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THE REACTIONS OF THIOMETHOXYMETHYL HEXACHLOROANTIMONATE WITH POTASSIUM t-BUTOXIDE AND OTHER BASES

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Abstract—The major product isolated from the treatment of thiomethoxymethyl hexachloroantimonate (II) with potassium t-butoxide is 3,5,5-trimethyl-1,3-oxathiolanium hexachloroantimonate (V). Experiments designed to elucidate the mechanism of this process are described along with the reactions of II with some other representative nucleophiles.

IN 1968 a general method for the generation of carbenes by the deprotonation of carbonium ions with sterically hindered bases was reported from this laboratory.[2] Recently in an attempt to extend this reaction to the formation of thiomethoxycarbene (III) we have treated the thiomethoxymethyl cation (II) with potassium t-butoxide.

$$\underset{\text{I}}{MeSCH_2Cl} \xrightarrow[CH_2Cl_2]{SbCl_5} \underset{\text{II}}{MeSCH_2^+\ SbCl_6^-} \xrightarrow{:B} \underset{\text{III}}{[MeS\ddot{C}H]} \rightarrow \underset{\text{IV}}{MeSCH_2OCMe_3}$$

The results of this experiment and the derived corroborative studies are described here to illustrate some of the limitations and complications involved in attempts to use isolable but highly reactive carbonium ions as reagents and precursors in synthetic organic chemistry.

As our source of the thiomethoxymethyl cation, we were not required to utilize or adapt the very inefficient procedures outlined in the control experiments of the two preceding papers[3,4] because coincident with the appearance of our preliminary communication.[5] Meerwein, Zenner, and Gipp[6] published a practical method for its preparation and isolation as the $SbCl_6^-$ salt. They found that II precipitated from solution in high yield when I was added to $SbCl_5$ in CH_2Cl_2. Though it was very hygroscopic and moisture reactive, II could be isolated in reasonable purity: NMR in CD_3NO_2: 5·78δ (s. 2). 3·87δ (s. 3)‡ (NMR of I: 4·84 and 2·30δ).

Potassium *t*-butoxide was chosen here for two reasons. First, we induced from kinetic C–H acidity studies in heteroaromatic systems[7] that a base of at least this strength would be required to abstract H^+ from II. Second, the most likely alternative reaction

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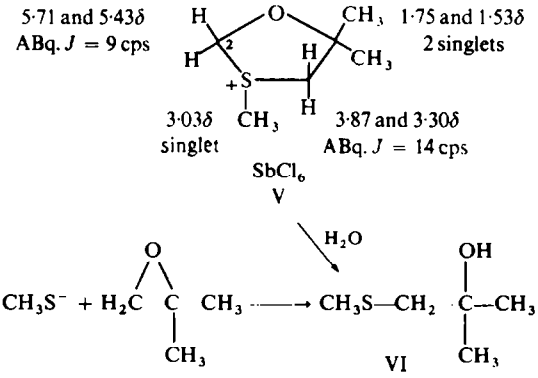
† Abstracted from the Ph.D. Thesis of D.W.H.[1] NIH predoctoral fellow, 1966–1970. Additional discussion and experimental data can be found in this reference.

‡ Note that NMR of II is in accord with a structure in which the plus charge is divided between carbon and sulfur. The names, thiomethoxymethyl cation and methyl-methylene-sulfonium cation, which describe the two extreme canonical forms of the resonance hybrid will be used interchangeably in this text.

is addition at C^+ (II + $tBuO^- \rightarrow$ IV) and though we suspected that a much more hindered base than t-butoxide would be needed to favor the deprotonation pathway. such bases are not available and there was a chance that carbene formation could compete successfully with addition.

The reaction of potassium t-butoxide with II was performed by slowly adding the solid base under N_2 to a stirred suspension at 0° of one equivalent of II in CH_2Cl_2. The isolated product. however. was neither the adduct (IV) nor any compound obviously derived from the carbene (III). It was a crystalline salt whose analysis agreed with the formula, $C_6H_{13}OSSbCl_6$. and whose NMR spectrum (CD_3NO_2) led us to assign it the 3.5.5-trimethyl-1.3-oxathiolanium salt structure (V). Note that the



NMR nonequivalence of the CH_2 hydrogens and also the two Me groups on carbon is expected from the known tetrahedral non-inversion-prone stereochemistry at sulfonium S[8] which in V would cause the top of the ring to be different from the bottom. The small geminal coupling constant at C_2 is normal for CH_2 groups constrained between two electronegative atoms in 5-membered rings.[9] As further structure proof. V was hydrolyzed with H_2O to the expected ring cleavage product. methyl 2-hydroxy-2-methylpropyl sulfide (VI. 85%). A comparison sample of VI was synthesized by the reaction of isobutylene oxide with thiomethoxide (epoxides are known to undergo nucleophilic attack in basic solution at the least substituted carbon[10]).

In our initial speculations we were best able to rationalize the production of V from II and t-butoxide as an example of a process in which a single formally unactivated Me group in the latter reactant has somehow been selectively oxidized and functionalized. The high yield* (62%) under probably nonoptimum conditions provided a strong argument against an alternative indiscriminate oxidation pathway affording V only as the most easily isolated of several products formed. Selective Me functionalization procedures are rare and also in great demand by synthetic chemists so a new preparative method for this purpose could be valuable if readily generalized. Thus in the hope of ultimately translating our reaction into a useful synthetic method. we began a mechanistic study.

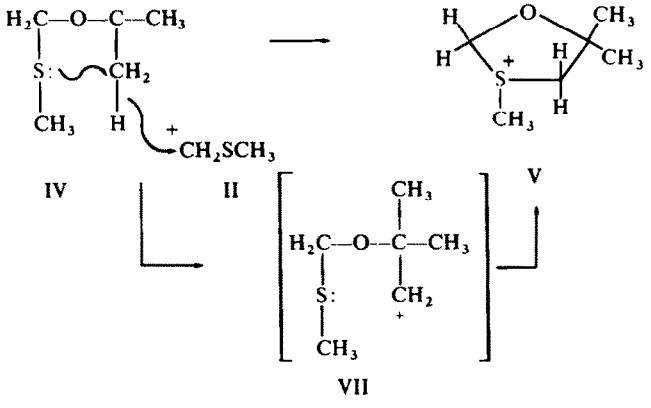
All plausible pathways for the formation of V have as their first step the addition of t-butoxide to the carbonium ion center in II to yield the adduct (IV). In the further

* Assuming a required stoichiometry of two moles of II per mole of t-butoxide. The yield is actually lower at this experimental reagent ratio for reasons given later.

transformation of IV to V an oxidation step is required at some point and the only reasonable oxidizing reagent available is a second molecule of II. In order to verify this analysis the mixed acetal (IV) was prepared and isolated (though with difficulty) and then reacted with II. As expected the cyclized product (V) was obtained. Though this result simplifies the problem, an attractive mechanism for the process IV + II → V, is still difficult to formulate.

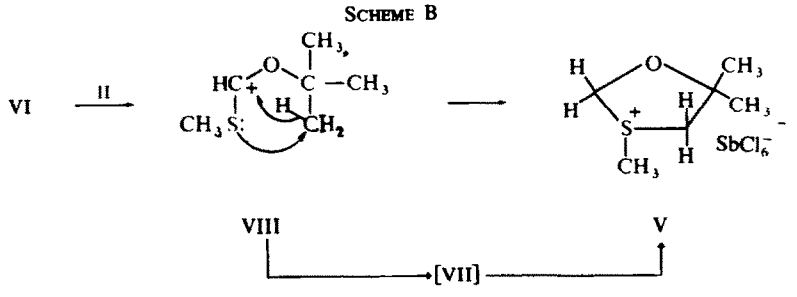
The most direct route from IV to V is depicted in Scheme A where it is postulated that II initiates the ring closure simply by abstracting hydride from IV. Since the

SCHEME A



discrete intermediacy of an unstabilized primary carbonium ion (VII) can nearly be excluded from thermodynamic considerations, such a process must almost necessarily be concerted with the sulfide lone electron pair assisting the hydride transfer. Authenticated examples of back side participation in hydride abstraction are, however, very rare.[11] Also the best position for hydride removal in IV is not the Me group but the acetal carbon since the cation (VIII) thus generated would be resonance stabilized by both O and S and therefore energetically downhill versus II. It is conceivable that VIII is the precursor to V (Scheme B), but again, in order to circumvent

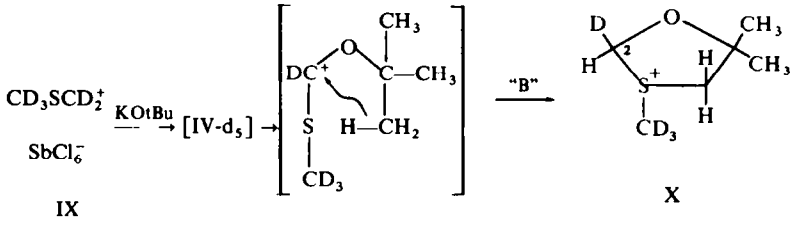
SCHEME B



the opposition to the primary carbonium ion (VII) as an intervening reaction intermediate, it is necessary to invoke sulfur lone pair participation (this time front side assistance). The process, VIII → V, might be more palatable if viewed as a cycloaddition[12] of a C—H bond with an $\overset{+}{\underset{\cdot\cdot}{S}}{=}C$ bond.

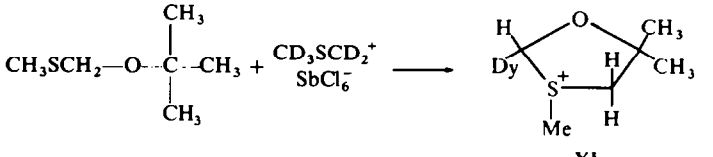
The mechanism (Scheme B) is easily tested by reacting thiomethoxymethyl-d_5

$SbCl_6^-$ (IX) with tBuOK. If it is correct, the product (X) must contain at least 50% H at C_2 (and more if VIII ⇌ VII). When the experiment was performed with IX containing >98%D at both positions by NMR analysis, the product isolated contained <3%H at the SMe position and <1%H at C_2, thus eliminating Scheme B as a viable pathway.



IX X

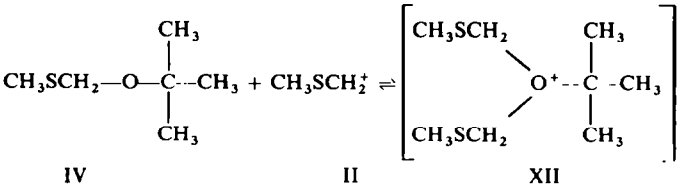
When a similar tracer experiment was carried out using unlabeled IV and deuterated IX as the reactants, the product (XI) incorporated deuterium at both the acetal CH_2 and the SMe positions. In fact the data for two different reactant ratios require that there be complete equilibration between the thiomethoxymethyl unit of IV and IX under the reaction conditions. This equilibration is most easily visualized as occurring



IV IX XI

ratio IV/IX	*%D at C_2*	*%D at SMe*
1:1	49%	51%
1:2	65%	62%

via the symmetrical oxonium cation (XII) though a reversible acid-induced fragmentation of IV to II initiated by complex formation of the oxygen in IV with some other unspecified acid in the reaction medium is also possible. This experiment does



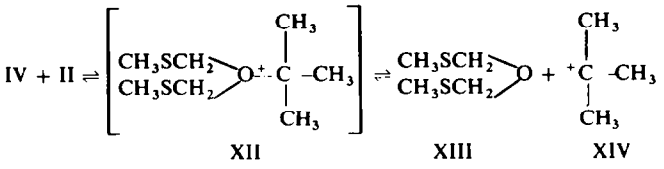
IV II XII

not rule out A as the mechanism of oxathiolanium salt (V) formation since the process IV + II ⇌ XII or its equivalent, can be considered a side equilibrium having nothing to do with product formation.

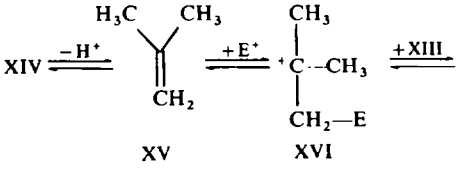
However, with the detection of XII in the reaction medium it becomes essential to elucidate and evaluate those reaction pathways which require this species (or its equivalent) as an intermediate. Mechanisms in this class are summarized in Scheme C.

In this new sequence an alternative fragmentation of XII* to the acetal (XIII) and the stabilized t-Bu cation (XIV) is visualized as being competitive with the previously demonstrated reversion of XII to IV and the sulfur stabilized cation (II). Proton loss

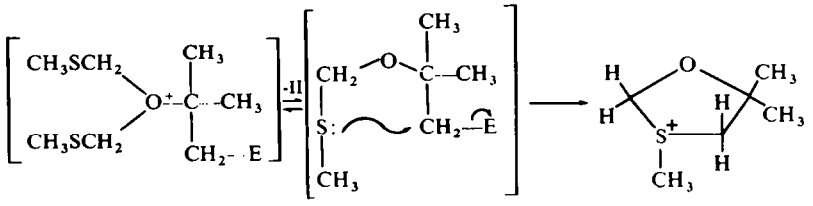
SCHEME C



XII XIII XIV



XV XVI



XVII XVIII V

from XIV gives isobutylene (XV) which is then attacked by some electrophile in solution. E^+. chosen for its ability to become a good leaving group as E^- in a later step. The substituted t-Bu cation (XVI) generated from XV then adds to the acetal (XIII) to yield the oxonium salt (XVII). This is postulated to be in equilibrium with II and the E-substituted ether (XVIII) which finally cyclizes to the product using the sulfur lone electron pair to displace E^- from carbon. Note that Scheme C is symmetrical about structure XV. that is XVI. XVII. and XVIII are just E-substituted analogues of XIV. XII. and IV. respectively. and the rationalizations given for the transformations of the unsubstituted species also apply to the E-derivatives. In C the mandatory oxidation has formally been accomplished by reduction of the reactant. E^+ (to E^-). whose further characterization is necessary here. The most likely candidates are chlorine and various antimony chlorides which would be available from the following hypothetical equilibria:

$$CH_3SCH_2^+ SbCl_6^- \rightleftharpoons CH_3SCH_2Cl + SbCl_5$$
$$SbCl_5 \rightleftharpoons SbCl_3 + Cl_2 \rightleftharpoons SbCl_4^+ + Cl^- \rightleftharpoons SbCl_4^- + Cl^+$$
$$R + Cl_2 \rightleftharpoons R^+Cl + Cl^-$$
$$S: + R'Cl \rightarrow {}^+S\text{–}R' + Cl^-$$

or

$$R + SbCl_5 \rightleftharpoons R^+SbCl_4 + Cl^-$$
$$S: + R'SbCl_4 \rightarrow {}^+S\text{–}R' + SbCl_4^- \rightleftharpoons SbCl_3 + Cl^-$$

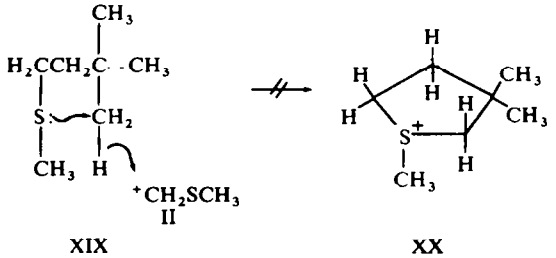
* Or its equivalent: replace one thiomethoxy methyl unit in XII, XIII, and XVII by some other unspecified acid group.

In Scheme C as in Scheme A the salt (II) still functions as the oxidizing agent, but, instead of the cationic site being reduced ($CH_3SCH_2^+ \rightarrow CH_3SCH_3$), the anion undergoes the change in oxidation state ($Sb^{+5} \rightarrow Sb^{+3}$).

The greatest deficiency of Scheme C is that it is not consistent with the 62% product yield. A reaction medium containing both a powerful enough Lewis acid and a strong enough oxidizing agent to induce the multiple fragmentations and recombinations required in this mechanism should also be harsh and unselective enough to siphon off the intermediates in numerous side reactions. For example, the starting mixed acetal (IV) undergoes rapid disproportionation in acid and XIII and XVIII should be given more susceptible to acid-catalyzed decomposition. Also, multiple substitution of XV should not be significantly more difficult than addition of only one E group. Even the product (V) does not have the advantage of being insoluble in the solvent and thus immune to further reaction or reversion to its precursors. However, the fact that the highest product yield is obtained when exposure to the acid and oxidant are minimized by adding excess $t\text{-}BuO^-$ is compatible with pathway C.

Since isobutylene (XV) is an obligatory intermediate in mechanism C, the absence of deuterium in the C-Me and C-CH_2 positions of the product (V) when the reaction is performed in the presence of deuterated isobutylene would rule out this route. However, when this control experiment was carried out using deuterated isobutylene[13] (83·5%D at Me, 53·5%D at CH_2), salt (II), and t-BuOK in a ratio of 1:1:1, product D incorporation to the extent of 34% at the C-Me positions was found. Similar D content in the C-CH_2 position was detected but the value was much less precise because of difficulties inherent in the NMR analysis. If a symmetrical t-Bu cation (or radical or anion) derived from both the deuterated isobutylene (by addition of one nonisotopic H) and the t-Bu group of t-BuOK are the equilibrating species, complete equilibration would give 34%D at the two C-Me's. Complete direct hydrogen transfer equilibration between isobutylene and the t-Bu from t-BuOK (isobutylene-D + t-Bu-H $\rightleftharpoons$ isobutylene-H + t-Bu-D) leads to a prediction of 36%D incorporation at the C-Me's, also in agreement with the experimental data.

The isobutylene experiment does not conclusively eliminate A as the mechanism of oxathiolanium salt formation since XII–XV could be rapid side equilibrium products whose further conversion to V depends on their ability to revert to the starting acetal (IV). The demonstrated presence of these intermediates in the reaction medium, however, strongly favors pathway C and, in so far as Occam's razor is applicable, rules out A. The fact that the sulfide (XIX) does not yield the sulfonium salt (XX) on treatment with II (see accompanying paper[14]) is also inconsistent with Scheme A but in accord with C.

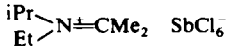


XIX XX

As an additional test of the involvement of the powerful oxidant and Lewis acid, $SbCl_5$, in the reaction of t-BuO^- with II, this salt was treated with other nucleophiles. In analogy with our studies above many of the products obtained should only be explainable by invoking multiple acid catalyzed equilibria and oxidation state changes. This analysis seems to be correct as is seen in the examples below.

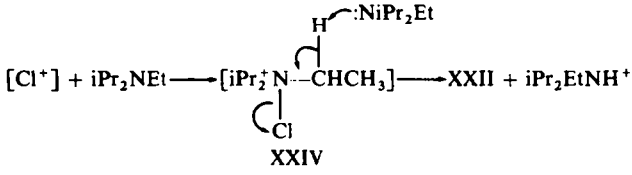
The nitrogen containing products obtained from the reaction of II with diisopropylethylamine at 0° were the salt, $iPr_2EtNH^+SbCl_6^-$ (over 50%) and the adducts, $iPr_2EtN:SbCl_x$ (x = 3 and 5). The hydrogen excess and chlorine deficiency of these substances are accounted for in the stoichiometry as Cl_2CHSCH_3(XXI) which along with $ClCH_2SCH_3$(I) was also isolated. When the experiment was performed at −78°, ethylidine-diisopropyl-immonium $SbCl_6^-$ (XXII) was also a major product (33%). None of the related salt (XXIII) was found though as little as 5% would have *never* found. Previously published work on the chemistry of II consists of one reaction

XXII



XXIII

been easily detected. The immonium salt (XXII) could be derived by hydride abstraction from the amine or by a base-induced elimination from an N-chlorocation (XXIV). By abstracting hydride from I, XXII could be the oxidant in the production of XXI.



XXIV

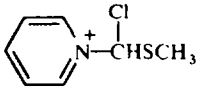
When the salt (II) was treated with Py or PPh_3, the chlorinated sulfides (I and XXI) were again obtained and also in analogy with the reaction of iPr_2NEt the extra hydrogen was found as the protonated nucleophile (Py · $H^+SbCl_6^-$ or $Ph_3PH^+SbCl_6^-$) and the chlorine deficiency in the stoichiometry accounted for as the $SbCl_3$ adduct of the nucleophile. In the Py reaction the chlorinated salt (XXV) was also isolated in low yield. Since an intermediate like XXII cannot be drawn in these reactions, alternative oxidation-reduction mechanisms must be available. The acidity and oxidizing power of a medium containing II was further verified by the isolation of 1,2-dichlorocyclohexane and much polymeric tar from the decomposition of II with cyclohexene.

In other experiments reaction of II with the weak base, butyric acid, in CH_2Cl_2 followed by addition of ether yielded $Et_2O:SbCl_5$ complex,[15] $nPrCO_2CH_2Cl$,[16] CH_3SSCH_3, and I while reaction with the strong base sodium acetylacetonate afforded 3,3-dichloro-2,4-pentanedione[17] (10%) as the major volatile product along with traces of acetylactone, AcOH, and CH_3SSCH_3 but no I or XXI.

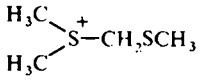
In many of the above studies the most obvious and expected of all possible products is the adduct from attack of the nucleophile at C^+ in II but such a substance was *never* found. Prviously published work on the chemistry of II consists of one reaction with Me_2S in which the adduct (XXVI) was the *only* product isolated.[6] This latter

process and related reactions of other sulfides with II and its analogues have been investigated in detail and the results published in the following paper.[14]

In summary it would appear that though we embarked on a study of the reactions of the cationic component of II. what we uncovered was primarily the chemistry of



XXV



XXVI

the anion. Our inability to apriori predict reaction course and products with any confidence is. however. a complication which should normally be encountered in attempts to utilize highly activated compounds for synthetic purposes. When a superabundance of reactivity is bound up in a single reactant many reaction pathways will be energetically downhill and thus easily negotiated. Since the rewards for successfully controlling and selectively channeling this reactivity in desired directions more than compensate for its disadvantages. further research is indicated. An initial success in this area—a simple procedure for generating adducts in high yield from reaction of II and related compounds with nucleophiles—is outlined in the next article.[14]

EXPERIMENTAL

M.ps were taken in soft glass capillary tubes using a calibrated thermometer. NMR spectra were recorded on a Varian Model A-60 or Model A-60A (internal TMS standard except where noted). A Perkin–Elmer 257 Spectrophotometer was used for IR spectra and mass spectra (MS) were obtained on an MS-902 High Resolution Mass Spectrometer. A Varian 700 Autoprep Gas Chromatograph with a thermoconductivity detector was employed for all gas chromatography (GC).

Thiomethoxymethyl hexachloroantimonate. The procedure was adapted from that of Meerwein.[6] A 250 ml 3-neck flask. stirrer. a pressure equalizing dropping funnel (teflon stopcock required). and condenser were oven dried. assembled. and flushed with N_2. the reaction was carried out under N_2. $SbCl_5$ (45 ml. 0·35 mol) dissolved in 80 ml CH_2Cl_2 was placed in the ice cooled flask and 22·65 g (0·25 mol) $ClCH_2SCH_3$ in 20 ml CH_2Cl_2 was added dropwise (45 min) with vigorous stirring, during which a pale yellow solid continuously precipitated. Stirring was prolonged for 1 hr at 0° and the liquid was removed from the solid with a medium frit filter stick attached *via* a drying tube to an aspirator, during which N_2 was blown through. The thiomethoxymethyl $SbCl_6^-$ was washed with CH_2Cl_2 (filter stick) until washes were colourless and dried *in vacuo* in the original reaction vessel; yield 62·0 g (63%); m.p. 144–147° (lit.[6] 142–144°). Increased yields could be obtained by using a higher ratio of $SbCl_5$ to sulfide. Product was stable if kept in the refrigerator but slowly decomposed at room temp. unless under CH_2Cl_2 or $ClCH_2CH_2Cl$. Special use precautions are described below. NMR (δ) CD_3NO_2: 5·78(s), 3·87(s); ratio: 2:3.

Reactions of thiomethoxymethyl hexachloroantimonate. General precautions. The title compound was very hygroscopic. and also decomposed rapidly on contact with moisture. Minute amounts of the species generated in the decomposition could drastically affect reaction course. Precautions must be taken to keep the reaction systems moisture free.

Often reaction products were hygroscopic and even when this was not the case some impurities. by-products. and leftover starting materials could react with trace water yielding substances which were able to partially decompose the desired product. Therefore. at least the initial steps of most isolation and purification procedures including filtrations were performed under N_2. A filter stick (connected via a collecting vessel and drying tube to an aspirator) inserted into the mixture was usually used for filtration. In later steps in the purification of acid stable nonhygroscopic solids. simple suction filtration under an N_2 blanket was a satisfactory substitute for the filter stick procedure.

3,5,5-*Trimethyl*-1,3-*oxathiolanium hexachloroantimonate.* t-BuOK (33·04 g, 0·295 mol) was placed in a 125 ml Erlenmeyer flask with an N_2 inlet. The joint was fitted with a 3" length of Tygon tubing of just large enough diameter to slip over its surface with an air tight seal. The other end of the tubing was slipped over one end of a 3" length of 2 cm diameter glass tubing which was itself inserted through a rubber stopper plugging the side neck of the reaction vessel, a 1 l. 3-neck flask. This latter apparatus was immersed in an ice bath and was also equipped with a mechanical stirrer and a condenser connected to a standard setup for the maintenance of a slight positive N_2 pressure within the system with concomitant exclusion of O_2 and moisture. The reaction flask was charged with 115·5 g (0·295 mol) thiomethoxymethyl $SbCl_6^-$ and 300 ml CH_2Cl_2 and then purged of the last traces of air. The solid KOtBu was slowly tapped into the stirred sulfonium salt suspension with the aid of a moderate N_2 flow (required to keep the CH_2Cl_2 vaporized in the exothermic reaction from clogging the solid addition tube). After the addition (30 min) the dark yellow mixture was stirred at 0° for 2 hr, then warmed to room temp, and stirred overnight. A gray white solid (mostly $KSbCl_6$) was removed by filtration (under N_2) and washed with CH_2Cl_2. The total filtrate was evaporated at reduced pressure to a volume of 200 ml and the product crystallized overnight in the refrigerator. (The product could also be isolated by reducing the soln volume to 300 ml, then adding 300 ml of CCl_4 thus precipitating a dark red viscous oil. The supernatant was decanted, the residual oil dried on a vacuum pump overnight and then dissolved in 150 ml CH_2Cl_2 and crystallized as above). The pale yellow solid was filtered, washed with CH_2Cl_2, and dried *in vacuo*: yield: 24·2 g (36% based on required stoichiometry of 2 eq salt per eq base); m.p. 141–143° (dec). Further crops could be isolated from the filtrate which contained an additional 26% of the product; NMR (δ) CD_3NO_2: 5·71 and 5·43 (ABq, J = 9 cps), 3·87 and 3·30 (ABq, J = 14 cps), 3·03(s), 1·75(s); 1·53(s); ratio: 1:1:1:1:3:3:3. (Found: C, 15·67; H, 2·63; Cl, 45·02; S, 6·76. $C_6H_{13}Cl_6OSSb$ requires: C, 15·41; H, 2·81; Cl, 45·48; S, 6·85%).

When the ratio of thiomethoxymethyl $SbCl_6^-$ to KOtBu was 2:1 the yield was 23%.

Hydrolysis of 3,5,5-*trimethyl*-1,3-*oxathiolanium hexachloroantimonate.* H_2O (20 ml) was added to the title compound (3·0 g, 0·0064 mol) followed by 100 ml 0·7 Naq NaOH. After stirring overnight the mixture was acidified with HCl and the solid (from hydrolysis of $SbCl_6^-$) filtered. The filtrate was ether extracted, the extracts dried over $MgSO_4$, and evaporated. The residual, almost pure methyl 2-hydroxy-2-methylpropyl sulfide (0·65 g, 85%) was purified for analysis by GC; NMR(δ) CCl_4: 2·58(s), 2·16(s), 1·25(s); ratio: 2:3:6; IR(μ) CCl_4: 2·82(OH). (Found: C, 49·82; H, 9·94; S, 26·49. $C_5H_{12}OS$ requires: C, 49·95; H, 10·08; S, 26·66%).

Methyl 2-*hydroxy*-2-*methylpropyl sulfide.* Isobutylene oxide (3 g, 0·042 mol) was reacted with a soln of NaSMe (0·05 mol) in absolute EtOH. After 5 hr H_2O was added and the mixture worked up by acidification to pH 7, extraction with Et_2O, and distillation yielding 3·3 g (66%) of colorless liquid (b.p. 30° 2 mm) identical with the product obtained by hydrolysis of 3,5,5-trimethyl-1,3-oxathiolanium $SbCl_6^-$.

Thiomethoxymethyl t-butyl ether. (This procedure should be carried out in a hood because of extremely obnoxious odors). KOtBu (56 g, 0·5 mol) and dried distilled THF (150 ml) were placed in an ice bath cooled 500 ml 3-neck flask equipped with a pressure equalizing dropping funnel, condenser topped by a drying tube, and magnetic stirring bar. $ClCH_2SCH_3$ (48 g, 0·5 mol) in 25 ml of THF was added (15 min) to the stirred mixture at a rate slow enough to maintain a controlled reflux, for 4 hr. The dark brown heterogeneous mixture was diluted with H_2O, extracted with n-hexane, dried over $MgSO_4$, and distilled. The fraction distilling at 144–147° (25 ml) was collected and separated by prep. GC. Formaldehyde di-t-butyl acetal, thiomethoxymethyl t-butyl ether, and formaldehyde dimethyl thioacetal were isolated in a ratio of 1:6·6:2·1. The $CH_2(SMe)_2$ was identical to an authentic sample:[18] NMR(δ) $CDCl_3$: 3·68(s); 2·17(s); ratio: 1:3. $MeSCH_2OtBu$: NMR(δ) $CDCl_3$: 4·52(s); 2·17(s); 1·25(s); ratio: 2:3:9. (Found: C, 54·03; H, 10·31; S, 23·76. $C_6H_{14}OS$ requires: C, 53·68; H, 10·51; S, 23·89%). $CH_2(OtBu)_2$: NMR(δ) $CDCl_3$: 4·73(s), 1·26(s); ratio: 1:9. (Found: C, 67·24; H, 12·42. $C_9H_{20}O_2$ requires: C, 67·45; H, 12·58%).

Reaction of thiomethoxymethyl hexachloroantimonate with thiomethoxymethyl-t-butyl ether. A soln of 0·845 g (0·063 mol) of $MeSCH_2OtBu$ in 20 ml CH_2Cl_2 was added (10 min) with stirring to a CH_2Cl_2 (50 ml) suspension of thiomethoxymethyl $SbCl_6^-$ (2·47 g, 0·0063 mol) at 0°. CCl_4 (100 ml) was added to the homogeneous yellow soln precipitating a yellow oil. The supernatant was decanted, the residual oil pumped under vacuum, and then crystallized from CH_2Cl_2 yielding 1·0 g (34%) of 3,5,5-trimethyl-1,3-oxathiolanium $SbCl_6^-$.

Thiomethoxymethyl-d_5 hexachloroantimonate. The procedure reported previously was followed except that $ClCD_2SCD_3$ (from DMSO-d_6 > 99·5% and $SOCl_2$[19]) was substituted for the undeuterated sulfide. The product contained >98% D at both positions by NMR analysis.

Reaction of thiomethoxymethyl-d_5 hexachloroantimonate with potassium t-butoxide. The procedure for

the preparation of the undeuterated compound was followed using 21·5 g (0·053 mol $CD_3SCD_2^+$ $SbCl_6^-$. On workup this reaction gave 2·2 g (18%) of deuterated oxathiolanium salt; m.p. 142–143° (dec). The product contained <3% H on the S-Me group and <1% H at the acetal carbon (NMR analysis).

Reaction of thiomethoxymethyl-d_5 hexachloroantimonate with thiomethoxymethyl t-butyl ether. When 0·783 g (0·0058 mol) of $MeSCH_2OtBu$ in 10 ml CH_2Cl_2 was reacted with a CH_2Cl_2 (65 ml) suspension of CD_3SCD_2 $SbCl_6^-$ (2·2 g, 0·0058 mol) by the method above in the nonisotopically labelled system. 0·50 g (19%) of deuterated 3,5,5-trimethyl-1,3-oxathiolanium $SbCl_6^-$ (m.p. 140–141° dec) was isolated. This material was shown by NMR to contain ~49% D at the acetal carbon and ~51% D at the S-Me (NMR analysis).

When the $CD_3SCD_2^+$ $SbCl_6^-$ to $MeSCH_2OtBu$ ratio was increased to 2:1, salt containing ~65% D at the acetal carbon and ~62% D at the S-Me was isolated.

Deuterium Labeled Isobutylene. This was prepared from acetone-d_6 (>99·5%, Diaprep) and triphenylphosphonium methylide by the method of Atkinson.[13] After 2 bulb-to-bulb distillations on a vacuum line 6·66 g (77%) of deuterated isobutylene was obtained. The % D at the vinyl and Me positions was calculated using low temp NMR (−27·5°) with $CDCl_3$ as solvent and $CHCl_3$ as an internal weight standard; Me: δ 3·5% D and CH_2: 53·5% D.

Reaction of thiomethoxymethyl hexachloroantimonate with potassium t-butoxide in the presence of deuterated isobutylene. $CD_3SCD_2^+$ $SbCl_6^-$ (39·2 g, 0·1 mol) suspended in 100 ml CH_2Cl_2 was reacted with 11·2 g (0·1 mol) solid KOtBu as described in the basic experiment (*vide supra*) except that the water condenser was replaced by a CO_2 acetone condenser, the main reaction vessel was immersed in a CO_2 acetone bath instead of an ice bath, and the KOtBu addition was accomplished in 10 min. Only a slight color change was observed. The solid addition apparatus was immediately exchanged for a CO_2-acetone jacketed pressure equalizing dropping funnel containing (9·4 mL 6·66 g, 0·107 mol) deuterated isobutylene and 10 ml CH_2Cl_2. After converting the N_2 gas bubbler to a system for maintaining a slight positive N_2 pressure, the isobutylene soln was added (5 min) to the mixture (no reaction). This was allowed to warm to room temp. and stirred overnight yielding a reddish soln over a white solid. The product, isolated in the usual manner, contained ~34% D at the $(CH_3)_2C$ position.

Reaction of thiomethoxymethyl hexachloroantimonate with diisopropylethylamine at 0°. A stirred dispersion of thiomethoxymethyl $SbCl_6^-$ (39·4 g, 0·1 mol) in 100 ml CH_2Cl_2 in a 250 ml 3-neck flask equipped with a condenser topped with an N_2 inlet stopcock and a pressure equalizing dropping funnel containing 12·9 g (0·1 mol) of iPr_2NEt (redistilled) in 25 ml CH_2Cl_2 was immersed in an ice bath. As the amine was added (30 min) white fumes appeared but these slowly subsided. The yellow mixture was stirred at 0° for 1 hr and stored in a refrigerator overnight. A pale yellow solid was separated (suction filtration) from the dark orange mother liquor, washed with 100 ml CH_2Cl_2 and dried at high vacuum; yield: 21·5 g (46%) of iPr_2EtNH^+ $SbCl_6^-$; m.p. 220–224° (dec) after recrystallization from CH_2Cl_2; NMR(δ) CD_3CN: 3·7(m), 3·2(m), 1·4(d and t); ratio: 2:2:15. (Found: C, 20·58; H, 4·22; Cl, 45·85; N, 3·03. $C_8H_{20}Cl_6NSb$ requires: C, 20·68; H, 4·34; Cl, 45·77; N, 3·01%).

The addition of 300 ml CCl_4 to the filtrate from removal of the amine salt precipitated a second solid which was filtered, washed with CCl_4, and dried *in vacuo* (18 g). The NMR (CD_3CN; especially the Me region which showed the presence of at least 2 slightly different plus charged iPr_2NEt compounds) led us to identify it as a mixture of iPr_2EtNH^+ $SbCl_6^-$ and $iPr_2EtN{:}SbCl_x$ (x = 3 and 5). In accord with this assignment hydrolysis of the solid with aq NaOH afforded iPr_2NEt as the only volatile product. Mixtures (1:1) of $SbCl_3$ or $SbCl_5$ with iPr_2NEt gave NMR spectra very similar to that of the diisopropylethylammonium cation further confirming our structural assignment.

The combined mother and wash liquor obtained after removal of the mixture of amine complexes and salts was found to contain only 2 volatile products. $ClCH_2SCH_3$ (0·031 mol, 31%) and Cl_2CHSCH_3 (0·045 mol, 45%) which were isolated by GC and compared with authentic samples.[20]

Reaction of thiomethoxymethyl hexachloroantimonate with diisopropylethylamine at −78°. Thiomethoxymethyl $SbCl_6^-$ (34·7 g, 0·088 mol) was reacted with iPr_2NEt (11·35 g, 0·088 mol) in CH_2Cl_2 using the procedure above except that a CO_2-acetone bath was used in place of the ice bath. Following addition of the amine, the mixture was stirred for 1 hr at −78°, warmed to 0°, and stirred for another hr then placed in a refrigerator overnight. Both the white solid initially filtered off (9·3 g) and the solid precipitated by addition of CCl_4 (17·3 g) were shown to be mixtures of iPr_2EtNH^+ $SbCl_6^-$ and ethylidene-diisopropylimmonium $SbCl_6^-$ (5:3 and 9:5, respectively) by spectral analysis and hydrolysis in dil NaOH to a mixture of iPr_2NEt and iPr_2NH. The amines were isolated by GC and identified by comparison of their IR and NMR with commercial samples. No iPrEtNH was found in this reaction or in similar experiments with other solid

fractions though it was specifically looked for and a comparison sample (Aldrich) was easily separable by GC. The mixture of the ammonium and immonium salts could not be separated by fractional crystallization though the ratio of compounds could be changed. A combustion analysis was performed on a mixture which analyzed by NMR as a 10:7 mixture of immonium to ammonium salt; m.p. 197–199° dec; (Found: C, 21·04; H, 4.35; Cl, 45·57; N, 3·05. $C_{8}H_{18.8}Cl_6NSb$ requires: C, 20·74; H, 4·09; Cl, 45·89; N, 3·02%). NMR(δ) CD_3CN of immonium salt by difference: 8·48(q), 4·5(m), 2·55(broad d), 1·33(m); ratio: 1:2:3:12.

The filtrate after removal of the solids above was shown to contain (in addition to solvent) only 2 volatile substances, $ClCH_2SCH_3$ (0·031 mol, 35%) and Cl_2CHSCH_3 (0·033 mol, 38%). During distillation part of the isolation procedure, a solid identified as a mixture of the ammonium salt and $SbCl_x$ complex of iPr_2NEt (*vide supra*) precipitated in the still pot.

Reaction of thiomethoxymethyl hexachloroantimonate with pyridine. Pyridine (7·7 g, 0·097 mol) in 25 ml CH_2Cl_2 was reacted with a stirred CH_2Cl_2 (75 ml) suspension of thiomethoxymethyl $SbCl_6^-$ (33·5 g, 0·097 mol) at 0° as above. A solid (28·9 g) was obtained by filtration followed by washing with 150 ml CH_2Cl_2 and a second solid (2·8 g) was isolated by concentrating the first filtrate to 100 ml then adding 200 ml CCl_4 to ensure complete precipitation. The filtrate contained in addition to the solvent only 2 volatile components, $ClCH_2SCH_3$ (0·040 mol, 42%) and Cl_2CHSCH_3 (0·033 mol, 34%).

The second solid was identified as thiomethoxychloromethyl pyridinium $SbCl_6^-$ (m.p. 157–158° after recrystallization from CH_2Cl_2, moisture sensitive) by independent synthesis;[14] NMR(δ) CD_3NO_2: 9·4(m); 8·9(m), 8·5(m), 7·63(s), 2·43(s); ratio: 2:1:2:1:3. (Found: C, 16·46; H, 1·65; Cl, 48·81; N, 3·16. $C_7H_9Cl_7NSSb$ requires: C, 16·51; H, 1·78; Cl, 48·74; N, 2·75%).

The first solid was identified by NMR as a mixture of N-thiomethoxychloromethylpyridinium $SbCl_6^-$ (5 mmol, 5%), pyridinium $SbCl_6^-$ (0·06 mol, 62%), and pyridine $SbCl_x$ complexes (5 mmol, 5%).[21,22] The second compound could be isolated by recrystallization and compared with an authentic sample[22] (m.p. 245–250°).

Reaction of thiomethoxymethyl hexachloroantimonate with triphenylphosphine. Ph_3P (26·2 g, 0·01 mol) in 60 ml CH_2Cl_2 was reacted with a CH_2Cl_2 (75 ml) suspension of thiomethoxymethyl $SbCl_6^-$ (39·4 g, 0·01 mol) cooled by an ice bath as above. Using standard workup for this section, $ClCH_2SCH_3$ (0·047 mol, 47%), Cl_2CHSCH_3 (0·01 mol, 10%) were found. The only solid material isolated was tentatively identified as a mixture of $Ph_3PH^+SbCl_6^-$ and the various $Ph_3P \cdot SbCl_x$ complexes by NMR. Since the NMR did not contain peaks outside the Ph region indicating the lack of a thiomethoxymethyl derived residue, it was not further investigated.

Reaction of thiomethoxymethyl hexachloroantimonate with n-butyric acid. Using the standard procedure, n-butyric acid (4·4 g, 0·05 mol) in 10 ml CH_2Cl_2 was added (15 min) to a stirred mixture of thiomethoxymethyl $SbCl_6^-$ (20·0 g, 0·05 mol) and CH_2Cl_2 (75 ml) at 0°. The mixture was stirred for 1 hr, warmed to room temp and left overnight. Anhyd. Et_2O (200 ml) was added to the light, yellow homogeneous soln precipitating a hygroscopic fluffy white solid identified as $Et_2O \cdot SbCl_5$ complex;[15] NMR(δ) CD_3NO_2: 4·27(q, J = 7 cps), 1·50(t, J = 7 cps); ratio: 2:3. The filtrate was separated and assayed by a combination of distillation and GC and shown to contain n-$PrCO_2CH_2Cl$ (0·0074 mol, 15%), CH_3SSCH_3 (0·0012 mol, 5%), $ClCH_2SCH_3$ (0·0033 mol, 7%), and unreacted n-$PrCO_2H$ (0·017 mol, 34%). n-$PrCO_2CH_2Cl$: b.p. 118–119° 730 mm, lit.[16] 72° 42 mm; NMR(δ) $CDCl_3$: 5·72(s), 2·4(m), 2·7(m), 1·0(m); ratio: 2:2:2:3; IR(μ) $CHCl_3$: 5·68. (Found: C, 44·14; H, 6·74; Cl, 26·05. $C_5H_9ClO_2$ requires: C, 44·15; H, 6·62; Cl, 25·87%).

Reaction of thiomethoxymethyl hexachloroantimonate with sodium acetylacetonate. Powdered sodium acetylacetonate (6·1 g, 0·05 mol) was added to a cooled stirred suspension of $CH_3SCH_2^+$ $SbCl_6^-$ (19·7 g, 0·05 mol) in CH_2Cl using the solid addition apparatus described above. $NaSbCl_6$ and a dark red viscous oil composed of Sb salts and complexes (precipitated with CCl_4) were obtained. The major volatile product was 3,3-dichloro-2,4-pentanedione (10%); b.p. 176–176·5°, lit.[17] 77° 20 mm; NMR(δ) $CDCl_3$: 2·50. (Found: C, 35·68; H, 3·55; Cl, 41·84. $C_5H_6Cl_2O_2$ requires: C, 35·53; H, 3.58; Cl, 41·95%). Traces of acetylacetone, CH_3CO_2H, and CH_3SSCH_3 were also found but no $ClCH_2SCH_3$ or Cl_2CHSCH_3.

Reaction of thiomethoxymethyl hexachloroantimonate with cyclohexene. Excess cyclohexene (0·25 mol) in CH_2Cl_2 was added dropwise to a cooled CH_2Cl_2 suspension of $CH_3SCH_2^+$ $SbCl_6^-$ (0·1 mol) using the standard procedure. The volatile fraction (after precipitation of a black tar with n-pentane) was analyzed by GC, IR, and NMR: 1,2-dichlorocyclohexane (major product), chlorocyclohexane (little), cyclohexene (traces).

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