Substituent Effects of Positive Poles in Aromatic Substitution. III. The Chlorination and Bromination of Sulfonium and Selenonium Salts[1a,b]

H. M. GILOW, R. BRADFORD CAMP, JR., AND ERNEST C. CLIFTON[1c]

Department of Chemistry, Southwestern at Memphis, Memphis, Tennessee 38112

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Chlorination and bromination of dimethylphenylsulfonium and selenonium methyl sulfate in the presence of silver ion are reported. The *meta/para* ratio for chlorination, bromination, and nitration are similar. However, the *ortho/para* ratio for bromination and chlorination is higher than for nitration.

Halogenation of unreactive aromatic rings can be accomplished at high temperatures. The high temperature not only makes rearrangements more likely but also apparently favors a free radical rather than an ionic mechanism.[2] Pearson and co-workers have developed a method in which 1 equiv of a strong electrophilic reagent, such as aluminum chloride, is used to complex the substrate and 1 more equiv is used to generate an active attacking species of reagent. This method has been termed the swamping catalyst effect and has been used to effect electrophilic substitution of unreactive systems.[3-5]

Iodination in organic solvents can be accomplished using silver perchlorate as a catalyst.[6,7] Substances that are difficult to halogenate under normal conditions are easily substituted by a solution containing the halogen and silver sulfate in concentrated sulfuric acid. This method of bromination and iodination was introduced by Derbyshire and Waters[8] and for chlorination by Gorvin.[9] Numerous types of unreactive benzene derivatives[10,11] as well as heterocyclic systems have heen halogenated.[12] The exact structure of the electrophilic halogenating species is not known.[13]

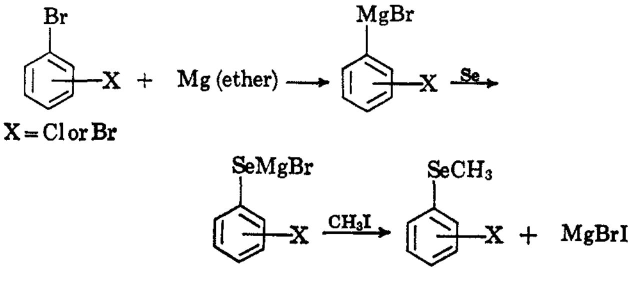
Recent investigations[1b,14] of electrophilic aromatic nitration of sulfonium and selenonium salts have shown orientations somewhat different from those previously reported.[15] For this reason it was of interest to investigate these unreactive aromatics toward bromination and chlorination reactions in the presence of silver ions.

Results and Discussion

The orientation results of chlorination and bromination of dimethylphenylsulfonium methyl sulfate (1) and dimethylphenylselenonium methyl sulfate (2) with and without a silver ion catalyst as well as the bromination of methyl phenyl sulfide are given in Table I.

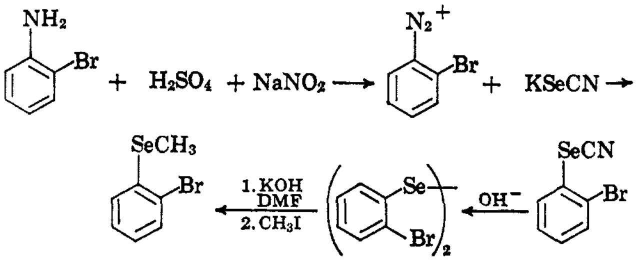
Bromination and chlorination of 1 and 2 take place rapidly at room temperature in the presence of silver ion. In concentrated sulfuric acid, using a silver sulfate catalyst, the progress of the reaction can be observed by the formation of the silver halide precipitate. This is not as obvious in the case of silver trifluoroacetate in trifluoroacetic acid since a silver halide precipitate is formed without aromatic substitution and hence an excess of silver trifluoroacetate was necessary in this case. The reactions were run to approximately 50% completion in order to prevent extensive disubstitution. Isomer distributions were nearly the same up to 90% completion.

Analysis of the reaction mixture from the halogenation reaction was similar to the method used to analyze the nitration reaction mixtures described earlier.[1b] Each individual halophenyl methyl selenide was synthesized in good yield without isolation of any of the intermediates, with the exception of *o*-bromophenyl methyl selenide, according to the equation



Since the Grignard reagent of *o*-dibromobenzene cannot be formed, *o*-bromophenyl methyl selenide was prepared by the sequence of reactions given in Scheme I.

SCHEME I



The halophenyl methyl sulfides were prepared from the corresponding haloanilines by well-known procedures. Conversion of the sulfides and selenides into the sulfonium and selenonium salts was readily effected by heating with dimethyl sulfate.

Known mixtures of the halosulfonium and selenonium salts were treated in the same manner as the halo-

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[1] (a) A preliminary report on part of this work has been given at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., 1966, p A42; (b) for part II, see H. M. Gilow and G. L. Walker, *J. Org. Chem.*, **32**, 2580 (1967); (c) National Science Foundation Undergraduate Research Participant.

[2] H. S. Mosher in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 504.

[3] D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, *J. Org. Chem.*, **23**, 1412 (1958).

[4] D. E. Pearson, W. W. Hargrove, J. K. T. Chow, and B. R. Suthers, *ibid.*, **26**, 789 (1961).

[5] M. Gordon and D. E. Pearson, *ibid.*, **29**, 329 (1964).

[6] L. Birckenback and J. Boubeau, *Ber.*, **65**, 395 (1932).

[7] L. Birckenback and J. Boubeau, *ibid.*, **66**, 1280 (1933).

[8] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573, 3694 (1950).

[9] J. H. Gorvin, *Chem. Ind.* (London), 910 (1951).

[10] J. H. Gorvin, *J. Chem. Soc.*, 1237 (1953).

[11] I. R. L. Barker and W. A. Waters, *ibid.*, 150 (1952).

[12] P. B. D. De La Mare, M. Kiamud-Din, and J. H. Ridd, *Chem. Ind.* (London), 361 (1958).

[13] E. Berliner, *J. Chem. Educ.*, **43**, No. 3, 124 (1966).

[14] H. M. Gilow and G. L. Walker, *Tetrahedron Letters*, No. 48, 4295 (1965).

[15] J. W. Baker and W. G. Moffitt, *J. Chem. Soc.*, 1722 (1930).

TABLE I

CHLORINATION AND BROMINATION OF AROMATIC SULFONIUM AND SELENONIUM SALTS

Compd	Reaction time,[a] min	Reagent	Catalyst	Solvent	*ortho*,[c] %	*meta*,[c] %	*para*,[c] %	Unsubstituted products,[b] %	Monosubstituted products,[b] %	Disubstituted products,[b] %
1	120	Cl_2	Ag_2SO_4	H_2SO_4	15.0 ± 0.3[d]	79.9 ± 0.4	5.1 ± 0.2	65	33	2
1	90	Cl_2	AgO_2CCF_3	CF_3CO_2H	18.3 ± 0.2	78.7 ± 0.2	3.0 ± 0.2	53	44	3
1	10	Br_2	Ag_2SO_4	H_2SO_4	4.9 ± 0.2	91.3 ± 0.4	3.7 ± 0.2	45	53	2
1	5	Br_2	AgO_2CCF_3	CF_3CO_2H	5.5 ± 0.2	91.2 ± 0.3	3.4 ± 0.2	38	59	3
1	180	Br_2	None	CH_3CO_2H	1	. . .	99	50	50	. . .
2	20	Cl_2	Ag_2SO_4	H_2SO_4	17.4 ± 0.2	74.9 ± 0.3	7.7 ± 0.2	52	43	5
2	20	Cl_2	AgO_2CCF_3	CF_3CO_2H	24.5 ± 0.2	71.1 ± 0.3	4.4 ± 0.2	61	37	2
2	10	Br_2	Ag_2SO_4	H_2SO_4	6.4 ± 0.2	88.1 ± 0.3	5.5 ± 0.1	50	48	2
2	0.75	Br_2	AgO_2CCF_3	CF_3CO_2H	6.4 ± 0.3	89.3 ± 0.3	4.2 ± 0.2	53	45	2
2	180	Br_2	None	CH_3CO_2H	9.4 ± 0.3	. . .	90.6 ± 0.6	48	27	25
$C_6H_5SCH_3$	15	Br_2	None	CH_3CO_2H	2.4 ± 0.1	. . .	97.6 ± 0.1	20	80	. . .
$C_6H_5SCH_3$	15	Br_2	None	CF_3CO_2H	8.0 ± 0.2	. . .	92.0 ± 0.2	35	65	. . .
$C_6H_5SCH_3$	15	Br_2	None	CS_2	<1	. . .	>99	. . .	100	. . .

[a] All reactions were run at room temperature except the bromination of **1** and **2** without a catalyst in acetic acid which was run at the temperature of a hot water bath and the bromination of $C_6H_5SCH_3$ in CS_2 which was run at reflux temperature of CS_2. [b] These are approximate values. [c] Each value is an average of three different reactions. Each reaction mixture was analyzed five times by gas chromatography. [d] Standard deviation.

genation mixtures of **1** and **2**. Good agreement was obtained from the gas chromatographic analysis and the actual values.

Each individual halodimethylphenyl sulfonium or selenonium methyl sulfate was treated in a manner identical with conditions for halogenation. Gas chromatographic analysis of the reaction mixtures indicated that there was no rearrangement under the conditions of the reaction and work-up. The disubstituted products could not be distinguished gas chromatographically with the column used, but did not interfere with the monosubstituted products.

The sulfonium salt **1** or selenonium salt **2** and silver sulfate were dissolved in concentrated sulfuric acid and diluted with methanol. The appropriate halogen was then added to the methanol solution and treated with sodium methoxide in the normal fashion. Gas chromatographic analysis indicated only methyl phenyl sulfide or methyl phenyl selenide. This indicated that there was no substitution occurring during the work-up of the reaction mixture.

It is relatively certain that the halogenation of **1** and **2** in the presence of silver ion is actually taking place with the sulfonium and selenonium salt and not the sulfide or selenide. The strongly electron-withdrawing groups direct mainly *meta* whereas bromination of methyl phenyl sulfide does not result in *meta* substitution. In all cases of silver ion catalyzed halogenation of **1** and **2** a higher percentage of the *ortho* isomer, as compared with *para*, is formed than in the bromination of methyl phenyl sulfide. Under the conditions of the reaction the chlorination of methyl phenyl sulfide does not result in aromatic substitution and both the bromination and chlorination of methyl phenyl selenide result in the addition of the halide to selenium. Hence it is clear that the sulfonium and selenonium salts are actually undergoing the electrophilic aromatic substitution. The orientation results obtained in the nitration of **1** and **2** have been discussed previously.[1b] Halogenation in the presence of silver ion is also thought to be electrophilic and hence the electronic effects of the aromatic ring should be similar. This is evidenced by the *meta/para* ratios which are roughly similar for the different reactions given in Table II.[16] The *ortho/para* ratios for bromination and chlorination are considerably higher than for nitration and in a number of cases even higher than the statistical factor of 2. This is somewhat surprising since nitration,[17,18] chlorination, and bromination[10] of anilinium salts do not give any *ortho* substitution products. The high *ortho/para* ratios for bromination and chlorination of **1** and **2** must be due to an additional factor which is not present in electrophilic nitration of aromatics containing positive poles or halogenation of anilinium ion in the presence of silver ion.

TABLE II

ortho/para AND *meta/para* RATIOS FOR ELECTROPHILIC AROMATIC SUBSTITUTION OF SULFONIUM AND SELENONIUM SALTS

Compd	Reaction	Catalyst	Ratio, *ortho/para*	Ratio, *meta/para*
1	Nitration[a]	H_2SO_4	0.6	15
1	Chlorination	Ag_2SO_4	2.9	16
1	Chlorination	AgO_2CCF_3	6.1	26
1	Bromination	Ag_2SO_4	1.3	25
1	Bromination	AgO_2CCF_3	1.6	27
2	Nitration[a]	H_2SO_4	0.4	15
2	Chlorination	Ag_2SO_4	2.3	9.7
2	Chlorination	AgO_2CCF_3	5.6	16
2	Bromination	Ag_2SO_4	1.2	16
2	Bromination	AgO_2CCF_3	1.5	21

[a] See ref 1b.

Although the silver ion is necessary for electrophilic halogenation of unreactive aromatics, the exact function of the silver ion is not known.[13] Arotsky and co-workers[19,20] have evidence for the formation of AgX_2^+ (X_2 = Cl_2, Br_2, and I_2) when the halide and silver sulfate are dissolved in concentrated sulfuric acid. This may be the active halogenating agent. There is

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(16) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam, The Netherlands, 1965, Chapter 11.

(17) M. Brickman and J. H. Ridd, *J. Chem. Soc.*, 6845 (1965).

(18) M. Brickman, J. H. P. Utley, and J. H. Ridd, *ibid.*, 6851 (1965).

(19) J. Arotsky and M. C. R. Symons, *Quart. Rev.* (London), **16**, 282 (1962).

(20) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 2582 (1962).

no evidence for a chloronium, bromonium, or iodonium ion under these conditions; however, it is possible that some other positive species, probably highly solvated, might be the reactive species. Since no appreciable silver halide forms until after the addition of the aromatic compound, it might be that as halogenation proceeds, a very unfavorable equilibrium, involving a positive halogen compound, is shifted to completion by precipitation of silver halide,[8] or that the silver salt functions only after the halogen and the aromatic compound have reacted to form an intermediate.

Even though the exact nature of the halogenating species is not known, it appears that some type of cyclic intermediate may exist which will aid in *ortho* substitution. It should be noted that the *ortho/para* ratio for chlorination is always larger than for a comparable bromination and the *ortho/para* ratio for halogenation of a sulfide is always larger than for a comparable halogenation of a selenide. This is no doubt due to steric factors. An alternate, or additional, explanation could involve the *ortho–meta* directing effect of the sulfonium and selenonium groups.[1b] The bromination and chlorination reactions, in the presence of silver ion, may be more selective toward *ortho* substitution than is nitration. Since the *meta/para* ratios differ by approximately a factor of 2 indicating similar electronic effects, and the *ortho/para* ratios by approximately a factor of 10, this explanation does not appear as satisfactory. Definite identification of the structure of the intermediate is not possible before the actual mechanism of the reaction is determined.

Bromination of methyl phenyl sulfide in carbon disulfide is a well-known reaction for the preparation of *p*-bromophenyl methyl sulfide.[21] Gas chromatographic analysis of the reaction mixture also indicated a small amount of *ortho* substitution but no *meta* substitution was observed. Similar results were obtained in acetic and trifluoroacetic acid except that in the more polar solvent, trifluoroacetic acid, more *ortho* substitution was observed. This could be the result of the more rapid reaction in trifluoroacetic acid being more nonselective but this is contrary to Brown and Wirkkala's[22] findings that the more rapid bromination of toluene in trifluoroacetic acid is also more selective toward the *para* product. Chlorination of methyl phenyl sulfide, under the same conditions as bromination, does not yield any of the corresponding chlorophenyl methyl sulfides but apparently caused oxidation or substitution in the methyl group. Bromination and chlorination of methyl phenyl selenide in acetic acid under the conditions of these reactions resulted in the formation of the dibromide or dichloride of methyl phenyl selenide and no aromatic substitution.

Bromination of **1** and **2** in actic acid without silver ion takes place very slowly but surprisingly does not result in *meta* substitution. Some *ortho* and mostly *para* substitution is observed. Appreciable bromination does not occur in concentrated sulfuric acid at 100° for 8 hr or refluxing trifluoroacetic acid.

Experimental Section[23]

Materials.—Dimethylphenylsulfonium methyl sulfate (**1**) and dimethylphenylselenonium methyl sulfate (**2**) were prepared and purified as previously described.[1b]

Halogenation of 1 and 2.—Sulfonium salt **1** (1 g, 0.004 M) and silver sulfate (0.4 g, 0.013 M) (Aldrich Chemical Co.) were dissolved in 5 ml of concentrated sulfuric acid (reagent grade, meets ACS specifications, sp gr 1.84, 95.5–96.5%). To this solution was added 0.55 g (0.0031 M) of bromine (J. T. Baker purified grade) and shaken for 10 min at room temperature and then analyzed. The reaction time was increased to 20, 30, and 40 min with no appreciable change in isomer distribution. Bromination of selenonium salt **2** was carried out in a similar manner except a shorter reaction time (Table I). Chlorination of **1** and **2** was also carried out in a similar manner except that chlorine gas (The Matheson Co.) was bubbled into the solution until it was saturated and then shaken in a glass-stoppered container until the reaction was complete.

Bromination in trifluoroacetic acid was accomplished by dissolving 1 g (0.004 M) of **1** and 2.5 g (0.011 M) of silver trifluoroacetate (Aldrich Chemical Co.) in 5 ml of trifluoroacetic acid ($n^{20}{}_{\mathrm{D}}$ 1.2800, Aldrich Chemical Co.). To this solution was added 1 g (0.0062 M) of bromine and it was then shaken for 5 min at room temperature and analyzed. Bromination of selenonium salt **2** was carried out in a similar manner as the chlorination of **1** and **2** except that chlorine was slowly bubbled into the reaction mixture during the entire reaction period.

Bromination of **1** and **2** in acetic acid was accomplished by dissolving 1 g of the salt in 5 ml of acetic acid and dropwise addition of bromine (2.5 g) to this solution over a period of 3 hr while heating on a hot water bath. The reaction mixture was then analyzed. Bromination of **1** was attempted by heating a concentrated sulfuric acid solution of **1** and bromine at 100° for 8 hr. Substitution of **2** was also attempted by refluxing a solution of trifluoroacetic acid, bromine, and **2** for 3 hr. In both cases only evidence for starting material could be obtained.

Halogenation of Methyl Phenyl Sulfide and Methyl Phenyl Selenide.—Methyl phenyl sulfide (1 g, 0.008 M) dissolved in 5 ml of trifluoroacetic acid and bromine (1.28 g, 0.011 M) dissolved in 5 ml of trifluoroacetic acid were combined and allowed to react at room temperature for 15 min and analyzed gas chromatographically. The bromination was also carried out in acetic acid using a similar procedure. Results are given in Table I. Attempted chlorination of methyl phenyl sulfide by slowly bubbling chlorine into an acetic acid solution of the sulfide did not result in the formation of *o*-, *m*-, or *p*-chlorophenyl methyl sulfide as evidenced by gas chromatographic analysis. The bromination and chlorination of methyl phenyl selenide in a similar manner resulted in the immediate formation of dibromomethyl phenyl selenide (mp 114–115°)[24] and dichloromethyl phenyl selenide (mp 132–133°),[25] respectively, but no substitution products.

Analysis of Reactions Mixtures.—The halogenation reaction mixtures were added to 200 ml of methanol and cooled to the temperature of Dry Ice in methanol. A concentrated solution of sodium methoxide in methanol ($\sim$10%) was added dropwise with stirring until the solution was basic to litmus paper. After the mixture came to room temperature, it was filtered, the filtrate evaporated to a small volume on a rotary evaporator, and analyzed gas chromatographically. An F & M Model 700 gas chromatograph was used with an 8-ft $^1/_8$-in. copper column. The column packing consisted of 5% Bentone 34 and 5% UCON 50HB 280X Polar on 60–80 mesh Chromosorb W (nonacid wash).

Synthesis of Halophenyl Methyl Selenides.—The procedure of Foster[26] was used to convert *o*-, *m*-, and *p*-bromochlorobenzene and *m*- and *p*-dibromobenzene into the corresponding *o*-, *m*-, and *p*-chlorobenzeneselenol and *m*- and *p*-bromobenzeneselenol by way of a Grignard reagent and selenium powder. Instead of isolating the selenol as in Foster's procedure, an equivalent amount of methyl iodide was added dropwise to the reaction mixture and hence the halophenyl methyl selenide was isolated. The halophenyl methyl selenides were obtained in yields of 45–55%. *o*-Bromophenyl selenocyanate was synthesized according

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[21] M. P. Balfe, R. E. Dabby, and J. Kenyon, *J. Chem. Soc.*, 382 (1951).

[22] H. C. Brown and R. A. Wirkkala, *J. Am. Chem. Soc.*, **88**, 1447 (1966).

[23] All melting points are uncorrected. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

[24] D. G. Foster and S. F. Brown, *ibid.*, **50**, 1182 (1928).

[25] O. J. K. Edwards, W. R. Gaythwaite, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 2293 (1928).

[26] D. G. Foster, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 771.

TABLE III

HALOPHENYL METHYL SULFIDES AND SELENIDES

Ether	Bp (mm) or mp, °C
o-Chlorophenyl methyl sulfide	99–100 (3.5)[a]
m-Chlorophenyl methyl sulfide	82–83 (2.5)[a]
p-Chlorophenyl methyl sulfide	74–76 (1)[a]
o-Bromophenyl methyl sulfide	73–74 (1.25)[b]
m-Bromophenyl methyl sulfide	78–79 (1.5)[c]
p-Bromophenyl methyl sulfide	36–37[d]
o-Chlorophenyl methyl selenide	72–73 (1.25)[e]
m-Chlorophenyl methyl selenide	80–81 (1.5)[e]
p-Chlorophenyl methyl selenide	99–100 (4.5) 25–26[f]
o-Bromophenyl methyl selenide	111–112 (3.5)
m-Bromophenyl methyl selenide	88–89 (1.75)
p-Bromophenyl methyl selenide	46–47[g]

[a] R. S. Hoshi, V. R. Dani, S. N. Kulkarni, and K. S. Nargund, *J. Karnatak Univ.*, **4**, 38 (1959); *Chem. Abstr.*, **55**, 27201 (1961). [b] G. M. Gasperini, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 3 (1960). [c] E. A. Nodiff, S. Lipschuts, P. N. Craig, and M. Gordon, *J. Org. Chem.*, **25**, 60 (1960). [d] See ref 16. [e] See ref 28. Crystallized from methanol. [f] Crystallized from methanol. [g] Crystallized from low-boiling petroleum ether.

to the procedure of Challenger, Peters, and Halevy[27] (mp 55–56°, crystallized from low-boiling petroleum ether). The crude selenocyanate was converted into the diselenide by treatment with base in a 44% yield based on *o*-bromoaniline, mp 95–96°, crystallized from isopropyl alcohol.[28] The procedure of Parker and Brody[29] was followed to convert the diselenide into *o*-bromophenyl methyl selenide, 53% yield. The boiling points of the selenides are given in Table III.

Synthesis of Halophenyl Methyl Sulfides.—*o*- and *m*-bromo- and *o*-, *m*-, and *p*-chloroaniline (Aldrich Chemical Co.) were diazotized[30] and then treated with potassium ethyl xanthate followed by hydrolysis[31] yielding the corresponding halothiophenols. The crude halothiophenols were alkylated with dimethyl sulfate using the procedure of Gilman and Martin.[32] *p*-Bromophenyl methyl sulfide was prepared by the bromination of methyl phenyl sulfide in carbon disulfide according to the procedure of Balfe, Dabby, and Kenyon.[21] Boiling and melting points of the halophenyl methyl sulfides are given in Table III.

Synthesis of Halodimethylphenylsulfonium and Selenonium Methyl Sulfates.—*o*-Bromophenyl methyl sulfide (5 g, 0.021 *M*) and 3.1 g of dimethyl sulfate (0.024 *M*) were heated in an oil bath at 95° for 2 hr. The reaction mixture crystallized on cooling, was ground in a mortar and pestle under acetone, and filtered. The crude product was crystallized from isopropyl alcohol. *m*- and *p*-Bromophenyl as well as *o*-, *m*-, and *p*-chlorophenyl methyl sulfide were converted into the corresponding sulfonium salts in a similar manner. *o*-, *m*-, and *p*-bromophenyl and *o*-, *m*-, and *p*-chlorophenyl methyl selenide were similarly converted into the corresponding selenonium salt except that a temperature of 70° and a reaction time of 1 hr was used. Analytical data for these salts are given in Table IV.

TABLE IV

SULFONIUM AND SELENONIUM SALTS

Compound[a]	Registry no.	Formula	Mp,[b] °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
o-$BrC_6H_4S(CH_3)_2^+$	14734-48-6	$C_9H_{13}O_4S_2Br$	110–111	90	32.83	3.98	32.66	3.86
m-$BrC_6H_4S(CH_3)_2^+$	14734-49-7	$C_9H_{13}O_4S_2Br$	115–116	86	32.83	3.98	32.76	3.99
p-$BrC_6H_4S(CH_3)_2^+$	14746-20-4	$C_9H_{13}O_4S_2Br$	137–138	83	32.83	3.98	32.93	3.91
o-$ClC_6H_4S(CH_3)_2^+$	14746-21-5	$C_9H_{13}O_4S_2Cl$	92–93	83	37.96	4.60	38.12	4.59
m-$ClC_6H_4S(CH_3)_2^+$	14734-50-0	$C_9H_{13}O_4S_2Cl$	103–104	81	37.97	4.60	38.10	4.61
p-$ClC_6H_4S(CH_3)_2^+$	14734-51-1	$C_9H_{13}O_4S_2Cl$	127–128	95	37.96	4.60	38.09	4.52
o-$BrC_6H_4Se(CH_3)_2^+$	14746-22-6	$C_9H_{13}O_4SSeBr$	105–106	88	28.74	3.48	28.58	3.60
m-$BrC_6H_4Se(CH_3)_2^+$	14746-23-7	$C_9H_{13}O_4SSeBr$	102–103	70	28.74	3.48	28.91	3.61
p-$BrC_6H_4Se(CH_3)_2^+$	14746-24-8	$C_9H_{13}O_4SSeBr$	150–153	78	28.74	3.48	28.59	3.42
o-$ClC_6H_4Se(CH_3)_2^+$	14746-18-0	$C_9H_{13}O_4SSeCl$	88–89	91	32.58	3.59	32.70	3.91
m-$ClC_6H_4Se(CH_3)_2^+$	14746-19-1	$C_9H_{13}O_4SSeCl$	73–74	60	32.58	3.59	32.74	4.00
p-$ClC_6H_4Se(CH_3)_2^+$	14734-45-3	$C_9H_{13}O_4SSeCl$	137–138	91	32.58	3.59	32.60	3.91

[a] All compounds are methyl sulfate salts ($CH_3SO_4^-$). [b] All salts were crystallized from isopropyl alcohol.

Registry No.—**1**, 6203-16-3; **2**, 13118-29-1; $C_6H_5SCH_3$, 100-68-5.

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(27) F. Challenger, A. T. Peters, and J. Halevy, *J. Chem. Soc.*, 1648 (1926).

(28) N. Marziano and R. Passerini, *Gazz. Chim. Ital.*, **94** (11), 1137 (1964).

(29) A. J. Parker and D. Brody, *J. Chem. Soc.*, 4067 (1963).

(30) P. F. Wiley, *J. Org. Chem.*, **16**, 810 (1951).

(31) G. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 6019 (1953).