poses equals the limiting conductance at zero field strength. It will be seen that a marked Wien effect is present; at only 10 kv./cm., the conductance is increased by 13%. For comparison, the lower curve is for 0.0001 molar magnesium sulfate[6] in water; this is a salt which is considered to have a fairly large Wien effect. By way of further contrast, the upper curve is for tribenzylammonium picrate[7] in toluene at 35°. We see that the polyelectrolyte in water gives about as large a Wien effect as does a 1-1 salt in a solvent whose dielectric constant is only 2.35. If we interpret our result as a second Wien effect in terms of Onsager's theory,[8] the polyelectrolyte is behaving approximately like a salt in which the cation has a charge of +33 (the ratio of the dielectric constants of water and toluene); in other words, the presence of about 1.7% of the counter ions in the peripheral zone mentioned above would be sufficient to account for our result.

The balance patterns (Fig. 2) observed on the oscilloscope for different pulse lengths are significant, if we consider the distances a bromide ion can travel during a pulse. At 10 kv./cm., a counter ion travels about 3000 Å. in 4 μsec. The balance patterns are tracings taken from the oscilloscope; a horizontal line coinciding with the center graticule marking is an indication of impedance balance. On the 11 μsec. tracing, balance was achieved after a preliminary excursion (*i.e.*, unbalance) lasting almost 5 μsec. On the shorter pulses balance was apparently not reached during the period of the pulse. Measurements taken with pulse lengths shorter than that necessary to give a steady state conductance value are accordingly only approximate estimates of the conductance. This behavior is, however, a clear indication of a time of relaxation effect in which the relaxation time is of the order of 1–5 microseconds. In such a time any free counter ions could travel several thousand Å. under the influence of a field of 10 kv./cm.

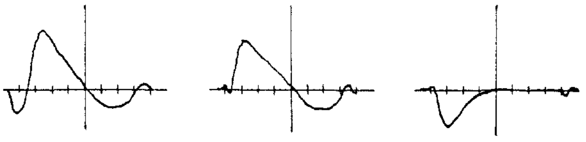
4 μsec. 6 μsec. 11 μsec.

Fig. 2.—Balance patterns.

In addition to this relaxation time phenomenon, it was noticed that the low field conductance of the solution was not regained instantaneously, as is usually the case with ordinary electrolytes. Figure 3 shows approximately the behavior observed. The low field conductance was regained slowly after the increase due to the high field, and then a decrease was observed, followed by a return to the normal low field conductance after a few minutes. This behavior was reproducible. On the other hand, two high field measurements made one immediately after the other were quite reproducible. The same phenomenon could be obtained with the application of a d.c. potential of 3 volts applied to the cell for a few seconds. In all cases the power dissipated in the cell was sufficient to raise the temperature of the electrolyte no more than 0.002°. The phenomenon of Fig. 3 is presumed to require more explanation than to ascribe it to electrode effects.

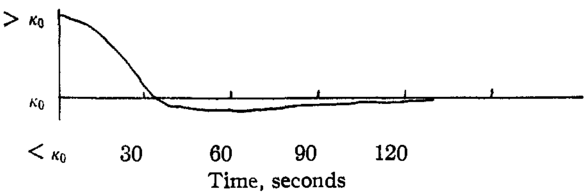

Fig. 3.—Time dependence of balance.

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Preparation and Properties of Some Unsaturated Sulfonium Salts[1]

By George B. Butler and Ben M. Benjamin

Ray and Levine[2] found that in the reaction between organic sulfides and alkyl halides, the sulfonium salt first formed can decompose in a variety of ways, the tendency being toward formation of the salt having the organic radicals of lowest molecular weight. The possibility exists that each alkyl radical may exist at some time as the alkyl halide. The final result is formation of the most stable product. These workers obtained trimethylsulfonium bromide by treating dimethyl sulfide with phenyl-2-fluorenylbromoethane and by treating phenyl-2-fluorenylmethylmethyl sulfide with methyl iodide, obtained trimethylsulfonium iodide.

In attempting to prepare unsaturated sulfonium halides, we have observed that when an alcohol is used as solvent, the alkyl radical of the alcohol may enter the sulfonium salt. Methanol[3] has been recommended as a suitable solvent for sulfonium salt formation. In attempting to prepare sulfonium halides of diallyl sulfide in methanol solution, only trimethylsulfonium halides were obtained. Methyl iodide, isopropyl iodide, phenacyl bromide and *p*-phenylphenacyl bromide were used as reactants. Diallyl-*p*-phenylphenacylsulfonium bromide has been reported[2]; however, in our attempts to prepare this compound, only trimethylsulfonium bromide was obtained. Dimethylallyl sulfide in methanol solution when treated with allyl iodide resulted in formation of trimethylsulfonium iodide. One previous unsuccessful attempt[4] to prepare triallylsulfonium salts has been reported, although allyldipropylsulfonium iodide was obtained. It has been stated[5] that dialkenyl sulfides, *e.g.*, diallyl sulfide, part with their sulfur when treated with excess of methyl iodide. In addition to diallyl-*p*-phenylphenacylsulfonium bromide[2] and allyldipropylsul-

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(6) M. Wien, *Ann. Physik*, **85**, 795 (1928); F. E. Bailey, unpublished results.

(7) R. M. Fuoss, D. Edelson and B. I. Spinrad, This Journal, **72**, 327 (1950).

(8) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(1) This work was done under the sponsorship of the Office of Naval Research under Contract No. N7 onr-346.

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

(3) R. W. Bost and H. C. Schultz, This Journal, **64**, 1165 (1942).

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

(5) P. D. Ritchie, "Chemistry of Plastics and High Polymers," Cleaver-Hume Press, Ltd., London, p. 186.

TABLE I

TRIALKYL SULFONIUM HALIDE MERCURIC HALIDE COMPLEXES

Compound	Formula	M.p., °C.	Analyses, % Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.	Decomposition upon standing at room temperature
Triallylsulfonium bromide mercuric iodide	$C_9H_{15}SBr \cdot HgI$	19–22	15.92	15.70	2.41	2.20	Slow but noticeable within an hour
Triallylsulfonium iodide mercuric iodide	$C_9H_{15}SI \cdot HgI_2$	64.5	14.85	14.67	2.23	2.05	None
Methyldiallylsulfonium iodide mercuric iodide	$C_7H_{13}SI \cdot HgI_2$	15–18	12.92	11.84	2.11	1.84	Noticeable within 15 hours
Triallylsulfonium iodide mercuric chloride	$C_9H_{15}SI \cdot HgCl_2$[a]	−47–−45	19.0	19.54	2.94	2.74	Starts immediately after isolation
Triallylsulfonium bromide mercuric chloride	$C_9H_{15}SBr \cdot HgCl_2$[b]	−46–−43	20.01	21.38	2.87	2.99	Noticeable within an hour
Ethylene-bis-(diallylsulfonium iodide) tetramercuric iodide	$C_{14}H_{24}S_2I_2 \cdot 4HgI_2$	84–84.7	7.26	7.23	1.28	1.04	Noticeable after two weeks
Ethylene-bis-(diallylsulfonium bromide) dimercuric iodide	$C_{14}H_{24}S_2Br_2 \cdot 2HgI_2$	25–28	12.79	12.71	1.94	1.83	Noticeable within an hour

[a] $n^{25}{}_D$ 1.6814; $d^{25}{}_4$ 2.4400. [b] $n^{25}{}_D$ 1.6382; $d^{25}{}_4$ 2.1849.

fonium iodide the only other unsaturated sulfonium salt located in the literature was acetylmethionineallylsulfonium bromide.[6] By treating diallyl sulfide with dimethyl sulfate in methanol solution, methyldiallylsulfonium methyl sulfate was obtained in this Laboratory.

Even though dialkyl sulfides and alkyl halides rarely are completely converted to sulfonium salts before the reaction reaches equilibrium,[7,8] in the presence of mercuric halides they combine more rapidly and completely.[9–11] These compounds retain the mercuric halide as part of the molecule. Even though unsaturated sulfides are very reluctant to form sulfonium salts, these compounds readily form sulfonium halide mercuric halide complexes. Even though these derivatives of saturated sulfides appear to be entirely stable, we have observed that in general, similar derivatives of the unsaturated sulfides decompose after standing for a short time. This decomposition appears to be accelerated by contact with light. For example, triallylsulfonium iodide mercuric chloride decomposes almost immediately after isolation to produce allyl chloride as one of the products. Other derivatives showed no signs of decomposition up to two weeks, while triallylsulfonium iodide mercuric iodide appears to be entirely stable.

When bis-(allylthio)-ethane was treated with allyl iodide and mercuric iodide, the product contained four mercuric iodide molecules. Substitution of allyl bromide in the above reaction resulted in the formation of a compound containing only two mercuric iodide molecules.

Some of the mercuric iodide complexes decomposed before they could be isolated. When diallyl sulfide, isopropyl iodide and mercuric iodide were mixed in acetone, the solution began to darken before all of the mercuric iodide dissolved. Only a black tarry mass could be isolated. The same was true when dimethallyl sulfide, methallyl chloride and mercuric iodide or chloride were mixed.

Experimental

Materials.—Diallyl sulfide was obtained from Eastman Kodak Company and used as received. Di-(2-methylallyl)-sulfide was prepared by the method described in the literature.[12] 2,4,6-Trithiane was prepared by the method o Chattaway and Kellett.[13] 2,4,6-Trimethyltrithiane was prepared by the method of Baumann and Fromm.[14] Ethylene mercaptan was prepared by the method of Meyer[15,16] and by reaction of ethylene bromide with potassium xanthate and basic hydrolysis of the product. The latter method gave better results.

1,2-Di-(allylthio)-ethane.—One mole of ethylene mercaptan was slowly added to two moles of potassium hydroxide in ethanol at 0°. To the suspended potassium mercaptide was added two moles of allyl bromide at 0°. The cooling bath was removed and the reaction mixture allowed to reach room temperature. Most of the alcohol was removed by distillation and the residue extracted with ether. After evaporating the ether, the oily liquid was distilled in vacuum, b.p. 109° (7 mm.), n_{25} 1.5345, d_{25} 0.9998. *Anal.* Calcd. for $C_8H_{14}S_2$: S, 36.78. Found: S, 36.64.

The methyl analog was prepared in a similar manner substituting methyl iodide for allyl bromide.

General Procedure for Preparing Sulfonium Salts.—One-hundredth mole of diallyl sulfide was dissolved in 10 ml. of dry methanol and placed in a heavy glass tube. To this was added 0.01 mole of methyl iodide and the tube was sealed, placed in a steam-cone, and heated with steam for three hours. The tube was cooled in Dry Ice–acetone and broken. To the contents was added dry ether until no more precipitation took place. The solid was purified by precipitating it from methanol solution with dry ether until constant melting. Analysis was performed by titration with standard silver nitrate. *Anal.* Calcd. for $C_7H_{13}IS$: I, 49.13. Found: I, 62.20.

This analysis and the melting point, 211°, correspond to trimethylsulfonium iodide which requires 62.19% I.

When the above mentioned reactants were refluxed for five hours the results were the same. A methanol solution of diallyl sulfide when treated with either methyl iodide or isopropyl iodide gave trimethylsulfonium iodide. Diallyl sulfide in methanol solution when treated with phenacyl bromide or *p*-phenylphenacyl bromide gave trimethylsulfonium bromide. Di-(2-methylallyl) sulfide, 2,4,6-trithiane and 2,4,6-trimethyltrithiane in methanol solutions when treated with allyl iodide or allyl bromide resulted in formation of the corresponding trimethyl sulfonium halide. 1,2-Di-(allylthio)-ethane did not react with allyl iodide or allyl bromide in the absence of a solvent. However, when its methanol solution was treated with methyl iodide, tetramethylethylenedisulfonium dibromide was obtained. *Anal.* Calcd. for $C_{10}H_{20}I_2S_2$, dimethyldiallylethylenedisulfonium dibromide: I, 53.6. Calcd. for $C_6H_{16}I_2S_2$: I, 62.3. Found: I, 59.5; m.p. 105–105.5° (dec.).

Methyldiallylsulfonium Methyl Sulfate.—To a methanol solution of 0.01 mole of diallyl sulfide was added 0.01 mole of dimethyl sulfate. The mixture was allowed to stand for five days in a sealed tube. The tube was broken and dry ether added to its contents. The light colored liquid which

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[6] G. Toennies and J. J. Kolb, THIS JOURNAL, **67**, 1141 (1945).

[7] M. P. Balfe, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 2554 (1930).

[8] S. Smiles, *ibid.*, 163 (1900).

[9] H. H. Cavell and S. Sugden, *ibid.*, 2572 (1930).

[10] F. H. Burstall and S. Sugden, *ibid.*, 229 (1930).

[11] P. C. Ray and N. Adhikary, *J. Indian Chem. Soc.*, **62**, 1752 (1940).

[12] M. Tamele, C. J. Ott, L. E. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[13] F. D. Chattaway and E. C. Kellett, THIS JOURNAL, **53**, 2187 (1931).

[14] Baumann and Fromm, *Ber.*, **22**, 2602 (1889).

[15] V. Meyer, *ibid.*, **19**, 3263 (1886).

[16] H. Fasbender, *ibid.*, **20**, 461 (1887).

settled to the bottom was washed several times with dry ether and all residual ether removed in vacuum. The liquid did not crystallize even at −78°. The same result was obtained when no solvent was used. No precipitate formed upon addition of 2% barium chloride solution.

To an aqueous solution of the above liquid was added a few drops of chloroplatinic acid. A yellow solid immediately precipitated. This was removed by filtration and washed with alcohol; m.p. 145°. *Anal.* Calcd. for $C_{14}H_{26}Cl_6PtS_2$: Pt, 29.3. Found: Pt, 28.4. This shows that the compound is bis-(methyldiallylsulfonium)-chloroplatinate.

General Procedure for Preparing Mercuric Halide Complexes.—One-hundredth mole of mercuric iodide was placed in a flask with 20 ml. of acetone. To this was added 0.01 mole of allyl bromide and 0.01 mole of diallyl sulfide. The mixture was shaken and when all the mercuric iodide had dissolved, the acetone was evaporated in vacuum. Dry ether was then added and the solid product recrystallized from methyl isobutyl ketone; m.p. 64.5°. *Anal.* Calcd. for $C_9H_{15}I_3HgS$: C, 14.67; H, 2.05. Found: C, 14.85; H, 2.23.

The compound formed from 1,2-di-(allylthio)-ethane, allyl iodide and mercuric iodide was purified by adding dry ether to its acetone solution. The liquid members were isolated by evaporating the acetone in vacuum, adding and decanting ether, and evaporating all residual ether in vacuum.

The properties and analyses of seven of these compounds are recorded in Table I. In addition, isopropyldiallylsulfonium iodide mercuric iodide, *n*-butyldiallylsulfonium iodide mercuric iodide, and methallyldiallylsulfonium chloride mercuric chloride were prepared, but decomposed before they could be isolated from solution.

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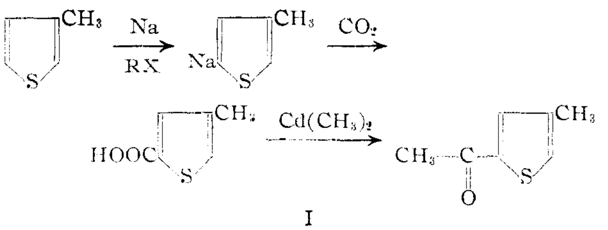
GAINESVILLE, FLORIDA RECEIVED NOVEMBER 23, 1951

Alkylation During Transmetalation of 3-Methylthiophene

BY JOSEPH A. BLANCHETTE AND ELLIS V. BROWN

RECEIVED OCTOBER 31, 1951

In the course of our investigation of the Willgerodt reaction in the heterocyclic series,[1] it became necessary to prepare 4-methyl-2-acetylthiophene by a method which would circumvent the isomeric mixture of 3-methyl- and 4-methyl-2-acetylthiophenes obtained by the direct acetylation of 3-methylthiophene. One of the possible routes available for the synthesis of 4-methyl-2-acetylthiophene is shown by equation I.



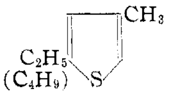
I

Schick and Hartough[2] reported that 3-methylthiophene metalated exclusively in the 5-position in the presence of alkyl or aryl halides such as ethyl chloride, bromobenzene or *n*-butyl bromide. On carbonation and acidification, they obtained a 42% yield of 4-methyl-2-thiophenecarboxylic acid with no trace of 3-methyl-2-thiophenecarboxylic acid being detected. The results obtained by us when this procedure of transmetalation was attempted with ethyl bromide and *n*-butyl bromide are shown in Table I.

TABLE I

Alkyl or aryl halide	3-Methylthiophene recovered, %	4-Methyl-2-thiophenecarboxylic acid, %	Organic residue, %	B.p., °C.
Ethyl bromide	60	10	40	164–166, 46–48 (13 mm.)
n-Butyl bromide	46	21	60	198–202

It can be seen that the highest yield of 4-methyl-2-thiophenecarboxylic acid obtained was 21% with *n*-butyl bromide which does not approach the 42% reported by Schick and Hartough using ethyl chloride. With both *n*-butyl bromide and ethyl bromide, high boiling liquid organic residues remained after the unreacted 3-methylthiophene had been recovered by fractional distillation. It seemed probable that these organic liquids were alkylated 3-methylthiophenes with the formulas I or II formed by Wurtz–Fittig coupling of 3-methylthienylsodium and the alkyl halides.



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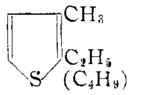
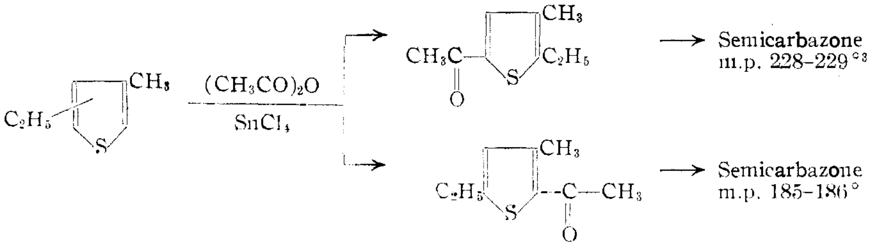


II

Since metalation takes place exclusively in the 5-position of 3-methylthiophene, as shown by the isolation of 4-methyl-2-thiophenecarboxylic acid after carbonation, I was the most probable and the scheme in equation II summarizes the experimental data which support this structure.



The two possible structures, I and II, are 2-ethyl-4-methylthiophene and 2-ethyl-3-methylthiophene. Acetylation would yield, either the known 2-ethyl-3-methyl-5-acetylthiophene, which can be converted to a known semicarbazone ($C_{10}H_{15}N_3OS$) with a melting point of 228–229°, or 2-ethyl-4-methyl-5-acetylthiophene. Acetylation of the compound obtained in this study gave a ketone whose semicarbazone had a melting point of 185–186° and analyzed for $C_{10}H_{15}N_3OS$. These results show that the original compound is a methylethylthiophene and seem to eliminate 2-ethyl-3-methylthiophene as a possibility. The structure is, therefore, most likely to be 2-ethyl-4-methylthiophene and, by analogy, the compound obtained with *n*-butyl bromide is 2-*n*-butyl-4-methylthiophene. A Willgerodt reaction on 2-ethyl-4-methyl-5-acetylthiophene gave the expected 2-ethyl-4-meth-

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[1] J. A. Blanchette and E. V. Brown, THIS JOURNAL, **73**, 2779 (1951).

[2] J. W. Schick and H. D. Hartough, *ibid.*, **70**, 1645 (1948).

[3] W. Steinkopf, A. Merckoll and H. Strauch, *Ann.*, **545**, 45 (1940).