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Activation of Weak Organic Bases. III.[1] The Reactions of Divalent Sulfides with Acid Chlorides in the Presence of Friedel-Crafts Catalysts

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The reaction of thioanisol with acetyl chloride in the presence of $SbCl_5$ was attempted hoping the isolation of acetylsulfonium cation (V). The product actually obtained was found to be the sulfonium ion (IXa), which was also isolated from thioanisol and $SbCl_5$ without using acetyl chloride. The same type of compounds (IXb, XII, and XIV) was obtained in an analogous fashion. The mechanism of these reaction has been discussed. When dialkyl sulfides were treated with benzoyl chloride in the presence of $AgClO_4$, the expected benzoyldialkylsulfonium ions were isolated. The reaction of these salts with nucleophiles has also been described.

The reactions of sulfides with an alkylating reagent have been widely studied[3] because the resulting sulfonium salts are not only a reactive species by themselves but also be convertible into the ylids,[4] which are used as versatile intermediates in organic synthesis. On the other hand, it has been reported that acetyl chloride is not effective on dialkyl sulfides at 100° after 7 days.[5] Only the active sulfides such as episulfides(I),[6] α-aminosulfides(II),[7] and α-thiosulfides[8] are known to react with acid chlorides affording corresponding thiol esters as shown in Chart 1.

Klages, *et al.*[9] have shown that diethyl ether reacts with acetyl chloride at —10——20° in the presence of $SbCl_5$ to afford crystalline acetyldiethyloxonium hexachloroantimonate(III).

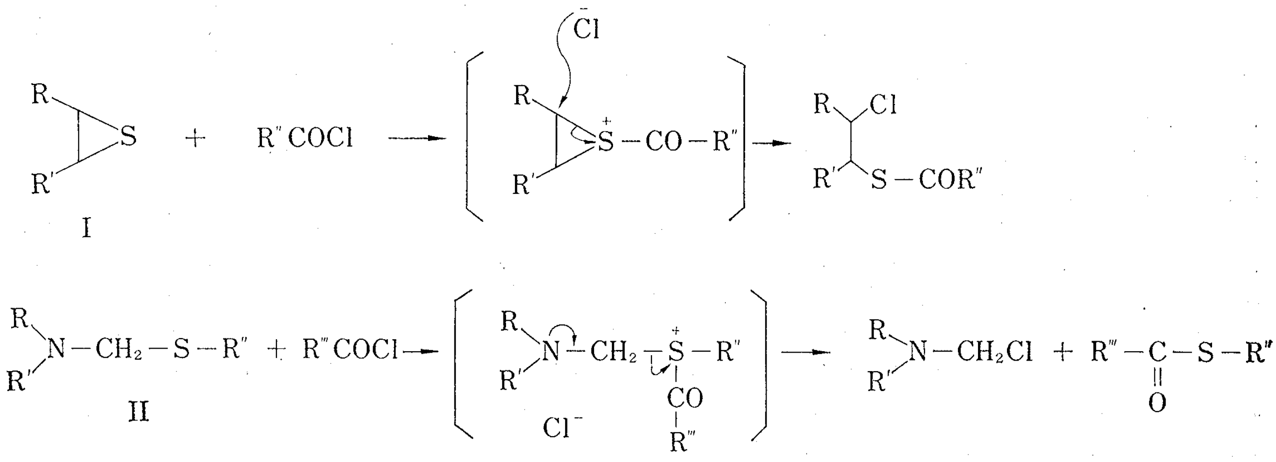

Chart 1

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[1] Part II: T. Oishi, K. Kamata, and Y. Ban, *Chemical Communication*, **1970**, 777.

[2] Location: *Kita*-12, *Nishi*-6, *Sapporo.*

[3] Houben-Weyl, "Methoden der Org. Chemie," 4th ed., Vol. IX, Georg Thieme, Stuttgart, 1955; T. Oishi and M. Mori, *Kagaku*, **25**, 510 (1970).

[4] A.W. Johnson, "Ylid Chemistry," Academic Press Inc., New York,, N.Y., 1966.

[5] E.L. Gustus and P.G. Stevens, *J. Am. Chem. Soc.*, **55**, 378 (1933).

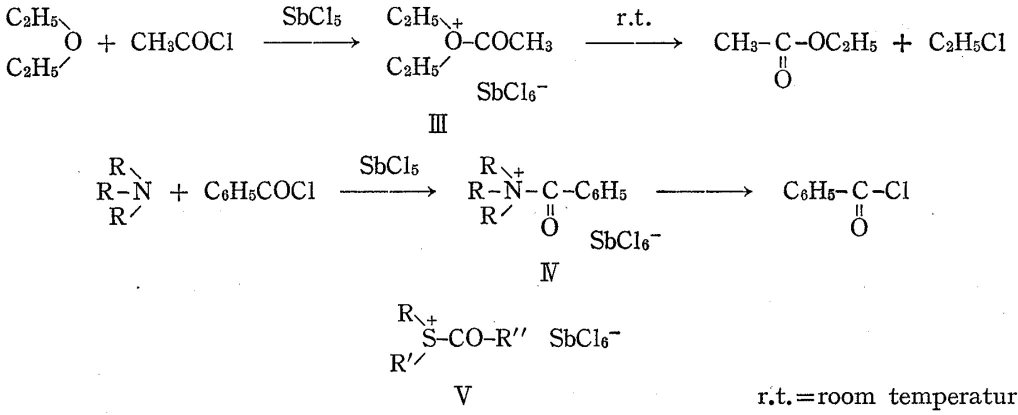
[6] C.C.J. Culvenor, W. Davies, and N.S. Heath, *J. Chem. Soc.*, **1949**, 282; E.M. Meade and F.N. Woodward, *J. Chem. Soc.*, **1948**, 1894.

[7] H. Bohme and G. Lerche, *Chem. Ber.*, **100**, 2125 (1967).

[8] G. Karmas, *Tetrahedron Letters*, **1964**, 1093.

[9] F. Klages, E. Muhlbauer, and G. Lukasczyki, *Chem. Ber.*, **94**, 1464 (1961).

Similarly, benzoyltrialkylammonium hexachloroantimonate(IV) has also been isolated in good yield[10] (Chart 2). Therefore, it was expected that acyldialkylsulfonium salts(V) could be isolated by using the same reagent system.[11] Moreovere, it has been reported that in the absence of nucleophile the oxonium salt (III) is cleaved to ethyl acetate and ethyl chloride on warming to room temperature,[12] whereas ammonium salts (IV) are stable at this temperature and decompose only at 80° under diminished pressure giving benzoyl chloride.[10] The above findings reveal that Cl^- which was generated from $SbCl_6^-$ and was known to be much stronger nucleophile than the latter, attacks on the metylene group adjacent to the electron-deficient oxygen ($\overset{+}{O}$-CO-) in III although such attack was not observed in IV. Thus, it seemed worthwhile to investigate the behavior of acylsulfonium salts(V) which is structurely related to III and IV in general.



r.t.=room temperature

Chart 2

The Reaction of Thioanisole with Acetyl Chloride in the Presence of $SbCl_5$

Friedel–Crafts acetylation of thioanisole in the presence of $AlCl_3$ is reported to give the para acetylated compound in good yield.[13] The reaction could proceed through initial S-acetylation accompanied by the irreversible migration of acetyl group from sulfur to aromatic ring because the electronreleasing conjugative effect of sulfur is known to be much less than that of oxygen whereas the nucleophilicity of the former is much stronger than that of the latter.[14] Thus, thioanisole was chosen as a sulfide and the isolation of the supposed intermediate(VI) was attempted.

To a solution of acetyl chloride in CH_2Cl_2 was added a molar equivalent of $SbCl_5$ and thioanisole successively at −70° and the solution was allowed to come to 0°. When CCl_4 was added to the solution and the whole was cooled again to −30°, a red crystalline product separated out. Recrystallization from a mixture of acetone–methanol yielded a red pillars of mp 154—157°. The nuclear magnetic resonance (NMR) spectrum of this compound shows two singlets at τ 6.33 (3H) and τ 7.42(3H). The higher field signal is apparentely

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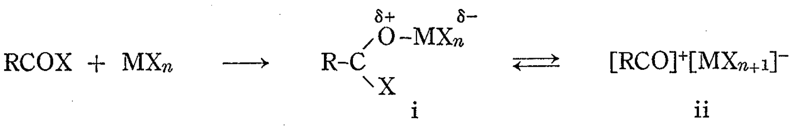
[10] F. Klages and E. Zang, *Ann.*, **607**, 35 (1957).

[11] Friedel–Crafts catalysts (MXn) are known to combine variously with acyl halides to form donor-



acceptor complexes (i) or to generate oxocarbonium ions (ii). For a review of this subject see ref. 16), p. 91—95, 665—680, 790—812. See also F.P. Boer, *J. Am. Chem. Soc.*, **90**, 6706 (1968); R. Weiss and B. Chevrier, *Chem. Commun.*, **1967**, 145.

[12] H. Meerwein and H. Maier-Huser, *J. Prakt. Chem.*, **134**, 51 (1932).

[13] R.A. Cutler, R.J. Stenger, and C.M. Suter, *J. Am. Chem. Soc.*, **74**, 5475 (1952).

[14] S. Oae, A. Ohno, and W. Tagaki, *Bull. Chem. Soc. Japan*, **35**, 681 (1962).

ascribed to S-methyl protons and the lower one to methyl orotons adjacent to sulfonium ion. Moreover, the spectrum shows that nine aromatic protons exist in its molecule and four protons out of them reveal typical AB splitting pattern, which indicates that two aromatic rings are involved in the molecule and one of them should be disubstituted on the 1,4-position. Based on the above data, the structure(VII) was assigned to this compound (Chart 3). Base induced hydrolysis of VII gave sulfide(VIII) in good yield, which further verified the structure (VII).

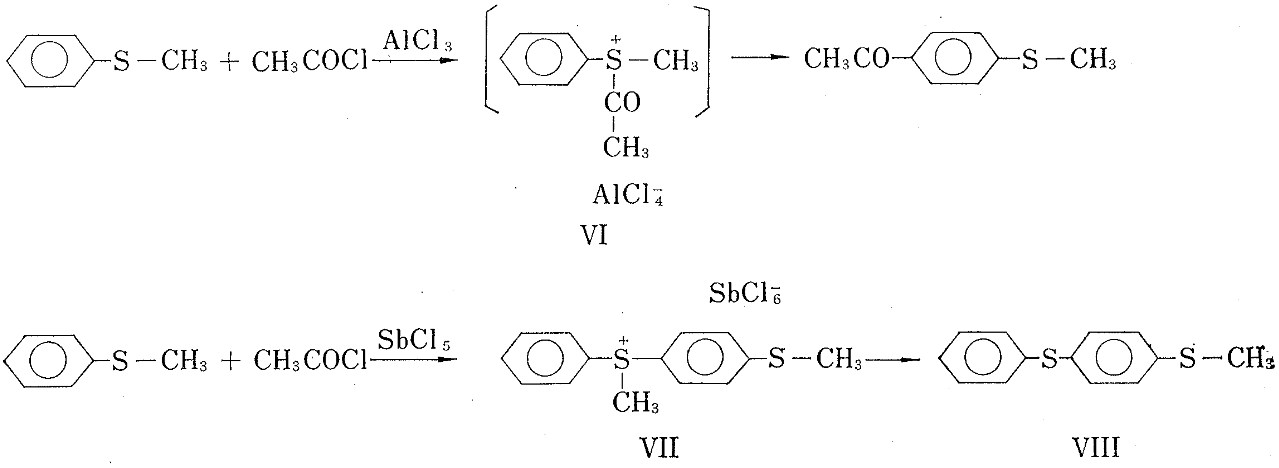


Chart 3

The Reaction of Phenyl Alkyl- and Diphenyl Sulfide with $SbCl_5$

The above result is rather unexpected and as an acetyl gruop is not involved in the compound(VII), it is assumed that the acylating agent may not be concerned with the formation of VII. Therefore, thioanisole was treated with $SbCl_5$ alone at $-70°$. After usual work-up, there was obtained a red crystalline material(IXa), which was found to be identical in every respect with VII. Analogously, phenyl ethyl sulfide reacted with $SbCl_5$ to afford sulfonium salt(IXb), which, without purification, was converted to the sulfide(Xb) in almost quantitative yield. When the *p*-methyl derivative(XI) was used, the salt(XII) was obtained. XII gave the sulfide(XIII) on alkaline hydrolysis. It should be emphasized that even a

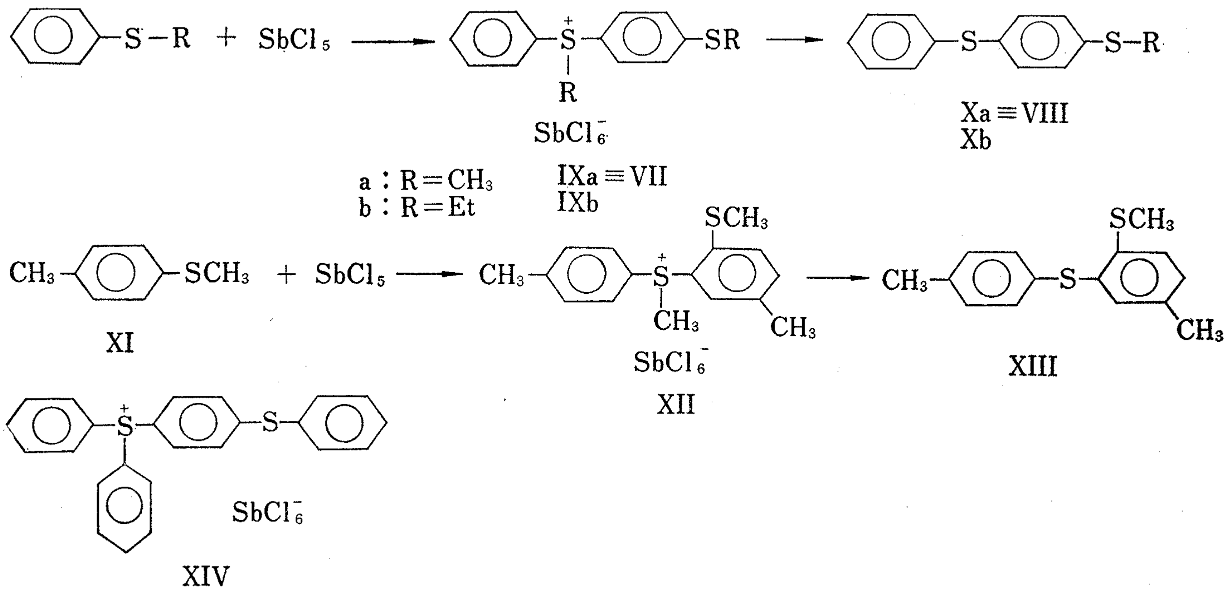


Chart 4

diphenyl sulfide undergoes the same reaction to give the triphenyl sulfonium salt(XIV) which is difficultly accessible by the other means.[15]

Antimony pentachloride is known to react as a chlorinating agent[16] as well as it works as a strong Lewis acid. In the present case, one might anticipate that the chlorosulfonium salt(XV) was initially formed by the attack of Cl^+ liberated from $SbCl_5$ and then this reactive intermediate condensed with the unchlorinated starting material affording the salt(IX)(Chart 5). Chlorodimethylsulfonium hexachloroantimonate(XVI) has been obtained by Meerwein, *et al.*[17] by the reaction of dimethyl sulfide and excess $SbCl_5$(Chart 6), which supports the presence of the chlorosulfonium ion(XV) as an intermediate. However, every effort to isolate it was unsuccessful. This failure would be ascribed to the extremely high reactivity of XV to thioanisole. Two routes may be considered for this reaction(Chart 5): one (pathway a)

$$2SbCl_5 \rightleftharpoons SbCl_6^- + SbCl_4^+ \longrightarrow SbCl_3 + Cl^+$$

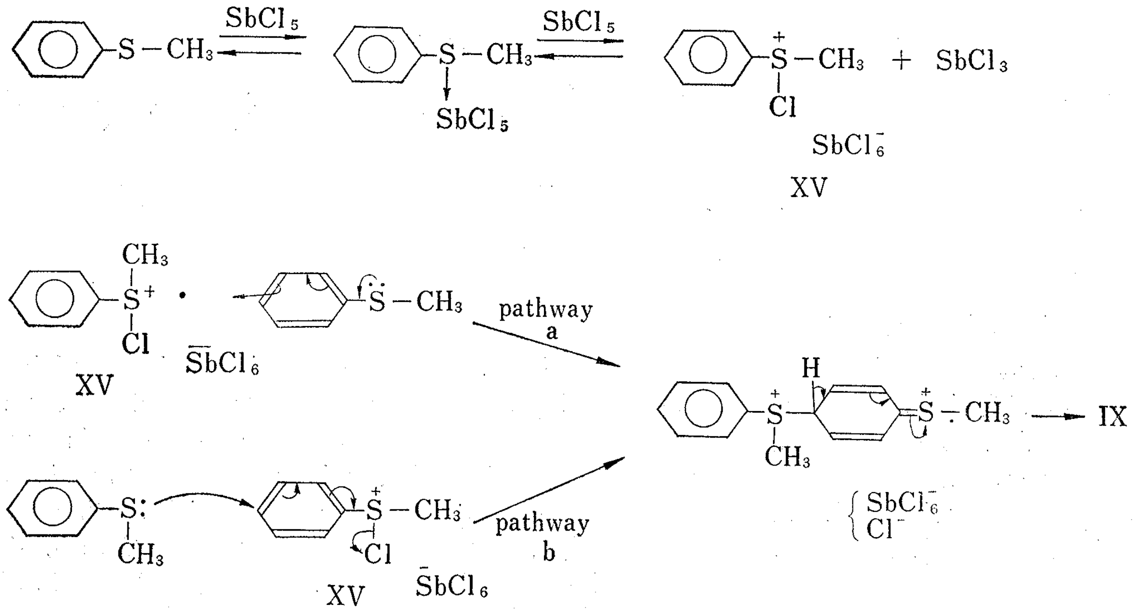


Chart 5

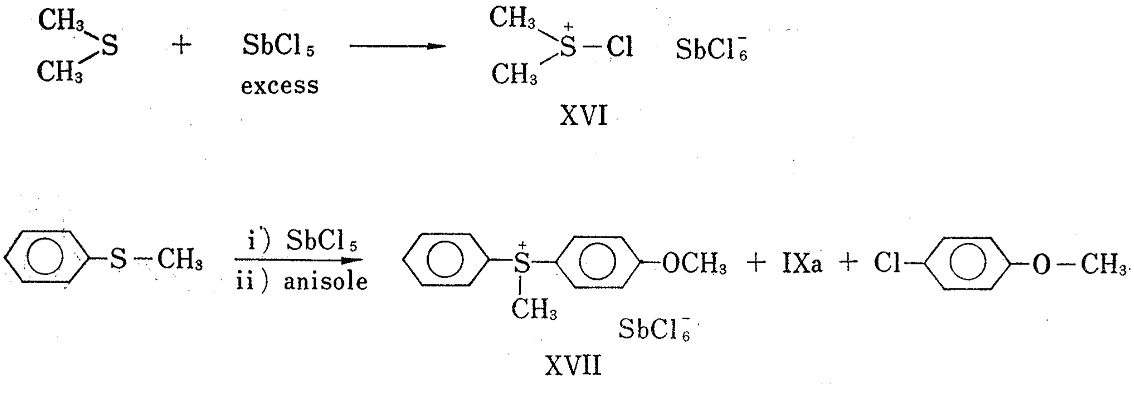


Chart 6

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15) J.W. Knapczyk and W.E. McEwen, *J. Am. Chem. Soc.*, **91**, 145 (1969), and references sited there in.
16) G.A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, ed. by G.A. Olah, Interscience Publishers, New York, N.Y., 1963, p. 270; W. Bracke, W.J. Cheng, J.M. Pearson, and M. Szwarc, *J. Am. Chem. Soc.*, **91**, 203 (1969).
17) H. Meerwein, K.F. Zenner, and R. Gipp, *Ann.*, **688**, 67 (1965).

involves substitution reaction on sulfur in the sulfonium salts(XV) and the other(pathway b) nucleophilic attack of the sulfur of thioanisole on the *para*-position of XV.

In order to clarify this point, the reaction of thioanisole with $SbCl_5$ was then carried out in the presence of anisole. If the reaction proceeds through the sulfonium salts(XV) and the pathway a is really operative, the main product would be the new sulfonium salt (XVII) because anisole is known to be more effective nucleophile than thioanisole. The products obtained were the mixture of XVII and IXa, of which the former was predominant. The result of this cross experiment supports the validity of pathway a(Chart 5). The reaction did not take place when the other Lewis acid such as BF_3·etherate and $FeCl_3$[18a] were employed. It has been reported that the same type of reaction took place when aryl alkyl sulfides were treated with conc. sulfuric acid[18b] or with 70% $HClO_4$–$POCl_3$–H_2O_2 system.[18c] It has been deduced that the initial step of these reactions is the oxidation of sulfides by conc. sulfuric acid or by H_2O_2, followed by the attack of unoxidized starting sulfides on the protonated sulfoxides to yield the products.

Halogenation of aryl alkyl sulfides by a variety of reagents has been reported by several workers. Side chain,[19,20] sulfur,[21] ring halogenation,[19,20] and S-alkyl bond cleavage reaction[22] have been reported to occur by altering the combination of sulfides and reagents. It is assumed that the initial attack of the reagents, however, occur on sulfur in every case and the resulting halosulfonium salts give products depending on the surrounding circumstances. In connection with the present work, the chlorination of phenylmercaptoacetic acid(XVIII) has attracted much attention. It has been reported[20] that XVIII was chlorinated by sulfuryl chloride on the side chain, whereas only ring chlorination was observed when $SbCl_5$ was used. The chlorination of side chain could proceed through XX, which might be produced from XIX as shown in Chart 7. On the other hand, $SbCl_6^-$ may be too weak a nucleophile to aid in the removal of hydrogen, which may explain the predominant occurence of the migration of

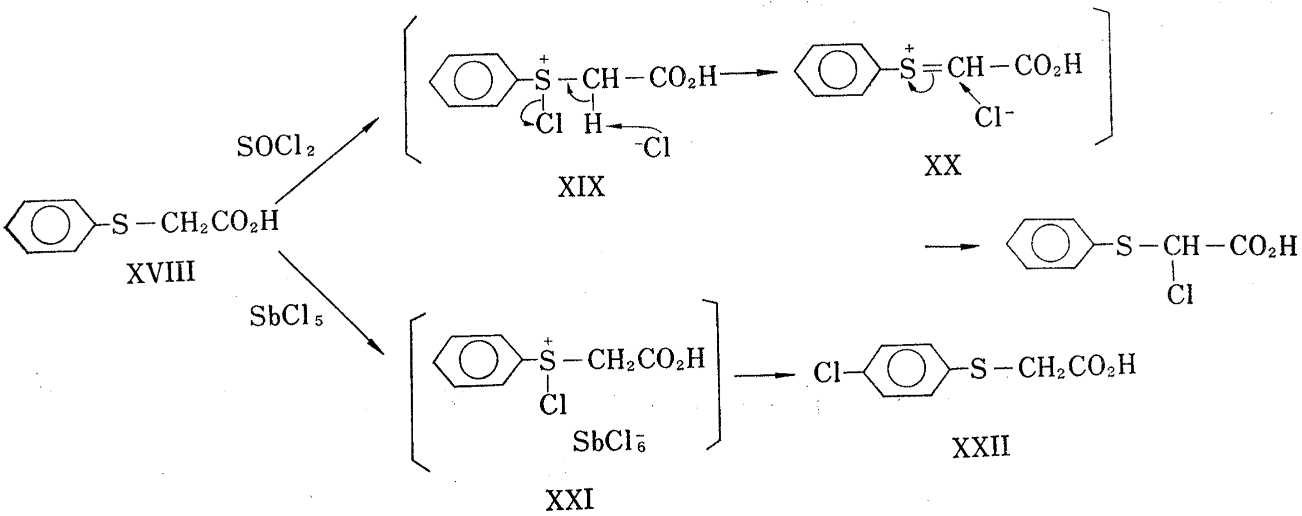

Chart 7

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18) *a*) After the present work had been completed, the reactions of diaryl sulfides with aromatic hydrocarbons in the presence of $AlCl_3$ were reported; C.H. Han and W.E. McEwen, *Tetrahedron Letters*, **1970**, 2629. However, the reaction conditions are not described in it; *b*) F. Krollpfeiffer and W. Hahn, *Chem. Ber.*, **86**, 1049 (1953); *c*) S. Ukai and K. Hirose, *Chem. Pharm. Bull.* (Tokyo), **16**, 202, 606 (1968).

19) D.L. Tuleen and T.B. Stephens, *Chem. Ind.* (London), **1966**, 1555; D.L. Tuleen and D.N. Buchanan, *J. Org. Chem.*, **32**, 495 (1967).

20) D. Walker and J. Leib, *J. Org. Chem.*, **27**, 4455 (1962).

21) R. Pummerer, *Chem. Ber.*, **42**, 2275 (1964); S. Oae, Y. Ohnishi, S. Kozuka, and W. Tagaki, *Bull. Chem. Soc. Japan*, **39**, 364 (1969).

22) W. Groebel, *Chem. Ber.*, **92**, 1887 (1959).

chloro cation from sulfur to the aromatic ring yielding the stable XXII(Chart 7). In sharp contrast with this observation, the nucleophilic substitution reaction on sulfur in XV was proved to occur in our case. The mode of the product formation might have been crucilally effected by a subtle difference in nucleophilicity between thioanisole and XVIII.

The Reaction of Dialkyl Sulfide with Benzoyl Chloride in the Presence of $AgClO_4$

It has been shown in the above experiments that $SbCl_5$ works as an oxidizing agent. For the purpose of isolating acylsulfonium ion, a different sort of Lewis acid should be employed. Thus, benzoyl chloride was treated with methyl *n*-octyl sulfide in the presence of $AgClO_4$[23] at −10° in methylene chloride. The solution was allowed to come to room temperature, filtered and evaporated to give an oil. From the *n*-hexane soluble fraction, there were obtained benzoic acid(78%) and from the residue, the protonated sulfide(XXIII)(49%). The above experiment showed that the initially formed intermediate(XXIV), if any, should have been hydrolyzed by the atmospheric moisture. To acertain the intermediacy of XXIV in the above reaction, methyl benzyl sulfide was subjected to acylation because the cleavage of sulfur-benzyl bond in XXV was expected during the reaction. The reaction proceeded smoothly affording methyl thiobenzoate(XXVI)(67.4%) and methyldibenzylsulfonium perchlorate(XXVII)(67%), which established that XXV was actually formed. Finally, the reaction of acylsulfonium salt with ether was carried out. The benzoyldiethylsulfonium salt(XXVIII) was prepared in the same way as described above in dichloroethane using diethylsulfide. After the solvent had been evaporated in a vaccum to remove any unreacted sulfide, the residual oil was washed once with *n*-hexane and dissolved again in dichloroethane. Excess di-*n*-propyl ether was then added and the solution was refluxed for 2 hr. After usual work-up, there were obtained *n*-propyl benzoate(38%) and diethylpropylsulfonium perchlorate (XXIX)(62%). It seemed that the attack of di-*n*-propyl ether on activated carbonyl carbon produced the corresponding benzoyl oxonium salt(XXX), which reacted with the sulfide to afford the observed products. It would appear that the progress of the reaction was facilitated by the irreversible formation of the stable sulfonium salts, XXVII and XXIX.

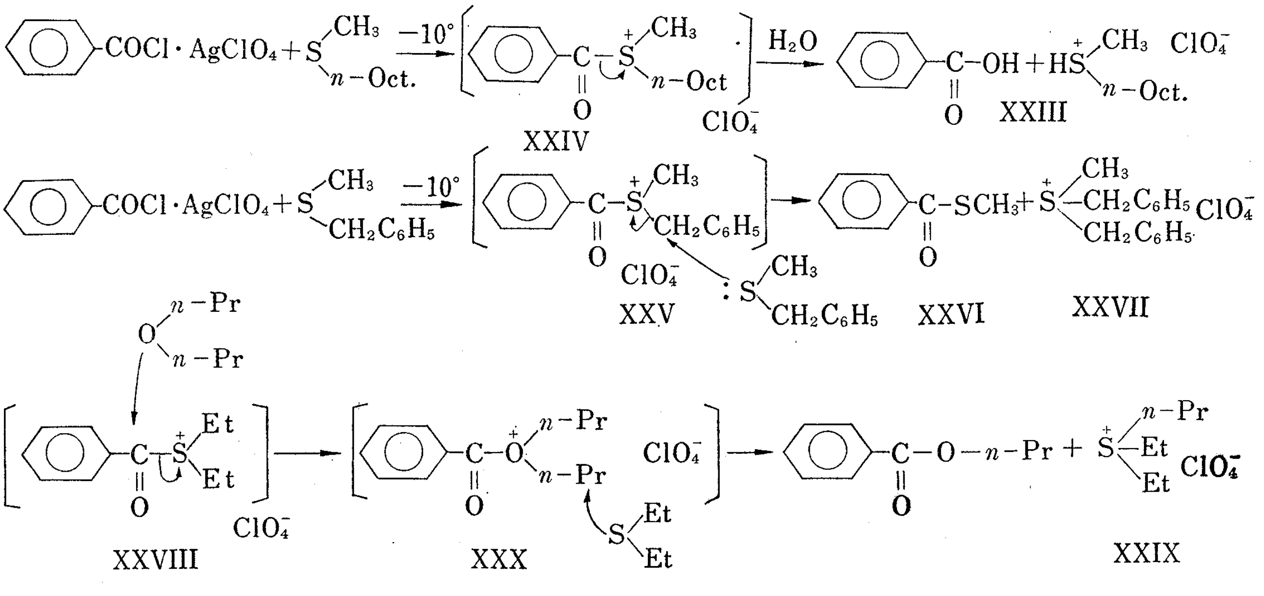

Chart 8

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[23] Klages, *et al.* have used $AgClO_4$ to generate *p*-toluenesulfonium cation as a perchlorate. F. Klages and F.E. Malecki, *Ann.*, **691**, 15 (1966).

On the bases of the above experiments, it was proved that benzoyldialkylsulfonium salts were formed when the dialkyl sulfides were treated with benzoyl chloride at 0° in the presence of $AgClO_4$. Moreover, it was demonstrated that their reactivity was similar to that of acetyltrialkylammonium salts (IV), and $\overset{+}{S}$-carbonyl bond cleavage $(\substack{R\\R}{>}\overset{+}{S}\text{–CO–})$ was found to take place in the acyldialkylsulfonium salt(XXVIII), whereas $\overset{+}{O}$-alkyl bond cleavage $(\substack{R\\R}{>}\overset{+}{O}\text{–CO–})$ was observed in the intermediary acyldialkylsulfonium salt (XXX) (see Chart 8).

Experimental[24]

Methylphenyl(*p*-methylmercaptophenyl)sulfonium Hexachloroantimonate (VII)——To a solution of 3.6 g of $SbCl_5$ in 10 ml of CH_2Cl_2 was added 0.8 g of acetyl chloride in CH_2Cl_2 at $-70°$ under stirring. After the addition had been completed, 1.24 g of methyl phenyl sulfide was added at this temperature. The orange crystalline precipitate separated out immediately. The homogenous solution was obtained when the suspension was allowed to come to room temperature. A red oil which deposited by the addition of CCl_4 to this solution solidified when the mixture was cooled to $-30°$. After filtration, 2.87 g of VII (crude) was obtained in almost quantitative yield. Recrystalization from acetone–ether gave red pillars of mp 154—157°. NMR (in CD_3NO_2) τ: 2.1—2.6 (9H, multiplet, aromatic protons), 6.33 (3H, singlet, $\overset{+}{S}\text{-C}\underline{H}_3$), 7.42 (3H, singlet, $\text{-}C_6H_5\text{-SC}\underline{H}_3$). *Anal.* Calcd. for $C_{14}H_{15}SSbCl_6$: C, 29.07; H, 2.60; Cl, 36.56; S, 11.02. Found: C, 29.24; H, 2.76; Cl, 36.40; S, 11.41.

The sulfonium salt (IX), which is identical in every respect with VII, was obtained by the reaction of methyl phenyl sulfide with $SbCl_5$ in almost quantitative yield. The procedure was almost same with that described above. The only difference is that acetyl chloride was not employed in this case. As noted above, orange crystals were separated out when $SbCl_5$ was added to methyl phenyl sulfide in CH_2Cl_2 at $-70°$. When water was added to this suspension, the starting sulfide was recovered in good yield, which showed that this product would be a donnor-acceptor complex $(C_6H_5\text{-}\underset{\substack{\downarrow\\ \delta\text{-}SbCl_5}}{\overset{\delta+}{S}}\text{-}CH_3)$. If this material were XV, methyl phenyl sulfoxide would be obtained on hydrolysis (see Chart 5).

Phenyl(4-methylmercaptophenyl) Sulfide (VIII)——Method i): A suspension of 1 g of VII in 20 ml of 10% NaOH solution was stirred vigorously at room temperature. While being stirred, a homogeneous solution was obtained. After 1 hr, the water layer was extracted with ether. The solvent was dried and evaporated to give 347 mg of an oil which was purified by silica gel chromatography. Elution with *n*-hexane yielded 320 mg of colorless oil of VIII (80%). NMR (in CCl_4) τ: 2.80 (9H, multiplet, aromatic protones), 7.58 (3H, singlet, $\text{-}C_6H_5S\text{-C}\underline{H}_3$). *Anal.* Calcd. for $C_{13}H_{12}S_2$: C, 67.19; H, 5.12; S, 27.59. Found: C, 66.79; H, 5.29; S, 28.02.

Method ii): To a solution of 500 mg of VI in CH_2Cl_2 was added 200 mg of piperidine. After standing for 1 hr, the solvent was evaporated off. The residue was digested well with ether and the ether insoluble material was filtered off. The solvent was evaporated to give 138 mg of colorless oil of VII (70%). The collected solid was recrystallized from acetone–methanol to give a crystalline doner-acceptor complex of piperidine with $SbCl_5$, mp 243—245°.

Phenyl(4-ethylmercaptophenyl) Sulfide (Xb)——Ethyl phenyl sulfide (1.38 g) was treated wiht $SbCl_5$ (3.3 g) in CH_2Cl_2 at $-70°$ in the same way as employed for the preparation of VII. An oily precipitate (739 mg) was subjected directly to the reaction with piperidine according to the method ii). After usual work-up, 317 mg of a colorless oil was obtained. This compound was proved to be Xb from NMR (in CCl_4) τ: 2.81 (9H, multiplet, aromatic protons), 7.12 (2H, quartet, $\text{-SC}\underline{H}_2CH_3$), 8.70 (3H, triplet, -SCH_2CH_3).

***p*-Tolyl (2-Methylmercapto-5-methyl)phenyl Sulfide (XIII)**——To a solution of 2.1 g of $SbCl_5$ in CH_2Cl_2 was added 886 mg of methyl *p*-tolyl sulfide in CH_2Cl_2 at $-10°$ and the solution was kept for 15 min at this temperature. Then, the solution was allowed to come to room temperature. After 30 min water was added to this solution. The CH_2Cl_2 layer was separated, dried and evaporated to give 1.8 g of XII as a brown oil. Purification by silica gel chromatography yielded 1.1 g (55%) of XII, which partially solidified. Without further purification, this compound was subjected to the further reaction. Cleavage of 473 mg of XII was carried out according to the method ii) yielding 159 mg (79% yield, after silica gel

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[24] Melting points are uncorrected. All NMR spectra were measured with a Hitachi H-60 spectrometer. Chemical shifts are reported as values measured from tetramethylsilane as an internal standard. $AgClO_4$ was dried over P_2O_5 for 24 hr under reduced pressure. $SbCl_5$ was distilled under reduced pressure before use.

chromatography) of XIII as an oil. NMR (in CCl_4) τ: 7.60 (3H, singlet), 7.70 (3H, singlet), 7.80 (3H, singlet). Mass Spectrum: M^+ 260. This compound has been synthesized by F. Krollpfeiffer and W. Hahn from methyl p-tolyl sulfide and conc. sulfuric acid.[18b)]

Diphenyl(4-phenylmercaptophenyl)sulfonium Hexachloroantimonate (XIV)——Diphenyl sulfide (1.62 g) was treated with $SbCl_5$ (3.3 g) at $-10°$ in the same way as employed for the preparation of XII to yield 2.7 g of XIV (76%). Recrystallization from acetone–ether gave yellow prisms of mp 178—181.5°. Only aromatic protons were observed in its NMR spectrum. *Anal.* Calcd. for $C_{24}H_{19}S_2SbCl_6$: C, 40.83; H, 2.71; S, 9.08; Cl, 30.13. Found: C, 40.87; H, 2.73; S, 9.07; Cl, 29.97.

Cross Experiment——To a solution of 6.6 g of $SbCl_5$ in CH_2Cl_2 was added 1.24 g of methyl phenyl sulfide at $-10°$. Successively, 1.08 g of anisol in CH_2Cl_2 was added at this temperature. The solution was allowed to come to room temperature and treated with water. The CH_2Cl_2 layer was separated and the water layer was extracted with CH_2Cl_2. The combined extracts were washed with water twice dried and evaporated to give 4.44 g of oily material, which solidified when ether was added. After filtration 3.7 g of crystalline compound was obtained. The NMR spectrum of this material reveals two singlets at τ 5.92 ($-C_6H_4OC\underline{H}_3$) and τ 7.35 ($-C_6H_4SC\underline{H}_3$). The former corresponds to O-methyl protons in XVII and the latter to S-methyl protons in IXa. The relative ratio of XVII and IXa (5:3) was calculated from the areas obtained by integration of the peaks. The solvent was evaporated off from the filtrate yielding 700 mg of p-chloroanisole which must have been obtained by the reaction of anisole-with $SbCl_5$.

***p*-Chloroanisole**——From 16.5 g of $SbCl_5$ and 5.4 g of anisole, there was obtained 4.23 g (60%) of p-chloroanisole in the same way as employed for the preparation of XIII.

The Reaction of Benzoyl Chloride with Methyl *n*-Octyl Sulfide in the Presence of $AgClO_4$——To a solution of 1.1 g of $AgClO_4$ in 5 ml of CH_2Cl_2 was added 0.7 g of benzoyl chloride at $-10°$. Then 0.8 g of methyl n-octyl sulfide in CH_2Cl_2 was added at this temperature. The turbide solution was allowed to come to room temperature and the white solid was filtered off. The solvent was evaporated off from the filtrate and the residue was treated with n-hexane. From n-hexane soluble fraction, there was obtained 0.47 g (78%) of benzoic acid. An oily insoluble material (0.63 g 49%) was proved to be methyl-n-octyl sulfide perchlorate (XXIII).

The Reaction of Benzoyl Chloride with Benzyl Methyl Sulfide in the Presence of $AgClO_4$——A mixture of 0.7 g of benzoyl chloride, 1.1 g of $AgClO_4$, and 0.7 g of benzyl methyl sulfide prepared in the same way as described above was stirred for 1 hr at room temperature. Water was added to this solution and the water layer was extracted with CH_2Cl_2. The solvent was dried and evaporated leaving an oil, which was digested with ether. The ether layer was washed with sat. $NaHCO_3$ solution to remove benzoic acid (0.25). The solvent was evaporated off to give 0.34 g of methyl thiobenzoate (67.4%, calcd. from benzyl methyl sulfide used). IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1665. The residue was recrystallized from acetone–ether yielding 0.56 g (67% calcd. from benzyl methyl sulfide used) of methyldibenzylsulfonium perchlorate (XXVII). NMR (in CD_3NO_2) τ: 5.25 (4H, broad singlet, $-SC\underline{H}_2C_6H_5$), 7.32 (3H, singlet, $SC\underline{H}_3$). *Anal.* Calcd. for $C_{15}H_{17}O_4SCl$: C 54.73; H, 5.21; S, 9.75. Found: C, 54.86; H, 5.24; S, 9.65.

The Reaction of *n*-Propyl Ether with the Intermediary Benzoylsulfonium Salt (XXVIII)——To a mixture of 0.7 g of benzoyl chloride and 1.1 g of $AgClO_4$ in CH_2Cl_2 was added 0.7 g of diethyl sulfide at $-10°$. The solution was allowed to come to room temperature and the solvent as well as unreacted diethylsulfide was evaporated off under reduced pressure leaving an oil, which was washed once with n-hexane. The residue was dissolved in 4 ml of dichloroethane containning 4 ml of n-propyl ether and the solution was refluxed for 2 hr. The solvent was evaporated off and the residue was digested with ether. The ether layer was separated and washed with sat. $NaHCO_3$ solution, dried and evaporated to yield 0.31 g (38%) of n-propyl benzoate. The ether insoluble fraction was identified as diethyl-n-propylsulfonium perchlorate (XXIX). Yield, 0.72 g (62%). Tetraphenylborate, mp 215—218°. *Anal.* Calcd. for $C_{31}H_{37}SB$: C, 82.21; H, 8.24; S, 7.08. Found: C, 82.20; H, 8.16; S, 6.98.

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