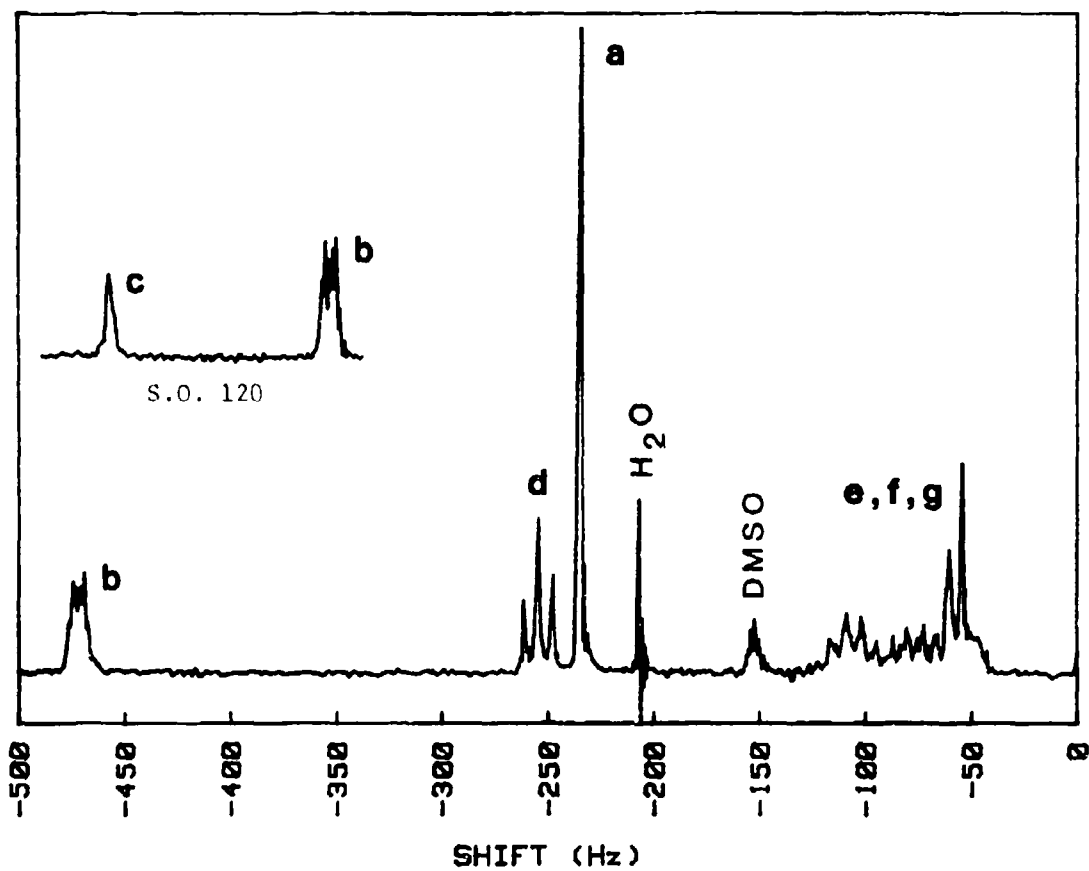


FIG. 5 -- NMR OF MeBzImCl (COMPOUND X)

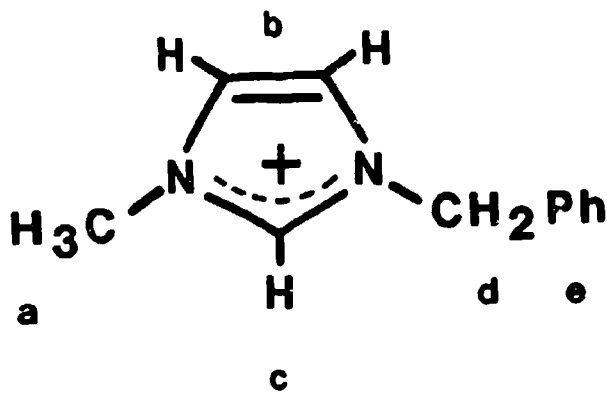
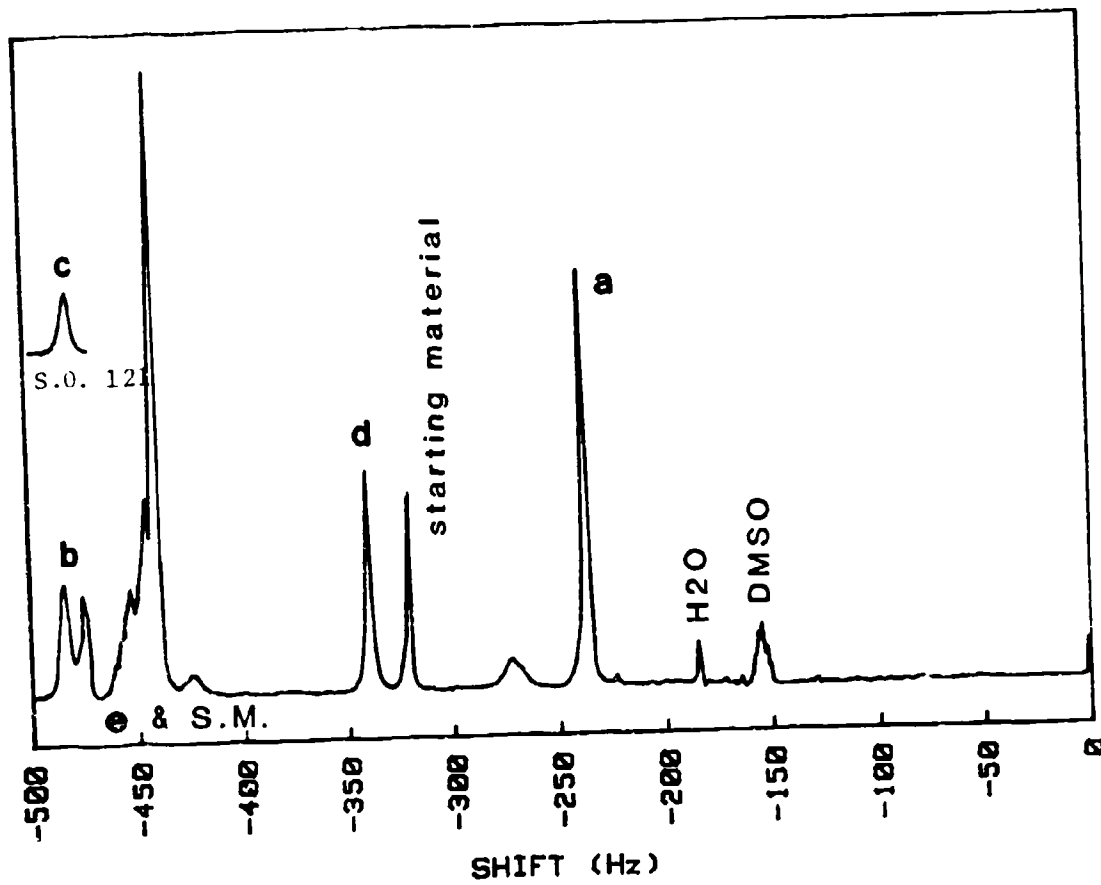


FIG. 6 -- IR OF Me_2ImCl (COMPOUND VI)

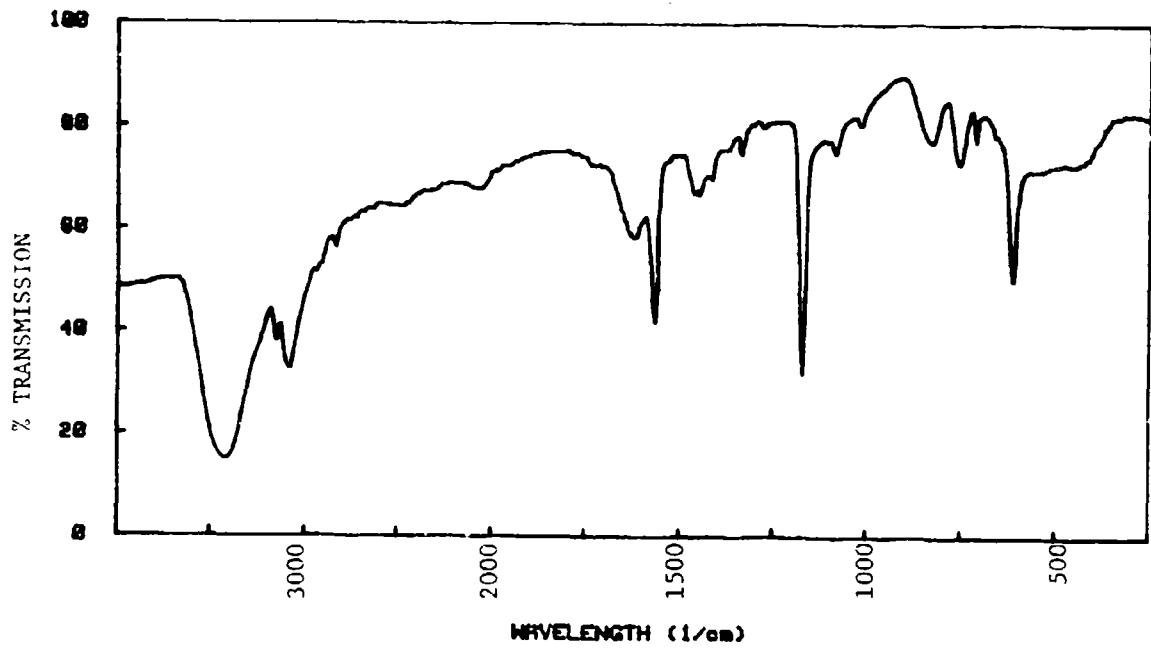


FIG. 7 -- IR OF MeEtImCl (COMPOUND VII)

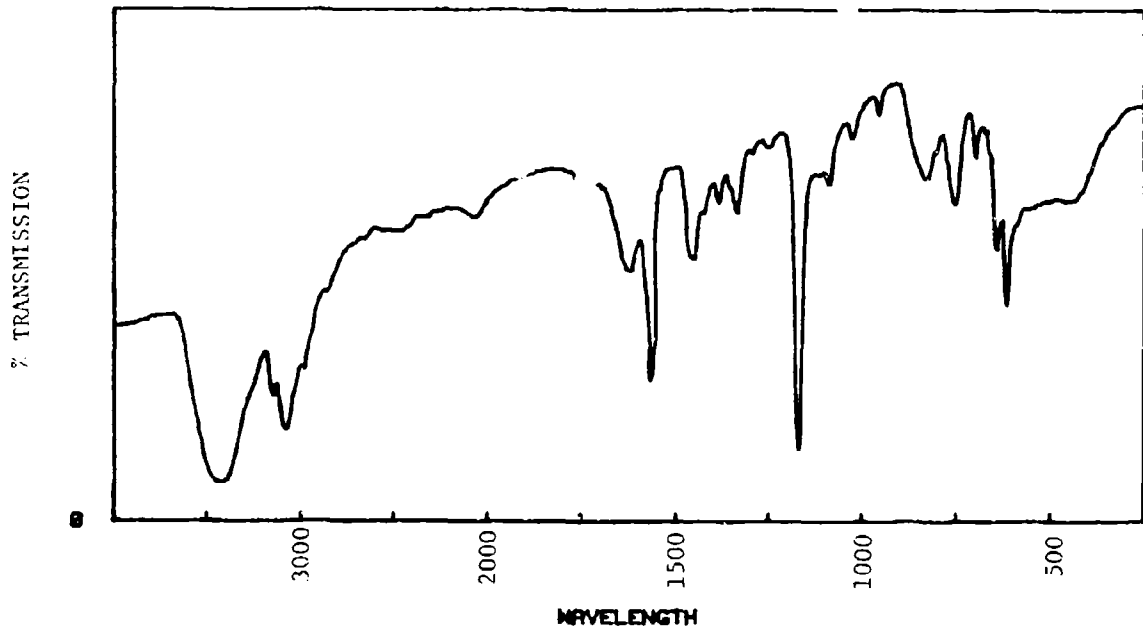


FIG. 8 -- IR OF MePrImCl (COMPOUND VIII)

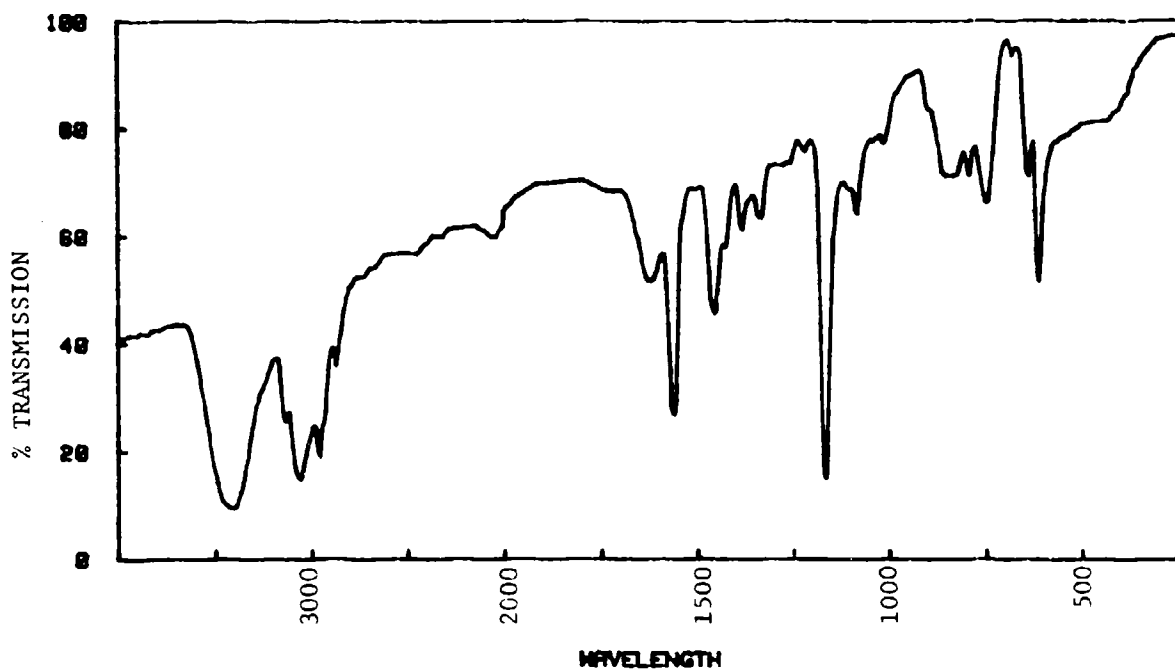


FIG. 9 -- IR OF MeBuImCl (COMPOUND IX)

