

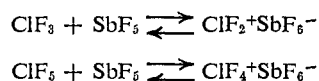
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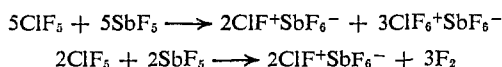
Radical Cations in the Chlorine Fluoride–Antimony Pentafluoride Systems

Sir:

Recently, Olah and Comisarow have reported¹ epr evidence for the existence of the two radical cations, Cl_2^+ and ClF^+ , in both the $\text{ClF}_3\text{-SbF}_5$ and the $\text{ClF}_5\text{-SbF}_5$ systems. These data are unexpected and disagree with the following, previously observed reactions.²⁻⁵



According to Olah and Comisarow¹ the ClF^+ cation forms directly by combination of SbF_5 with ClF_3 or ClF_5 . For ClF_5 , this reaction would involve a reduction of pentavalent chlorine to the divalent state, thus requiring the simultaneous oxidation of a second species. This could be achieved by either disproportionation of pentavalent chlorine or oxidation of fluoride to fluorine.



However, no evidence for either the formation of $\text{ClF}_6^+ \text{SbF}_6^-$ or F_2 evolution has been observed in the $\text{ClF}_5\text{-SbF}_5$ system.⁵ Furthermore, the Raman band at 819 cm^{-1} , observed by Olah and Comisarow in the $\text{ClF}_3\text{-SbF}_5$ system and ascribed to ClF^+ , strongly suggests the presence of ClF_2^+ , which in its AsF_6^- and SbF_6^- salts^{6,7} has its strongest absorptions between 805 and 830 cm^{-1} .

The interpretation of the epr signals reported by Olah and Comisarow has also been questioned. Thus, Eachus, Sleight, and Symons recently suggested⁸ the structures Cl_2O^+ and ClOF^+ for the epr signals attributed by Olah and Comisarow to Cl_2^+ and ClF^+ , respectively. The formation of the oxygen containing species Cl_2O^+ and ClOF^+ in the supposedly oxygen-free $\text{ClF}_3\text{-SbF}_5$ system presents a mystery. Whereas Eachus and coworkers have questioned the spectroscopic interpretation of Olah's epr data, we wish to clarify some of the discrepancies in Olah's work from a chemical synthesis point of view. Furthermore, we wish to report experimental details which are completely missing in both Olah's and Symon's papers and which (as can be seen from the data given below) are extremely important for duplication of the previous work.

Contrary to the results of Olah and Comisarow, we did not obtain any epr signal for $\text{ClF}_3\text{-SbF}_5$ and $\text{ClF}_5\text{-SbF}_5$, either in the solid state or in SbF_5 solution, provided the samples were freshly prepared in a well-passivated stainless steel–Teflon vacuum line, and the starting materials were fractionated on the line prior to use. The epr samples were prepared directly in Teflon FEP nmr tubes. It was found necessary to avoid contact of liquid phases with metal parts owing to their ability to dissolve paramagnetic metal salts, which give rise to epr signals. However, these metal ions cannot account for the fine structure in the spectra¹ observed by Olah and Comisarow, and there is no doubt that these epr signals are caused by chlorine containing species. Our attempts to reproduce the epr signal, ascribed by Olah and Comisarow to ClF^+ , in $\text{ClF}_3\text{-SbF}_5$ were successful when SbF_5 , distilled in a glass apparatus and stored in a Teflon container, was used in the sample preparation without further purification. In the latter case the SbF_5 was manually transferred to the epr tubes in the dry nitrogen atmosphere of a glove box. Unfortunately, Olah and Comisarow did not give any experimental details in their paper. According to a private communication,⁹ however, they handled their samples in glass vacuum systems and used quartz epr tubes. These facts might explain the difference in results and suggest that the observed paramagnetic species are due to handling procedures (such as SbF_5 purification) or to secondary reactions of the highly reactive fluorides with the container material or impurities contained in SbF_5 . Since chlorine oxyfluorides and oxides might be formed in the latter reactions,¹⁰ the observed epr signals might well be due to chlorine oxyfluorides or oxides, as suggested by Symons and coworkers.⁸ It should also be pointed out that fluorosulfonic acid interacts with chlorine fluorides,¹¹ and thus should not be used as an inert solvent for this type of investigation. Whereas ClF_3 and ClF_5 , when combined with SbF_5 under suitable conditions, do not produce paramagnetic species, ClF may behave differently. We did not study the ClF-SbF_5 system by epr but have previously observed¹² that the ClF-SbF_5 adduct produces upon melting a highly colored (from initial orange to dark brown-green) liquid. This strong color formation may be indicative of paramagnetic species.

In summary, the combination of carefully purified SbF_5 and ClF_3 or ClF_5 does not produce any paramagnetic species but results in the formation of diamagnetic $\text{ClF}_4^+ \text{SbF}_6^-$ and $\text{ClF}_2^+ \text{SbF}_6^-$, respectively. Using less stringent purification and handling conditions for SbF_5 , samples were produced exhibiting an epr spectrum which closely resembled that previously assigned¹ to ClF^+ . However, the intensity of the epr signal indicated the paramagnetic species to be a minor constituent. Obviously the previously reported¹ epr evidence alone is insufficient to prove the exact nature of these radicals. Further experimental work to establish the role of impurities in the starting materials and of side reactions with container materials is definitely required in order to positively identify the paramagnetic species.

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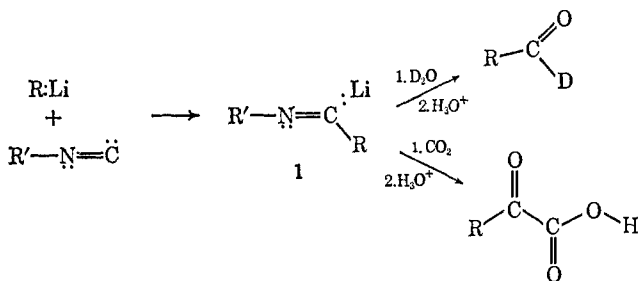
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Lithium Aldimines. A New Synthetic Intermediate¹

Sir:

The recent reports by Meyers² on his elegant syntheses of aldehydes and ketones prompts us to report our findings on the simple synthesis of lithium aldimines (1), which we have used as precursors for the preparation of aldehydes, 1-deuterio aldehydes, and α -keto acids.³



The lithium aldimine (1) reagent is prepared by the addition of an organolithium reagent to the appropriate isonitrile, which in this case is 1,1,3,3-tetramethylbutyl-isonitrile⁴ (TMBI). For example, when 1 equiv of *sec*-butyllithium and TMBI were combined, treated with D₂O, and then hydrolyzed, 1-deuterio-2-methylbutanal was isolated in 92% yield.⁵ This is, in our opinion, the cheapest and most convenient synthesis of C-1 labeled aldehydes yet reported.^{2,6} Moreover, carbonation of the intermediate lithium aldimine (1) yields, after hydrolysis, the corresponding α -keto acid in 80% yield.

Various types of α additions to isonitriles have been observed originally by Ugi and coworkers⁷ and later by Saegusa and coworkers,⁸ but our work represents the first successful 1:1 addition by an organometallic to an

(1) The support of this work by grants from the National Science Foundation and Public Service Research Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

(2) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzes, *J. Amer. Chem. Soc.*, **91**, 763 (1969); A. I. Meyers, *et al.*, *ibid.*, **91**, 764, 765 (1969); A. I. Meyers and A. C. Kovelesky, *ibid.*, **91**, 5887 (1969).

(3) It should be recognized that lithium aldimines (1) have the potential use as intermediates for the preparations of ketones, α -amino acids, and acylolins, just to name a few. We are in the process of exploring this potential.

(4) The reason for the choice of this particular isonitrile will be discussed in our full paper.

(5) Isotopic purity is greater than 97% by nmr analysis.

(6) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1966); D. Seebach, B. Erickson, and G. R. Singh, *J. Org. Chem.*, **31**, 4303 (1966); J. C. Craig, *ibid.*, **33**, 781 (1968); R. A. Olafson and P. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5058 (1967); D. J. Bennett, *Chem. Commun.*, 218 (1967).

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isonitrile.⁹ Table I lists the reactions carried out to date and the isolated yields of pure products.

Table I. Aldehydes and α -Keto Acids from Organolithium and 1,1,3,3-Tetramethylbutylisonitrile (TMBI)

RiLi	% crude 1	% overall yield	
		Aldehyde ^b	α -Keto acid ^b
<i>sec</i> -Butyl	100 ^a	96	80
	100 ^c	92 ^c	
<i>n</i> -Butyl	100 ^a	93	56
Phenyl	67	55	52

^a Reaction solvent was pentane. ^b All aldehydes and α -keto acids gave 2,4-dinitrophenylhydrazones which compared with the literature values. ^c Represents yield of 1-deuterio derivative.

The following is an experimental procedure which shows the simplicity of the synthesis. To a stirred solution of 3.76 g (0.027 mol) of TMBI¹⁰ dissolved in 27 ml of ether at 0° under a nitrogen atmosphere is added rapidly 0.027 mol of *sec*-butyllithium in hexane to yield a solution of 1.

(a) After 10 min, 1.6 ml (0.08 mol) of D₂O was added and stirring continued for an additional 10 min. The reaction mixture was filtered and the solvent evaporated to yield 5.45 g (quantitative crude yield) of aldimine. Steam distillation of the crude aldimine from 0.027 mol of oxalic acid yielded 2.16 g (0.025 mol 92%) of 1-deuterio-2-methylbutanal, bp 92°. Nmr analysis showed >97% deuterium incorporated.

(b) After 10 min, the solution of 1 was added dropwise to an ether slurry of Dry Ice. The solvent was evaporated and the carbonated imine was refluxed in an oxalic acid solution (7.5 g of oxalic acid in 60 ml of water) for 15 min. Extraction with methylene chloride, followed by evaporation of solvent, gave 2.8 g (80% yield) of 2-oxo-3-methylpentanoic acid which gave a 2,4-DNP derivative, mp 169–170°.

The scope and limitations of this¹¹ and related reactions are under current investigation.

K. Hirota, *ibid.*, 1273 (1967); (c) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967); (d) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968); T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1271 (1969).

(9) I. Ugi and U. Fetzer, *Ber.*, **94**, 2239 (1961), found that phenylmagnesium bromide did not undergo a simple addition to cyclohexylisonitrile, but rather several dimeric forms were isolated from the complex reaction mixture.

(10) Prepared in 93% yield from commercially available 1,1,3,3-tetramethylbutylamine by converting the amine to the formamide with formic acid and dehydrating the amide with thionyl chloride in *N,N*-dimethylformamide. The experimental procedure will be provided upon request. Available from Columbia Organic Chemicals.

(11) The use of different isonitriles and organometallics is now being investigated.

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Photodetachment Energies of Negative Ions by Ion Cyclotron Resonance Spectroscopy. Electron Affinities of Neutral Radicals

Sir:

The electron affinities of free radicals remain some of the most elusive quantities of chemical interest. Because of the great difficulty in obtaining gas-phase electron affinities and consequent lack of available data,