[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Preparation of Some Unsaturated Sulfonium Halide-Mercuric Halide Double Salts[1]

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Three unsaturated straight-chain alcohols were prepared, their double bonds being, respectively, two, three, and four carbon atoms removed from the carbinol carbon. The bromides of the respective alcohols were made; the physical constants of the hitherto unreported 5-hexen-1-ol and 1-bromohexene-5 were determined and they were characterized. The physical constants of the three new sulfides derived from the bromides were determined and these new compounds were characterized. Attempted syntheses of the three tris-sulfonium bromides were made. An attempt is made to explain the fact that the expected products were not obtained. Except for the tris(3-butenyl)sulfonium bromide–mercuric iodide, which could not be isolated, the eight new double salts of the tris(3-butenyl), -(4-pentenyl), and -(5-hexenyl) sulfonium bromides and, respectively, mercuric chloride, mercuric bromide, and mercuric iodide were made. Their physical states are reported and their respective constitutions were established by analysis. The effect of moving the double bond farther from the sulfur was an increase in the stability of the compound.

With a few exceptions, previous attempts to prepare unsaturated sulfonium salts have been unsuccessful. Steinkopf and Bessaritsch[2] prepared an addition compound of triallylsulfonium iodide and iodoform, but were unsuccessful in obtaining the free salt. Butler and Benjamin[3] were able to prepare methyldiallylsulfonium methyl sulfate and a number of unsaturated sulfonium halide–mercuric halide double salts, but were also unsuccessful in preparing triallylsulfonium iodide. Toennies and Kolb[4] were able to prepare acetyl methionineallylsulfonium bromide. Braun and Plate[5] reported preparing methylbis(1-cyclopentenyl)sulfonium iodide, but no analysis was given and the melting point of the product, crystallized from methyl alcohol, was identical with that of trimethylsulfonium iodide, 204°. Bost and Schultz[6] prepared diallyl -*p*-phenylphenacylsulfonium bromide by refluxing the reactants in absolute methyl alcohol. An attempt by Bloomfield[7] to prepare a sulfonium salt of dihydromyrcene tetrasulfide and methyl iodide yielded only trimethylsulfonium iodide. Lawson and Davson,[8] in their chlorination of mustard gas, reported some unsaturated sulfides and chlorosulfides whose sulfonium salts were unstable. Selker[9] reacted butylmethallyl sulfide and methyl iodide to produce dimethylbutylsulfonium iodide. From this they concluded that a double bond in the position α to a sulfur is unstable to methyl iodide.

The difficulty in preparing any sulfonium salt containing groups larger than methyl lies in the fact that the groups are subject to displacement by smaller groups. The smaller group might come from the solvent[3] or from the dissociation and subsequent recombination of the sulfonium salt, the larger groups having been eliminated in the interim. Cahours[10] obtained trimethyl sulfonium iodide from the reaction of benzyl bromide and methyl sulfide; Krüger[11] was able to change triethylsulfonium iodide to the trimethyl derivative by heating the former with excess methyl iodide at 150°. Masson,[12] in attempts to prepare a disulfonium salt from ethylene bromide and an alkyl sulfide obtained only trimethylsulfonium iodide. Platanov[13] and Anisimov reacted ethyl and methyl iodide with monothioparaldehyde, dithioparaldehyde, and ethyl monothioacetate, obtaining in every case the triethyl - or trimethylsulfonium iodide.

Ray and Levine[14] explained these apparently unrelated anomalies by postulating the dissociation of the sulfonium salt first formed with a subsequent recombination to give a sulfonium salt containing the smallest possible radicals. An apparent exception to this mechanism is shown by the work of P. C. Ray[15] who reacted methyl mercaptan with mercuric nitrite to form methyl mercury mercaptide nitrite. Subsequent reaction of this compound with butyl iodide gave a disulfide containing not one but two butyl groups, indicating the displacement of a lighter by a heavier radical. From this,

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[1] Taken from a thesis presented by G. D. Price to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science.

[2] W. Steinkopf and R. Bessaritsch, *J. prakt. Chem.*, **109**, 230 (1925).

[3] G. B. Butler and B. M. Benjamin, *J. Am. Chem. Soc.*, **74**, 1846 (1952).

[4] G. Toennies and J. J. Kolb, *J. Am. Chem. Soc.*, **67**, 1141 (1945).

[5] J. V. Braun and T. Plate, *Ber.*, **67**, 281 (1934).

[6] R. W. Bost and H. C. Schultz, *J. Am. Chem. Soc.*, **64**, 1165 (1942).

[7] G. F. Bloomfield, *J. Soc. Chem. Ind.*, **67**, 14 (1948).

[8] W. E. Lawson and T. P. Davson, *J. Am. Chem. Soc.*, **49**, 3119 (1927).

[9] M. L. Selker, *Ind. Eng. Chem.*, **40**, 1467 (1948).

[10] A. Cahours, *Compt. rend.*, **80**, 1317 (1875).

[11] F. Krüger, *J. prakt. Chem.*, [2] **14**, 193 (1877).

[12] O. Masson, *J. Chem. Soc.*, 233 (1886).

[13] M. S. Platanov and S. B. Anisimov, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 622 (1935).

[14] F. E. Ray and I. Levine, *J. Org. Chem.*, **2**, 267 (1937).

[15] P. C. Ray, *J. Chem. Soc.*, 603 (1916).

it is readily apparent then, that preparation of all but the simplest of sulfonium salts is very difficult.

Contrarily, double salts of the sulfonium halides and mercuric halides form with extraordinary speed and facility. Smiles[16] found the reaction at room temperature of ethyl iodide and methyl sulfide to be incomplete at the end of 3 days. Addition of mercuric iodide caused the reaction to be quantitatively complete in 15 min. In addition, they noted that the time element involved in rearrangement of the double salts was such as to allow preparation of mixed alkyl radical sulfonium halide–mercuric halide compounds.

There is still a lack of knowledge as to why the sulfonium halide-mercuric halides are formed with such ease. That they are ionic is shown by conductivity measurements, boiling point elevations, and parachor measurements. Cavell and Sugden[17] state that the structure $[R_3S]^+[HgI_3]^-$ is the most probable in view of the fact that silver iodide is readily soluble in the sulfonium iodides, probably with the formation of the more stable $[HgI_4]^=$ ion. Their statement that the sulfur is quadrivalent is borne out by the experiments of Ray and Adhikary.[18]

The ease of formation of a sulfonium bromide–mercuric bromide double salt is probably due to the abstraction by the mercuric bromide of the alkyl bromide bromine atom to form the $HgBr_3^-$ ion. The alkyl carbonium ion thereby formed is likely to attack an electron pair of the sulfur of the thioether. The reaction would be reversible only to the extent of the dissociation of the $HgBr_3^-$ ion to reform free bromide ion and mercuric bromide. The work of Cavell and Sugden[17] supports this hypothesis. That the $HgBr_3^-$ ion does dissociate is shown by the work of Smiles.

Attempts have been made in this laboratory to prepare unsaturated sulfonium halides preparatory to polymerizing them to form sulfonium ion exchange resins. That such attempts were unsuccessful is understandable in view of the failures of other workers to prepare even the simpler saturated sulfonium halides, probably because of the failure of the reaction, rearrangement of the groups present in the intermediate, or transalkylation by the solvent.

The attempts were carried out in sealed thick-wall glass tubes, both with and without solvents. Temperatures varying from 100° to 300° were used. The one case in which a reaction occurred was unsuccessful in that trimethyl sulfonium iodide was obtained and not the desired product.

Because of the instability of the triallyl sulfonium halide–mercuric halide double salts,[3] it was decided to prepare unsaturated sulfonium halide–mercuric halide double salts with the double bonds farther removed from the sulfur atom, in an attempt to correlate this distance with the instability of the salt. It was thought that a greater distance between the double bond and the sulfur atom would effect a behavior more nearly similar to the saturated analogs of the unsaturated salts chosen. For this reason, the mercuric chlorides, bromides, and iodides of the tris(3-butenyl), tris(4-pentenyl), and tris(5-hexenyl) sulfonium bromides were prepared.

Strömholm[19] was able to prepare sulfonium chloride–mercuric chloride double salts in which the ratios of sulfonium chloride to mercuric chloride were 2:1, 1:1, 1:2, 1:3, and 1:6, by varying the proportions of sulfonium chloride to mercuric chloride and by using different solvents. He states that the 1:1 ratio double salt is always obtained when the reaction is run in ether, and, further, that repeated ether washings of the higher salts (higher ratio of mercuric chloride to sulfonium chloride) remove mercuric chloride with the ultimate production of a 1:1 double salt. Smiles[20] found that the reaction to form dimethylethylsulfonium iodide–mercuric iodide was essentially complete in 2 min.; whereas 3 days were necessary to effect an incomplete reaction between dimethyl sulfide and ethyl iodide to give a highly impure product. His observation[21] that rearrangement occurs in the double salts is rendered unimportant by the fact that only tris-sulfonium halide–mercuric halide double salts were prepared in the present study.

Numerous other references to the preparation of sulfonium halide double salts using, to replace the mercuric halides, the halides[22] (to give polyhalides), antimony halides,[23] and the haloforms[24,2] are found in the literature. It is not clear what type of bonding is generally present, though if, as Cavell and Sugden[17] believe, the salts–mercuric halide salts are in the form $[R_3S]^+[HgI_3]^-$, it would seem possible to exchange the HgI_3^- ion for some other ion by passing a solution of the salt over the proper ion exchange resin, and thus indirectly arrive at the desired unsaturated sulfonium salt.

References to purification of the double salts[3,25] generally apply only to definite liquids or solids, not to exceedingly viscous oils. The solids need only be recrystallized from the proper solvent, while the liquids can be washed free of impurities, the reactants being quite soluble in ether. Attempts to purify the sulfonium halide–mercuric halide double

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[16] T. P. Hilditch and S. Smiles, *J. Chem. Soc.*, 1394 (1907).

[17] H. J. Cavell and S. Sugden, *J. Chem. Soc.*, 2572 (1930).

[18] P. C. Ray and N. Adhikary, *J. Indian Chem. Soc.*, 1, 297 (1930).

[19] D. Strömholm, *Ber.*, **32**, 2892 (1899).

[20] S. Smiles, *J. Chem. Soc.*, **87**, 450 (1905).

[21] S. Smiles and T. P. Hilditch, *J. Chem. Soc.*, 519 (1907).

[22] F. Dehn, *Ann.*, **4**, 83 (1865-66).

[23] P. C. Ray, N. Adhikary, and A. N. Ray, *J. Indian Chem. Soc.*, **8**, 251 (1931).

[24] W. Steinkopf and S. Müller, *Ber.*, **56**, 1926 (1923).

[25] D. Strömholm, *J. Chem. Soc.*, 138 (1903).

salts prepared below by 25 washings of each salt with 20-ml. portions of dry ether failed completely. It was finally decided to dissolve the oils in some solvent, then to precipitate them by the addition of dry ether. Solvents tried were *n*-hexane, methyl isobutyl ketone, diisobutyl ketone, acetone, diethyl ketone, methyl ethyl ketone, methyl isopropyl ketone, diisopropyl ketone, *n*-butyl ethyl ketone, methyl *n*-amyl ketone, dioxane, and dibenzyl ketone. Diisopropyl ketone was used for five of the eight double salts; solvents (which would give up the salts upon addition of dry ethyl ether) were not found for the other three. For those salts insoluble in diisopropyl ketone, another procedure was adopted. They were alternately washed with ether, and heated on a steam bath.

The effect of moving the double bond farther from the sulfur atom appears to have a stabilizing influence on the molecule. The severe treatment (heating them to 100° in purification attempts) did not decompose the salts for which solvents were not found, in sharp contrast to the salts of Butler and Benjamin,[2] which salts were unstable at room temperature.

As intermediates, 3-buten-1-ol, 4-penten-1-ol, 5-hexen-1-ol, the corresponding bromides, and the corresponding sulfides were prepared. The 3-buten-1-ol was made by the method of Pariselle,[26] as modified by Linstead and Rydon.[27] The 4-penten-1-ol and 5-hexen-1-ol were made[28] from tetrahydrofurfuryl alcohol and tetrahydro-pyran-2-methanol, respectively. The bromides were made by the addition of phosphorus tribromide to the respective alcohols.[29] The sulfides were made by the addition of a water solution of reagent grade sodium sulfide to the bromide, dissolved in alcohol.[30] Preparation of the sulfonium halide–mercuric halide double salts followed the procedure of Butler and Benjamin.[3]

EXPERIMENTAL

3-Buten-1-ol. Allyl bromide was added dropwise to a mixture of dry ether, magnesium shavings, and dry trioxymethylene, according to the procedure of Pariselle,[26] as modified by Linstead and Rydon.[27] Considerable difficulty was experienced in drying the trioxymethylene. The course finally taken was to heat the required amounts of magnesium shavings and trioxymethylene in the reaction flask while vigorously stirring and passing in a slow stream of air previously passed through Drierite. B.p. 112–114°. Yield 24.6%; n_D^{25} 1.4199; reported n_D^{25} 1.4189.

4-Penten-1-ol. This alcohol was prepared from tetrahydrofurfuryl alcohol by the procedure of Brooks and Snyder.[28]

5-Hexen-1-ol. To 860 g. (7.5 moles) of tetrahydropyran-2-methanol and 652 g. (8.25 moles) of pyridine contained in a 3-liter, three-necked, standard-taper flask equipped with stirrer, reflux condenser, addition funnel, and thermometer, and cooled in an ice bath, was added 940 g. (7.90 moles) of thionyl chloride at a rate such as to keep the reaction temperature below 60°. When the addition was complete, the mixture was stirred 4 hr. without the ice bath. Sufficient water to dissolve the pyridine hydrochloride was added, after which the mixture was extracted with eight 500 ml. portions of ether. Distillation of the ether left a residue which was dried over anhydrous magnesium sulfate. Distillation at 22–23 mm. gave 435.5 g. (43.1% yield) of tetrahydropyran-2-methyl chloride.

The chloride, dissolved in 1.5 l. of dry ether, was then added dropwise to 181.2 g. (7.88 moles) of sodium, covered with 1.0 l. of dry ether, and contained in a 3-liter, three-neck, standard-taper flask equipped as above except that a calcium chloride drying tube was fitted into the condenser. Upon completion of the reaction, the mixture was stirred for an additional 2 hr. without the ice bath, decanted into 2 l. of ice water, separated, dried over anhydrous magnesium sulfate, and distilled. The yield of 5-hexen-1-ol was 191.0 g. (25.5% yield) of material boiling at 71–73° at a pressure of 21 mm., n_D^{25} 1.4360.

Anal. Calcd. for $C_6H_{12}O$: C, 71.92; H, 11.07. Found: C, 72.01; H, 11.43.

1-Bromo-3-butene. To 70.8 g. (0.982 mole) of 3-buten-1-ol contained in a three-neck, 300-ml., standard-taper flask equipped with stirrer, addition funnel, thermometer, and reflux condenser and cooled in an ice-salt mixture, was added dropwise to 89.1 g. (0.330 mole) of phosphorus tribromide at such a rate as not to allow the reaction temperature to exceed 0°. Addition complete, the mixture was stirred and allowed to reach 20° over a period of 2 hr., left to stand overnight, and steam distilled. The lower layer of the distillate was separated, washed with 10% sodium carbonate solution, dried over Drierite, and fractionally distilled, yielding 42.5 g. (32.1%) of the product, boiling at 96–98° and having a refractive index, n_D^{25} 1.4595. The reported boiling point is 98.5–99° at 758 mm., the refractive index n_D^{20} 1.4621.[31]

1-Bromopentene-4. The bromination of 4-penten-1-ol was carried out in an exactly similar manner to that of 3-buten-1-ol. To 86.2 g. (1.0 mole) of 4-penten-1-ol was added 99.1 g. (0.336 mole) of phosphorus tribromide, giving, after final purification, 47.2 g. (31.6% yield) of 1-bromopentene-4, having a boiling point range of 51–53° at 52–53 mm. and a refractive index n_D^{25} 1.4651. Kharasch and Fuchs[32] state that the boiling point is 125–126°, the refractive index n_D^{20} 1.4632.

1-Bromohexane-5. Bromination of 247 g. (2.47 moles) 5-hexen-1-ol with 270.8 g. (1.0 mole) of phosphorus tribromide in the above manner gave 151.1 g. (37.5% yield) of the bromide boiling at 76–78° at a pressure of 4–5 mm., and having a refractive index of n_D^{25} 1.4630.

Anal. Calcd. for $C_6H_{11}Br$: C, 44.18; H, 6.80; Br, 49.00. Found: C, 44.31; H, 7.10; Br, 48.38.

Bis(3-butenyl) sulfide. To 10.0 g. (0.074 mole) of 1-bromo-3-butene dissolved in 30 ml. of 95% ethanol contained in a 300-ml. three-neck flask equipped with stirrer, addition funnel, and reflux condenser, and heated on a steam bath was added dropwise 8.9 g. (0.037 mole) of sodium sulfide nonahydrate. Stirring, while at reflux, was continued for 8 hr. after addition. When the refluxing was completed, the mixture was added to 50 ml. of 25% sodium chloride solution, the upper, oily layer separated and dried over Drierite, and five 20-ml. extracts of the sodium chloride solution with *n*-hexane were added. The hexane solution of the sulfide, after overnight drying, was distilled at atmospheric pressure until the pot temperature read 180°, at which point distillation was continued at 17 mm., giving 2.32 g. (43.3%

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(26) H. Pariselle, *Ann. Chim.*, **24,** 318 (1911).

(27) R. P. Linstead and H. M. Rydon, *J. Chem. Soc.*, 1998 (1934).

(28) L. A. Brooks and H. R. Snyder, *Org. Syntheses*, **25,** 84 (1945).

(29) D. A. Shirley, *Preparation of Organic Intermediates*, John Wiley & Sons Inc., New York, 1951, p. 94.

(30) Ref. 29, p. 32.

(31) A. Juvala, *Ber.*, **63,** 1992 (1930).

(32) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9,** 368–70 (1944).

yield) of material boiling at 78–80°, and having a refractive index, n_D^{25} 1.4825.

Anal. Calcd. for $C_8H_{14}S$: C, 67.57; H, 9.92. Found: C, 67.65; H, 10.03.

Bis(4-pentenyl) sulfide. Preparation of the sulfide in the above manner from 78.4 g. (0.526 mole) of the bromide, 150 ml. of 95% ethyl alcohol, 125 ml. of water, and 65.5 g. (0.273 mole) of sodium sulfide nonahydrate gave 19.8 g. (22.1% yield) of the product, boiling at 100–102° at 11–12 mm. pressure, and having a refractive index, n_D^{25} 1.4806.

Anal. Calcd. for $C_{10}H_{18}S$: C, 70.52; H, 10.65; S, 18.83. Found: C, 69.79; H, 10.32; S, 19.21.

Bis(5-hexenyl) sulfide. Preparation of the sulfide in the above manner from 50 g. (0.307 mole) of 1-bromo-5-hexene, 100 ml. of 95% ethanol, 37.2 g. (0.155 mole) of sodium sulfide nonahydrate, and 42 ml. of water gave 20.12 g. (66.0% yield) of the sulfide, boiling at 98–100.5°, at 4–5 mm. pressure and having a refractive index n_D^{25} 1.4782.

Anal. Calcd. for $C_{12}H_{22}S$: C, 72.63; H, 11.18; S, 16.16. Found: C, 72.88; H, 11.25; S, 15.71.

Attempted preparation of tris(3-butenyl)sulfonium bromide. In a heavy-walled glass tube were sealed 0.945 g. (0.007 mole) of 1-bromo-3-butene, and 0.994 g. (0.007 mole) of bis(3-butenyl) sulfide. The tube was enclosed in a heavy wire mesh in order to minimize the effects of a chance explosion and heated to 100° for 24 hr. Upon cooling the tube in an ice-salt bath there was no precipitation. After 24 hr. exposure at 200° no apparent reaction had occurred. To make certain that no reaction had occurred, the tube was immersed in a Dry Ice–acetone mixture and opened. Addition of ether did not cause precipitation.

Attempted preparation of tris(4-pentenyl)sulfonium bromide. In a heavy-walled glass tube were sealed 1.49 g. (0.01 mole) of 1-bromopentene-4 and 1.70 g. (0.01 mole) of bis(4-pentenyl) sulfide. After 48 hr. at 100° no precipitation was apparent upon placing the tube in an ice-salt bath. The tube was then heated at 200° for 48 hr. and was placed in a Dry Ice-acetone mixture before opening; addition of ether to the contents did not cause any precipitation.

Attempted preparation of bis(4-pentenyl)methylsulfonium iodide. In a heavy-walled glass tube was sealed 1.70 g. (0.01 mole) of bis(4-pentenyl) sulfide, methyl iodide, and 1.00 g. (0.01 mole) of 5-hexen-1-ol. The tube was heated at 100° for 48 hr., cooled in a Dry Ice–acetone bath, opened, and dry ether was added. The precipitate which formed was recrystallized from acetone. The crystals melted at 202–204°, the melting point of trimethyl sulfonium iodide.

Attempted preparation of tris(5-hexenyl)sulfonium bromide. In a heavy-walled glass tube was sealed 1.98 g. (0.01 mole) of bis(5-hexenyl) sulfide and 1.63 g. (0.01 mole) of 1-bromohexene-5. The tube was heated for 12 hr. at 300°. After cooling in a Dry Ice–acetone mixture, the tube was opened and dry ether added. No precipitation was apparent; the contents did not appear to be decomposed by the treatment.

Preparation of the double salts of tris(3-butenyl)sulfonium bromide with mercuric chloride, mercuric bromide, and mercuric iodide. To each of three 20 × 150 mm. test tubes were added 0.945 g. (0.007 mole) of 1-bromo-3-butene, 0.994 g. (0.007 mole) of bis(3-butenyl) sulfide, and 20 ml. of acetone. To the first tube was added 1.90 g. (0.007 mole) of mercuric chloride, to the second 2.52 g. (0.007 mole) of mercuric bromide, and to the third 3.18 g. (0.007 mole) of mercuric iodide. Because the mercuric iodide would not dissolve in the case of the third reaction, gentle reflux was maintained for 1 hr. in an effort to force solution. (It was necessary to decant the liquid from the undissolved mercuric iodide into another test tube before evaporation.) Subsequently, the acetone was evaporated from the tubes in a vacuum desiccator and the contents washed with ether. No product was obtained from the tube containing mercuric iodide. Attempts to find solvents for the reactions involving mercuric chloride and mercuric bromide failed; it was therefore necessary to adopt the method outlined in the general procedure. Each salt was alternately melted on the steam bath and washed ten times with dry ether. The two salts were obtained finally in the form of grey gums.

Anal. Calcd. for $C_{12}H_{21}SBr.3HgCl_2$: C, 13.22; H, 1.94. Found: C, 12.72; H, 2.00. Calcd. for $C_{12}H_{21}SBr.2HgBr_2$: C, 14.40; H, 2.12. Found: C, 13.50; H, 2.18.

Preparation of the double salts of tris(4-pentenyl)sulfonium bromide with mercuric chloride, mercuric bromide, and mercuric iodide. To each of three 20 × 150 mm. test tubes were added 1.49 g. (0.01 mole) of 1-bromo-4-pentene, 1.70 g. (0.01 mole) of bis(4-pentenyl) sulfide, and 20 ml. of acetone. To the first tube was added 2.71 g. (0.01 mole) of mercuric chloride, to the second 3.60 g. (0.01 mole) of mercuric bromide, and to the third, 4.54 g. (0.01 mole) of mercuric iodide. Again, the tube containing iodide was gently refluxed for 1 hr. in an attempt to force the reaction, and decanted into another test tube before evaporation. Subsequently, the acetone was evaporated from the tubes in a vacuum desiccator and the contents washed with ether. The contents of the tube to which the mercuric chloride had been added were ether insoluble in the solvents tried, or too soluble, so as to be difficult to precipitate out. Therefore, they were melted and washed with dry ether alternately ten times. The effect of the attempted purification is shown in the analyses. The contents of the tubes containing the mercuric bromide and the mercuric iodide were soluble in isopropyl ketone and were therefore dissolved in the minimum amount thereof and precipitated with dry ether. This was repeated five times. The mercuric chloride double salt was a very viscous, yellow oil, the mercuric bromide double salt a dark red oil, and the mercuric iodide double salt an orange oil.

Anal. Calcd. for $C_{15}H_{27}SBr.3HgCl_2$: C, 16.77; H, 2.38. Found: C, 16.73; H, 2.72. Calcd. for $C_{15}H_{27}SBr.HgBr_2$: C, 26.50; H, 4.00. Found: C, 25.85; H, 4.17. Calcd. for $C_{15}H_{27}SBr.HgI_2$: C, 23.28; H, 3.52. Found: C, 23.30; H, 3.51.

Preparation of the double salts of tris(5-hexenyl)sulfonium bromide and mercuric chloride, mercuric bromide, and mercuric iodide. To each of three test tubes was added 1.63 g. (0.01 mole) of 1-bromo-5-hexene, 1.98 g. (0.01 mole) of bis(5-hexenyl) sulfide, and 20 ml. of acetone. To the first tube was added 2.71 g. (0.01 mole) of mercuric chloride, to the second 3.60 g. (0.01 mole) of mercuric bromide, and to the third 4.54 g. (0.01 mole) of mercuric iodide. Reflux of the tube containing mercuric iodide was again carried out for 1 hr. After decanting the liquid from the mercuric iodide into another test tube, evaporation of the acetone was carried out in a vacuum desiccator. When evaporation was complete, the contents of the tubes were washed with ether and purified by alternately dissolving the contents in diisopropyl ketone and precipitating with dry ether. This cycle was repeated five times. As finally purified, both the mercuric chloride and the mercuric bromide double salts were light brown in color; the mercuric iodide double salt was pale yellow.

Anal. Calcd. for $C_{18}H_{33}SBr.HgCl_2$: C, 34.15; H, 5.26. Found: C, 34.70; H, 5.22. Calcd. for $C_{18}H_{33}SBr.HgBr_2$: C, 29.95; H, 4.61. Found: C, 29.65; H, 4.79. Calcd. for $C_{18}H_{33}SBr.HgI_2$: C, 26.50; H, 4.08. Found: C, 26.30; H, 4.15.

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