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THE THIOALKOXYALKYLATION OF SULFIDES AND OTHER NUCLEOPHILES*

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Abstract—A mild, high yield thioalkoxyalkylation procedure in which the active thioalkoxyalkyl cation reagent is generated *in situ* is described. The advantages of the new method over the use of a preformed reagent are demonstrated in the synthesis of a series of thioalkoxyalkylsulfonium salts and some similarly alkylated pyridines and tetrazoles.

IN THE preceding paper[1] we reported the reactions of $CH_3SCH_2^+$ $SbCl_6^-$ (I) with several simple nucleophiles including t-butoxide, diisopropylethylamine, pyridine, triphenylphosphine, and acetylacetonate. The products obtained were all most easily rationalized by invoking multistep equilibria including reversion of I to its precursors, $ClCH_2SCH_3$ (II) and $SbCl_5$, and participation of $SbCl_5$ or its equivalent as both a powerful Lewis acid and a strong oxidizing agent in the product determining steps. In no experiment was the simple adduct expected from addition of the nucleophile at C^+ in I among the products isolated. In the only previously published work[3]— the reaction of I with Me_2S— the adduct, Me_2S^+—CH_2SCH_3 $SbCl_6^-$ (III), was the only product found. The present research began with an investigation of this dichotomy in the hope that its resolution would yield clues on how to control the hyper-reactivity of I and thus selectively direct its reactions along predetermined pathways. The exploitation of highly activated compounds as reagents and synthetic precursors usually fails because of the multiplicity of easily negotiated reaction routes available to high energy species. The development of methods for the taming and channeling of such reactivity in a single direction has been a major part of our recent research effort. The present paper outlines one approach.§

As an introduction and verification, the reaction of I with Me_2S was first repeated. From the list of identified compounds and yields (Equation A), it is evident that though the simple adduct (III) reported by Meerwein[3] is indeed the major product, it is contaminated by other substances expected from the operation of the several equilibria and the redox system demonstrated in the preceding paper.

* This is Part II in a series; for Part I see preceding paper.[1]

† Abstracted from the Ph.D. Thesis of D. W. Hansen.[2] NIH predoctoral fellow, 1966–1970. Additional discussion and experimental data can be found in this reference.

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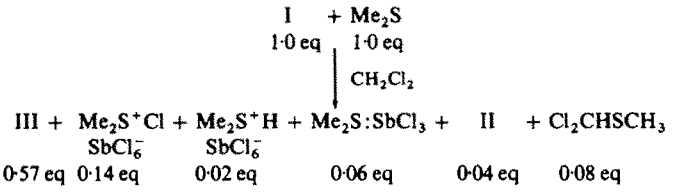
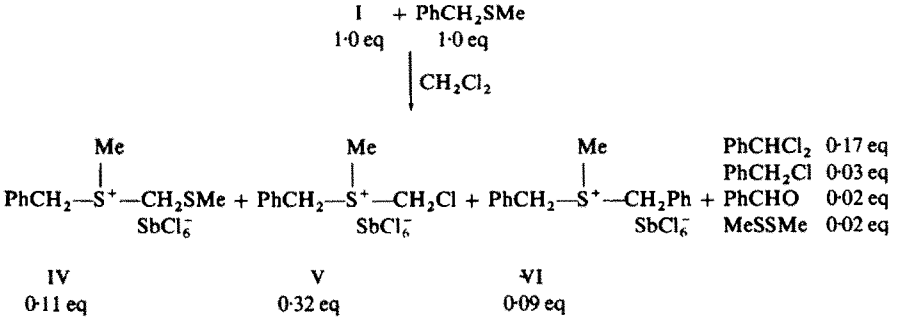
§ This is the latest example in a series beginning with ref. 4.

Equation A



When the related reaction of I with benzyl methyl sulfide was performed. the simple adduct (IV) was not even the major solid product (Equation B).

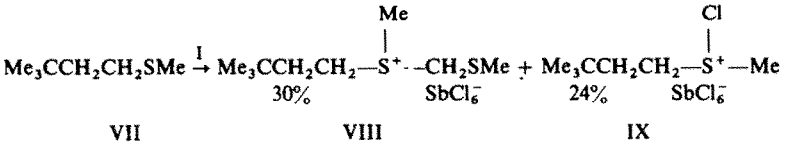
Equation B



The yields given are for 1 hr at −78° then 2 days at room temperature. When sulfide addition rates, reaction times, and temperatures were varied, the products remained the same but their ratios varied.

In a final illustrative experiment 3,3-dimethylbutyl methyl sulfide* (VII) gave two isolable salts on reaction with I, the adduct (VIII) and the S-chloro compound (IX).

Equation C

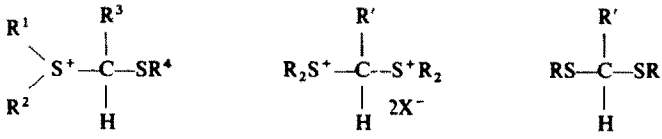


From our studies in the three representative series above it is obvious that the low thiomethoxymethylsulfonium salt yields (57%, 11%, 30%) and the difficulties encountered in separating these compounds from side products combine to make the reaction of I with sulfides a poor synthetic thiomethoxymethylation procedure.

A substantial role for thioalkoxyalkylated sulfides, amines, etc. in synthetic chemistry can be envisioned. Compounds such as X, for example, should stand in

* This experiment was performed because of its bearing on the mechanism of the reaction of I with t-butoxide.[1] Volatile products were not isolated.

the acidity of their central C—H midway between the dication (XI) and the thioacetal (XII).



X XI XII

Carbanions from XII are the most versatile nucleophilic acylation reagents employed in synthetic chemistry today[5] while the very readily formed related ylid-cations from XI have also found use in this area.[6] Thioalkoxyalkylated benzyl and allyl sulfides (X, R^1 = benzyl or allyl) might also be induced to undergo base-catalyzed masked acyl shifts related to the thioalkoxyalkyl shifts in the Stevens–Hauser rearrangement[7] of simple benzylsulfonium salts and the migrations in simple allylsulfonium salts which have recently been extensively investigated.[7] The potential value of thioalkoxyalkylation in the protection, activation and functionalization of amines and other nucleophilic moieties can be similarly documented.

Two direct methods are discernible for making salts of structure (X), the alkylation of thioacetals and the thioalkoxyalkylation of sulfides. Because unsymmetrical thioacetals are difficult to isolate and store, the second route has greater potential generality. Thus, with the special incentives for making X outlined above we were encouraged to attempt the modification of the reaction of I and its substituted analogues with sulfides in such a way as to not only maximize production of X but more important to get the reaction to proceed in consistently high yield.

The major problem is the hyper-reactivity of I and the equilibria beginning with its reversion to $ClCH_2SMe$ (II) and $SbCl_5$. One solution is to suppress the first equilibrium by using an excess of the less reactive equilibrium component (II). This result can be achieved in a practical way without using a stoichiometric excess of II by dripping $SbCl_5$ into a solution of II and the added sulfide with which I, when generated, is to react to yield X; the synthesis and reaction of I would thus be performed as two essentially simultaneous titrations. Since II doesn't react readily with sulfides and the fast reaction of $SbCl_5$ with simple sulfides is just a reversible equilibrium adduct formation, additional synthetic complications would not be expected unless this adduct or I precipitated from solution and thus decreased the rate of production of X. In the reactions of I which we have previously described, the main rate limiting factor is its insolubility in the usual reaction solvent, CH_2Cl_2,* and this factor accounts almost exclusively for the long reaction times required. In this new procedure though the reaction medium would probably be supersaturated in I, the danger of precipitation should be minimal because of the presence of the extra contaminants, the sulfide and III (we are taking advantage of the ordinarily discouraging axiom which promises that a very crude product will be more difficult to crystallize than the pure substance). If as argued above the synthesis of X from II can be carried out as one step without I precipitating, a further improvement in product

* Since more polar solvents either reacted with I or the other reaction substrate, a change in solvents was not feasible.

TABLE 1. THIOALKOXYALKYLATION OF SULFIDES. ONE STEP PROCEDURE AT $-80°$

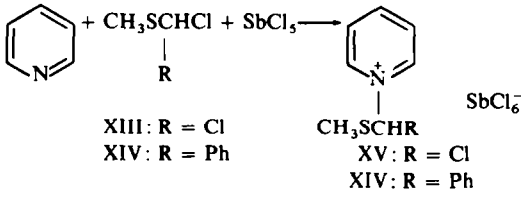
Rxn. No.	Alkylating Reagent	Nucleophile	Acid	Product Structure	Product Yield
A	$ClCH_2SMe$	Me_2S	$SbCl_5$	$Me_2S^+—CH_2SMe\ \ SbCl_6^-$	92%
B	$ClCH_2SMe$	$PhCH_2SMe$	$SbCl_5$	$PhCH_2—S^+(Me)—CH_2SMe\ \ SbCl_6^-$	80%
C	$ClCH_2SMe$	$CH_2=CHCH_2SMe$	$SbCl_5$	$CH_2=CHCH_2—S^+(Me)—CH_2SMe\ \ SbCl_6^-$	93%
D	$ClCH_2SMe$	$(CH_2=CHCH_2)_2S$	$SbCl_5$	$(CH_2=CHCH_2)_2S^+—CH_2SMe\ \ SbCl_6^-$	86%
E	$ClCH_2SMe$	$Me_3CCH_2CH_2SMe$	$SbCl_5$	$Me_3CCH_2CH_2—S^+(Me)—CH_2SMe\ \ SbCl_6^-$	75%
F	$PhCH(Cl)SMe$	Me_2S	$SbCl_5$	$Me_2S^+—CH(Ph)SMe\ \ SbCl_6^-$	96%
G	Cl_2CHSMe	Me_2S	$SbCl_5$	$Me_2S^+—CH(Cl)SMe\ \ SbCl_6^-$	69%
H	$ClCH_2SMe$	$PhCH_2SMe$	BF_3 gas	$PhCH_2—S^+(Me)—CH_2SMe\ \ BF_4^-$	80%
I	$ClCH_2SMe$	Me_2S	$BF_3 \cdot Et_2O$	$Me_2S^+—CH_2SMe\ \ BF_4^-$	52%

yield should be realized by performing the experiment at low temperature, a change which should increase the selectivity of I in its choice of reaction course.

The experimental results are in Table 1. The yields given are overall yields for two reactions, the generation of the sulfur stabilized cation and its attack by the added sulfide substrate. From the table it is evident that the thiomethoxymethylation (A–E) of sulfides including benzyl (B) and allyl (C, D) sulfides did go in high yield as predicted as did other thioalkoxyalkylations including thiomethoxybenzylation (F) and thiomethoxychloromethylation* (G). Finally the BF_4^- salts (H, I) could be obtained in addition to the $SbCl_6^-$ salts by using BF_3 as the reagent in place of $SbCl_5$. The reaction was cleaner with BF_3 gas than with BF_3 etherate.

We have considered the possibility that thioalkoxyalkyl cations are not intermediates on the route to product in the reactions of Table 1. The only feasible alternative pathway is S_N2 displacement by the sulfide lone pair at the chlorine bearing carbon to give the chloride salt of X which is siphoned off to product by complexation of the anion with the added Lewis acid. This mechanism has been discarded for three reasons. First, previous solvolytic studies on α-halo ethers and thioethers are only in accord with reaction by S_N1 type processes and specifically rule out S_N2 displacements except in strong base.[8] Second, there was ample positive evidence for the formation of thioalkoxyalkyl cations under the experimental conditions (*vide supra*). Third, an S_N2 displacement mechanism requires the rapid production of $X(Cl^-)$, but the only relevant data in the literature indicate that this step is very slow.† We have not been able to distinguish between the two possible routes for the generation of I: (a) reversible ionization of $ClCH_2SMe$ (II) followed by reaction of Cl^- with $SbCl_5$, and (b) ionization initiated by attack of $SbCl_5$ on II. However, $BrCH_2SMe$ was instantly converted to $ClCH_2SMe$ in $CDCl_3$ in the presence of an equivalent of $nBu_4N^+Cl^-$ so the activation implied by (b) is unnecessary for rapid reaction.

The thioalkoxyalkylation of heteroaromatic amines has also been achieved in the further generalization of the new procedure developed above. For example, py. on



XIII: R = Cl
XIV: R = Ph

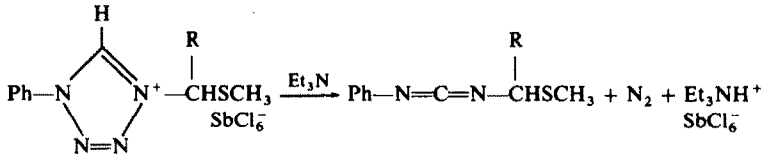
XV: R = Cl
XIV: R = Ph

* The replacement of the second Cl in the product of G by another Me_2S was not possible. In a control experiment the chloromethyl (i) and dichloromethyl (ii) cations were both prepared from the precursor chlorosulfides and $SbCl_5$ and the very hygroscopic salts isolated. Both compounds gave only intractable tars on treatment with Me_2S.

$CH_3S^+CHCl\ SbCl_6^-$ (i) $\qquad$ $CH_3S^+CCl_2\ SbCl_6^-$ (ii)

† We have treated $ClCH_2SMe$ with Me_2S. The salt ($X[R^1 = R^2 = R^4 = Me, R^3 = H]\ Cl^-$) oiled out to the extent of only 10% in a week at 30°. Decomposition or reversion of the isolated oil to starting materials was negligible in a 24 hr period (NMR analysis).

treatment with $SbCl_5$ and Cl_2CHSMe (XIII) or PhCHClSMe (XIV) was converted to the quaternary salts (XV and XVI) in 64% and 89% yields, respectively.* Similarly 1-phenyltetrazole[11] was alkylated by II and XIV to give the 1,4-disubstituted tetrazolium salts (XVII [95%] and XVIII [60%]).



XVII: R = H
XVIII: R = Ph

XIX: R = H
XX: R = Ph

To confirm the position of alkylation, both XVII and XVIII were titrated with Et_3N in CH_2Cl_2. Nitrogen was evolved and solutions of the novel bifunctional carbodiimides, XIX (IR 4·73μ) and XX (IR 4·72μ), were obtained as anticipated.[12] This is the first time that compounds with a carbodiimide function attached to an acetal type carbon have been generated and an investigation of their synthetic utility is in progress.

EXPERIMENTAL

The apparatus used for performing GC separations and for recording spectra and m.ps was described in the preceding paper.[1]

Reaction of thiomethoxymethyl hexachloroantimonate with dimethyl sulfide. Me_2S (3·1 g, 0·05 mol) in 25 ml CH_2Cl_2 was added (20 min) to a stirred dispersion of the title salt[1] (19·6 g, 0·05 mol) in 100 ml CH_2Cl_2 at 0° under N_2. The mixture turned yellow but remained heterogeneous so was allowed to warm to room temp and stirred for 2 days. A bright yellow solid separated (suction filtration), washed with 100 ml CH_2Cl_2, and dried *in vacuo*. Identified (NMR) as a mixture of $Me_2S^+CH_2SMe\ SbCl_6^-$, $Me_2S^+Cl\ SbCl_6^-$, and $Me_2S^+H\ SbCl_6^-$ in a mole ratio of 1:0·16:trace. The first compound could be isolated by repeated crystallization from CH_2Cl_2; m.p. 147–148° (lit.[3] 146–147°). A second yellow solid was precipitated from the combined mother and wash liquors with 300 ml CCl_4. This analyzed as a mixture of the 3 above compounds and $Me_2S:SbCl_3$ in a mole ratio of 1:0·7:0·2:0·7 (order of naming). The remaining filtrate contained $ClCH_2SMe$ (1·9 mmol, 4%) and Cl_2CHSMe (4·1 mmol, 8%) analyzed by GC and NMR.[1] $Me_2S^+CH_2SMe\ SbCl_6^-$ yield 0·0283 mol (57%); for spectral data see below. $Me_2S^+Cl\ SbCl_6^-$ yield 6·8 mmol (14%); NMR(δ) CD_3CN: 3·25(s). CD_3NO_2: 3·88(s); a comparison sample was made.[3] $Me_2S^+H\ SbCl_6^-$ yield 0·9 mmol (2%); NMR(δ) CD_3CN: 11·27(s), 3·27(s); ratio 1:3; previously synthesized from $Me_2S:SbCl_5$ and HCl.[13] $Me_2S:SbCl_3$ yield 2·9 mmol (6%) NMR(δ) CD_3CN: 2·72(s); adduct known from mixing components.[14]

Reaction of thiomethoxymethyl hexachloroantimonate with 3,3-dimethylbutyl methyl sulfide. The procedure described above was followed using $Me_3CCH_2CH_2SMe$ (6·6 g, 0·05 mol) in place of Me_2S. One solid was obtained by simple filtration of the mixture and a second precipitation from the mother liquors with 200 ml CCl_4. The less soluble S-chloro-3,3-dimethylbutyl-methylsulfonium $SbCl_6^-$ was purified by recrystallization from CH_2Cl_2, m.p. 129–131°, yield 6·0 g (24%). A comparison sample was prepared (92%) by chlorination of the sulfide $SbCl_5$ adduct with excess $SbCl_5$; NMR(δ) CD_3CN: 3·9(m), 3·65(s), 1·9(m), 1·03(s); ratio: 2:3:2:9. (Found: C, 16·74; H, 3·16; S: 6·71. $C_7H_{16}Cl_7SSb$ requires: C, 16·74; H, 3·21; S, 6·39%).

The second salt, 3,3-dimethylbutyl-methyl-thiomethoxymethyl-sulfonium $SbCl_6^-$, was washed with CH_2Cl_2–CCl_4 (1:1), recrystallized from CH_2Cl_2, and dried *in vacuo*; m.p. 139–140° dec; yield 8·0 g (30%); see below for analytical and spectral data.

* Pyridine has previously been thiomethoxymethylated with II directly on heating and with DCC–DMSO.[10]

Reaction of thiomethoxymethyl hexachloroantimonate with benzyl methyl sulfide. The reaction flask was cooled in a CO_2-acetone bath but otherwise the procedure used above was followed with $PhCH_2SMe$ (6·9 g, 0·05 mol) as substrate. After sulfide addition (20 min), the heterogeneous mixture was stirred for 1 hr at −78° and warmed to room temp giving a homogeneous yellow soln. After 2 days the precipitated light yellow benzyl-chloromethyl-methyl-sulfonium $SbCl_6^-$ was filtered, washed with CH_2Cl_2, and recrystallized from CH_2Cl_2. 3·4g, m.p. 140–141° dec; NMR(δ) CD_3CN: 7·56(s); 5·18 and 4·94 (ABq, J = 12 c/s), 4·68(s), 2·93(s); ratio: 5:1:1:2:3. (Found: C, 21·00; H, 2·17; Cl, 47·32; S, 6·42. $C_9H_{12}Cl_7SSb$ requires: C, 20·70; H, 2·32; Cl, 47·53; S, 6·14%).

A second solid fraction (17·6 g) was obtained from the combined filtrate and wash liquors by precipitation with 300 ml CCl_4. Though this material could not be separated, the 3 major constituents were benzyl-chloromethyl-methyl-sulfonium $SbCl_6^-$ (9 mmol, combined yield first fraction 32%), benzyl-methyl-thiomethoxymethylsulfonium $SbCl_6^-$ (5·7 mmol, 11%; see later experiment for analytical and spectral data), and dibenzyl-methyl sulfonium $SbCl_6^-$ (4·3 mmol, 9%, see below for data). An NMR peak (11·71δ) suggested the presence of some protonated sulfide and a broad peak in the S—Me region (2·80δ)was most easily explained as indicating the presence of some sulfide antimony chloride complex.

The filtrate after removal of all solids was reduced in volume and then analyzed by preparative GC and NMR: $PhCHCl_2$ (8·4 mmol, 17%), PhCHO (1·2 mmol, 2%), $PhCH_2Cl$ (1·6 mmol, 3%), MeSSMe (0·9 mmol).

When this experiment was performed using different sulfide addition rates, temps, and times, the products remained the same but their ratios varied. The yield of dibenzyl-methyl-sulfonium $SbCl_6^-$ was highest when the $PhCH_2SMe$ was added all at once at the beginning of the experiment. Under these conditions the compound could be isolated from the second solid fraction by leaching out other components with hot $CHCl_3$. The salt was recrystallized from $CHCl_3$: m.p. 158–159°. A comparison sample was synthesized by methylation of $(PhCH_2)_2S$ with $Me_3O^+SbCl_6^-$ at −78°; NMR(δ) CD_3CN: 7·53(s), 4·70 and 4·42 (ABq, J = 13 cps), 2·64(s); ratio: 10:2:2:3. (Found: C, 32·04; H, 2·99; S, 5·89. $C_{15}H_{17}Cl_6SSb$ requires: C, 31·95; H, 3·04; S, 5·69%).

Dimethyl-thiomethoxymethyl-sulfonium hexachloroantimonate. This reaction and subsequent isolation and purification procedures were performed under N_2. Although the product is not hygroscopic, impurities, by-products, and leftover $SbCl_5$ pick up H_2O and exposure of the mixture or purification solvent to this contaminant results in diminished yields and less pure product. The related reactions following this procedure were also carried out under N_2.

$SbCl_5$ (29·9 g, 0·01 mol) in 50 ml CH_2Cl_2 was added dropwise (20 min) to a stirred soln of Me_2S (6·8 g, 0·11 mol), $ClCH_2SMe$ (9·6 g, 0·1 mol) and 200 ml CH_2Cl_2 in a 500 ml 3-neck flask equipped with a pressure equalizing dropping funnel, stirrer, and N_2 inlet stopcock and immersed in a CO_2-acetone bath. After addition, the reaction was stirred at −78° for 1 hr and warmed to room temp. The yellow precipitate was filtered, washed with CH_2Cl_2, and dried *in vacuo*; yield: 42·5 g (92%); m.p. 145–146° (lit.[3] 146–147°); NMR(δ) CD_3CN: 4·50(s), 2·98(s), 2·40(s); ratio: 2:6:3.

Benzyl-methyl-thiomethoxymethyl-sulfonium hexachloroantimonate. The procedure of the above experiment was used with $PhCH_2SMe$ replacing the Me_2S. The non-hygroscopic yellow product was recrystallized from CH_2Cl_2 (80%); m.p. 104–105°; NMR(δ) CD_3CN: 7·57(s), 4·76 and 4·52 (ABq, J = 13 c/s), 4·40(s), 2·81(s), 2·38(s); ratio: 5:1:1:2:3:3. (Found: C, 22·62; H, 3·02; S, 12·14. $C_{10}H_{15}Cl_5S_2Sb$ requires: C, 22·50; H, 2·83; S, 12·01%).

Allyl-methyl-thiomethoxymethyl-sulfonium hexachloroantimonate. This experiment was performed with allyl methyl sulfide as test reagent. CCl_4 was slowly added to the yellow-orange clear mixture to precipitate the product. The salt was washed twice with CCl_4—CH_2Cl_2 (3:1) and dried *in vacuo* (93%); m.p. 80–82°. The yellow slightly hygroscopic salt was stable for a few weeks at room temp and longer at 0°. NMR(δ) CD_3CN: 5·8(m), 4·45(s), 4·10(d, J = 7 c/s), 2·90(s), 2·39(s); ratio: 3:2:2:3:3. (Found: C, 14·64; H, 3·04; Cl, 43·72; S, 13·40. $C_6H_{13}Cl_6S_2Sb$ requires: C, 14·90; H, 2·71; Cl, 43·97; S, 13·26%).

Diallyl-thiomethoxymethyl-sulfonium hexachloroantimonate. With diallyl sulfide as the nucleophile to be alkylated, the product was precipitated from the orange homogeneous reaction soln with CCl_4 as above (86%); m.p. 90–91°; NMR(δ) CD_3CN: 5·2–6·2(m), 4·40(s), 4·05(d), J = 7 c/s, 2·39(s); ratio: 6:2:4:3. (Found: C, 18·60; H, 3·18; Cl, 41·51; S, 12·77. $C_8H_{15}Cl_6SSb$ requires: C, 18·85; H, 2·97; Cl, 41·72; S, 12·58%). The slightly yellow hygroscopic salt decomposed after 3 months at 0°.

3,3-Dimethylbutyl-methyl-thiomethoxymethyl-sulfonium hexachloroantimonate. 3,3-Dimethylbutyl methyl sulfide[15] was thiomethoxymethylated by the standard procedure. The light yellow non-hygroscopic stable product was recrystallized from CH_2Cl_2 and dried *in vacuo*; yield: 75%; m.p. 140–141° dec.; NMR(δ)

CD_3NO_2: 4·52(s). 3·2–3·6(m). 3·02(s). 2·42(s). 1·4–1·9(m). 1·00(s); ratio: 2:2:3:3:2:9. (Found: C. 20·27; H. 3·81; S. 12·29. $C_9H_{21}Cl_6S_2Sb$ requires: C. 20·48; H. 4·01; S. 12·15%).

Dimethyl-α-thiomethoxybenzyl-sulfonium hexachloroantimonate. After completion of the alkylation of α-chlorobenzyl methyl sulfide[16] the stirred homogeneous red soln was reimmersed in a CO_2-acetone bath and CCl_4 added dropwise precipitating the granular yellow sulfonium salt. (Rapid addition of CCl_4 caused the salt to oil out). The supernatant was removed from the hygroscopic solid (filter stick) which was washed with CH_2Cl_2—CCl_4 (1:1) and dried *in vacuo* (96%); m.p. 90–94°; NMR(δ) CD_3CN: 7·4–7·7(m), 5·83(s). 2·75(s). 2·44(s); ratio: 5:1:6:3. Upon exposure of the title compound to air for a short time the odor of benzaldehyde became noticeable.

Dimethyl-thiomethoxychloromethyl-sulfonium hexachloroantimonate. A somewhat unstable light yellow product was obtained from alkylation of Cl_2CHSMe (69%); m.p. 142–144°. NMR(δ) CD_3NO_2: 6·75(s). 3·25 (2 singlets). 2·59(s); ratio: 1:6:3. (Found: C. 10·14; H. 2·10; S. 12·79. $C_4H_{10}Cl_7S_2Sb$ requires: C. 9·76; H. 2·05; S. 13·03%).

Benzyl-methyl-thiomethoxymethyl-sulfonium fluoroborate. $PhCH_2SMe$ (14·2 g. 0·11 mol). $ClCH_2SMe$ (9·6 g. 0·1 mol). and 200 ml CH_2Cl_2 were placed in a 3-neck flask with a gas introduction tube adjusted to below the surface of the soln. stirrer. and condenser attached to a gas flow meter. After purging the system with N_2. the flask was cooled in a CO_2-acetone bath and BF_3 bubbled at moderate rate through the system for 30 min. The mixture was warmed to room temp and excess BF_3 and solvent stripped off at reduced pressure (drying tube between the reaction flask and the water aspirator). The residual oil was triturated with ether which removed the remaining impurities and after evaporation of the last traces of ether *in vacuo* 20·2 g (80%) of the sulfonium BF_4^- was isolated as a light yellow somewhat hygroscopic moisture sensitive oil whose NMR spectrum was essentially identical to that of the $SbCl_6^-$ salt.

Dimethyl-thiomethoxymethyl-sulfonium fluoroborate. Freshly distilled $BF_3 \cdot Et_2O$ (19·9 g. 0·14 mol) was added (20 min) with stirring to a CH_2Cl_2 (75 ml) soln of Me_2S (6·2 g. 0·1 mol) and $ClCH_2SMe$ (9·6 g. 0·1 mol) at 0°. The mixture was stirred overnight. The clear red soln was evaporated giving a dark red fuming oil. washed and triturated with 3 × 100 ml anhyd. Et_2O. The yellow product oil was stripped of residual Et_2O on a vac. pump: yield: 12·9 g containing 84% (NMR) of the title compound (52% yield). This material was identical with that obtained by the methylation of $(MeS)_2CH_2$ with $Me_3O^+BF_4^-$; NMR(δ) CD_3NO_2: 4·53(s). 2·98(s). 2·38(s); ratio: 2:6:3.

Thiomethoxychloromethyl hexachloroantimonate. Cl_2CHSMe (0·53 g. 0·004 mol) in 10 ml CH_2Cl_2 was added dropwise (10 min) to a stirred soln of $SbCl_5$ (1·32 g. 0·0044 mol) and 35 ml CH_2Cl_2 in a flask equipped for reaction under N_2 and cooled by a CO_2-acetone bath. The white solid product began to precipitate from soln after half of the sulfide had been added. No change was observed on warming to 0° but at room temp the mixture began to yellow and a gas was slowly evolved. The mixture was therefore left in the ice bath while the supernatant was removed with the aid of a filter stick. The highly hygroscopic moisture sensitive product was washed with 3 × 25 ml CH_2Cl_2—CCl_4 (1:4) and dried *in vacuo*; yield 0·98 g (60%) m.p. 78–79° dec; NMR(δ) CD_3NO_2: 10·9 (broad s). 3·27(s); ratio: 1:3.

Thiomethoxydichloromethyl hexachloroantimonate. The experimental procedure above was followed using Cl_3CSMe. The precipitated white salt was purified by washing with 2 × 75 ml CH_2Cl_2—CCl_4 (2:1) followed by drying *in vacuo* (98%); m.p. 110–111°. The compound was very hygroscopic and moisture sensitive but seemed to have greater thermal stability than the monochloro analogue; NMR(δ) CD_3NO_2: 3·37(s).

N-Thioalkoxyalkylpyridinium hexachloroantimonates. Py. (0·43 g. 0·0054 mol) was added to a stirred soln of Cl_2CHSMe (0·70 g. 0·0054 mol) in 30 ml CH_2Cl_2 at −78° under N_2. There was no evidence of reaction. Then $SbCl_5$ (1·60 g. 0·0054 mol) in 10 ml CH_2Cl_2 was added (10 min) and the mixture stirred at −78° for 30 min before being warmed to room temp. The mixture was diluted with 200 ml CCl_4 the precipitated yellow solid filtered. washed with CCl_4. and dried *in vacuo*; yield 1·75 g (64%); m.p. 156–157° after recrystallization from CH_2Cl_2. lit.[1] 157–158°.

The procedure in the above experiment was followed using α-chlorobenzyl methyl sulfide.[16] The very hygroscopic pyridinium salt was isolated in 89% yield; m.p. 125–127°; NMR(δ) CD_3NO_2: 9·2–9·5(m). 8·6–9·1(m). 8·1–8·5(m). 7·54(s). 7·08(s). 2·33(s); ratio: 2:1:2:5:1:3.

1-Phenyl-4-thioalkoxyalkyltetrazolium hexachloroantimonates. The pyridine alkylation procedure was used with the following quantities: 1-phenyltetrazole[11] (0·73 g. 0·005 mol) and α-chlorobenzyl methyl sulfide (0·86 g. 0·005 mol) in 35 ml CH_2Cl_2 and $SbCl_5$ (1·50 g. 0·005 mol) in 10 ml CH_2Cl_2. The yellow hygroscopic tetrazolium salt was obtained in 60% yield (1·84 g); m.p. 96–98°; NMR(δ) CD_3NO_2: 10·58(s). 7·6–8·1(m). 7·60 (broad s). 7·13(s). 2·50(s); ratio: 1:5:5:1:3. As a test of structure a small amount of the

salt was treated with an equivalent of Et_3N in CH_2Cl_2. N_2 was evolved and the carbodiimide was generated (IR: 4·72μ).

The above procedure was followed with $ClCH_2SMe$ as the alkylating agent. The yellow hygroscopic product was isolated in 95% yield; m.p. 79–81°; NMR(δ) CD_3NO_2: 10·51(s), 7·7–8·2(m), 6·01(s), 2·49(s); ratio: 1:5:2:3. This salt also released N_2 and cleaved to the carbodiimide (IR: 4·73μ in CH_2Cl_2) on titration with Et_3N.

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