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New Synthetic Route to Trialkyloxonium Salts: Alkylation of Ethers with Acyldialkyl Cations

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Summary Acylium cations or complexes of acyl halides with nonmetal halides (*e.g.* $PhCO^+SbF_6^-$ or $PhCOCl{-}SbCl_5$) react at low temperature with an excess of alkyl ethers (*e.g.* Me_2O or Et_2O) giving the corresponding trialkyloxonium salts.

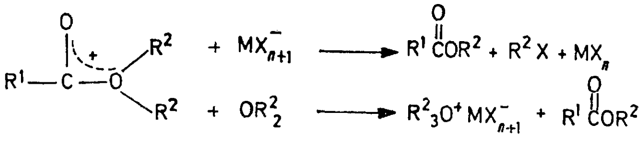
THE Meerwein[1] and other simple methods[2] for preparation of trialkyloxonium salts have been described only for salts with BF_4^- and $SbCl_6^-$ anions. These are unstable, however, because the BF_4^- and $SbCl_6^-$ anions easily break down into smaller fragments.[3] Recently salts with the PF_6^- anion have been described,[4] and salts with SbF_6^- have also been prepared but only either under 'magic' conditions[5] or in solution in anhydrous HF.[6] Both PF_6^- and, especially, SbF_6^- are stable and keep their integrity in chemical reactions thus eliminating undesirable side reactions.

TABLE 1.

Acylium salt or complex	Ether	Trialkyloxonium salt M.p. (t/°C)	Trialkyloxonium salt % Purity (^{1}H n.m.r.)
$PhCOCl{-}SbCl_5$	Me_2O	159	98·5
,,	Et_2O	127	96·0
$MeCO^+SbCl_6^-$	Et_2O	125	95·0
$PhCO^+SbF_6^-$	Me_2O	239—241	98·0
,,	Et_2O	139	98·5

We now report a new process, leading to trialkyloxonium (alkyl = Me and/or Et) salts with various anions, including SbF_6^-. The possibility of exchanging the alkyl groups in these salts should extend this method to other trialkyloxonium salts.

The process is based on the well known ether cleavage with acyl halides, leading to carboxylic esters and alkyl halides; acyldialkyloxonium ions (**1**)[7,8] are probably intermediates. Thus, we have two competing nucleophiles, the anion itself, MX_{n+1}^-, and the ether, R^2_2O (Scheme). When R^1 = Me, the formation of keten and the dialkyloxonium salt has also been reported.[7] At low temperatures and with an excess of ether, formation of the alkyl halides R^2X, as well as other side reactions can, as we have shown, be suppressed and trialkyloxonium salts are formed.



SCHEME

Typically (*e.g.* preparation of $Et_3O^+SbF_6^-$), benzoyl fluoride (0·01 mol) was added to a precooled solution of SbF_5 (0·01) mol in SO_2 (10 ml). Precooled Et_2O (10 ml, 10 mol. equiv.) was then added, with the temperature maintained below −50 °C. After 15 min SO_2 and Et_2O were evaporated off and white crystals of the triethyloxonium salt were dried *in vacuo*. If the salt is not sufficiently pure (n.m.r. spectroscopy in CH_2Cl_2 or $MeNO_2$) it can be recrystallized from $CH_2Cl_2{-}Et_2O$.

Freon 113 may also be used instead of SO_2 provided it is sufficiently pure. In this case the reaction between the

TABLE 2.

^{1}H N.m.r. chemical shifts (δ values) in the expected impurities and products

R	R_2O	$PhCO_2R$	$R_2O{\cdot}SbCl_5$	$R_2O{\cdot}SbF_5$	$R_3O^+SbCl_6^-$	$R_3O^+SbF_6^-$
Me	3·55	3·80	4·33	—	4·48	4·53
$\mathit{Me}CH_2$	1·15	1·32	1·48	1·41	1·65	1·65
$MeC\mathit{H}_2$	3·50	4·30	4·38	4·33	4·85	4·82

acyl fluoride–metal fluoride complex and ether apparently proceeds at the solid–liquid interface, because the complexes are insoluble in Freon 113.

The salts in Table 1 were prepared similarly. We think that this alkylation of ethers with (**1**) can also be used in other alkylation processes; the intermediates (**1**) so far have been known exclusively as acylating agents.[7]

The estimated purity is based on the ^{1}H n.m.r. data in Table 2.

The absence of benzoate impurities was confirmed by the absence of aromatic n.m.r. absorptions. The yields of the salts depend on the required purity. For $>95\%$ purity yields exceed 60% (based on the nonmetal halide).

The use of higher alkyl ethers leads to side reactions. However, we have developed a method for exchanging the alkyl groups in the trimethyl- or triethyl-oxonium salts for higher alkyl groups. *E.g.*, a solution of $Me_3O^+SbF_6^-$ and a higher dialkyl ether (10 mol. equiv.) in SO_2 in an ampoule closed with a Teflon glass stopcock was kept overnight and then evaporated *in vacuo*: the purity of the oxonium salt formed was checked by ^{1}H n.m.r. spectroscopy. This procedure was repeated until the required purity was attained. For $Pr^n{}_3O^+SbF_6^-$ after 1 cycle the purity was $> 90\%$; for $Bu^n{}_3O^+SbF_6^-$ after 2 cycles, the product contained $<10\%$ of the original Me groups.

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