Acknowledgment. The authors gratefully acknowledge the valuable comments of Professors Harold Hart and George A. Olah. We also thank Mr. Kenzo Iwai and Mr. Tetsuo Ishioka for their assistance in the laboratory.

Registry No.—**1**, 36230-30-5; **2**, 56908-77-1; **3**, 17384-76-8; **4**, 2717-39-7; **5**, 14558-12-4; **6**, 7383-94-0; **7**, 13764-18-6; **8**, 14558-14-6; **9**, 7435-50-9; **10**, 569-41-5; **11**, 575-37-1; **12**, 56908-78-2; **13**, 56908-79-3; **14**, 3031-15-0; **15**, 879-12-9; **15** picrate, 56908-80-6; **16**, 19063-11-7; **17**, 56908-81-7; **18**, 18623-61-5; **19**, 56908-82-8; **20**, 51958-57-7; **21**, 571-58-4; **22**, 581-40-8; **50**, 56908-83-9; **51**, 56908-84-0; **52**, 56908-85-1; **54**, 56908-86-2; **55**, 56908-87-3; 3,5-dimethylbenzyl bromide, 56908-88-4; diethyl allylmalonate, 2049-80-1; naphthalic anhydride, 81-84-5; dimsyl sodium, 15590-23-5; 1,3-dimethylnaphthalene, 575-41-7.

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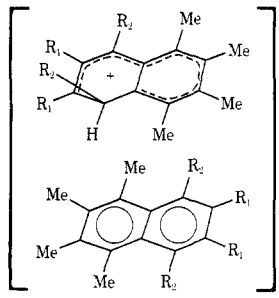
(16) One of the tentative models for the hypothetical complex ArH⁺Ar is illustrated below as an overlapping double-layered form. (1) Telomerization may take place via σ complex resulting in the strain relief at the position para to the protonated carbon; (2) hydrogen transfer may take place via π complex from the Me substituents of the basic Ar to the protonated ring most favorably when $R_1 = R_2 = H$.



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Ion Radicals. XXXV. Reactions of Thianthrene and Phenoxathiin Cation Radicals with Ketones. Formation and Reactions of β-Ketosulfonium Perchlorates and Ylides[1,2]

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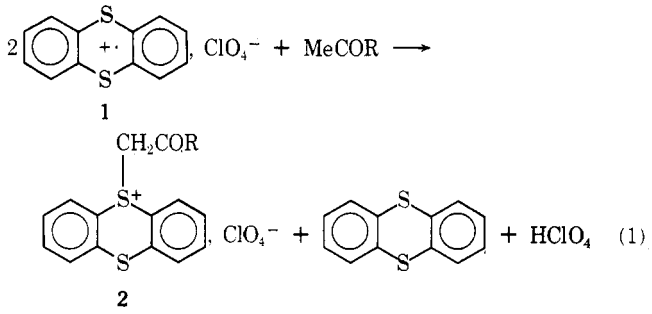
Thianthrene cation radical perchlorate (**1**) and phenoxathiin cation radical perchlorate (**3**) react with ketones to give, in most cases, a β-ketoalkylsulfonium perchlorate and the parent heterocycle (thianthrene or phenoxathiin) in equimolar amounts. Reaction with diketones or β-keto esters leads, in some cases, directly to a sulfur ylide. Some of the β-ketosulfonium perchlorates were themselves easily converted into sulfur ylides by treatment with base. Reaction of selected β-ketosulfonium perchlorates with nucleophiles led easily, also, to displacement of the parent heterocycle and formation of an α-substituted ketone bearing the nucleophile at the α-carbon atom.

Several methods of preparing β-ketosulfonium salts are to be found in the literature. Most common among these is the reaction of a dialkyl or alkyl aryl sulfide with an α-halogeno ketone or ester. Phenacyl bromide[3-6] and α-bromo esters[5,7] are often used. This method is quite old, having been used years ago by Clarke in measuring the reactivities of some dialkyl and cyclic sulfides,[8] but in those cases the salts were not isolated. Alternatively, in another common method, a β-ketoalkyl sulfide is alkylated. Methylation is most common, dimethyl sulfate,[9] methyl tosylate,[9] and trimethyloxonium fluoroborate[10,11] having been used.

Carbonyl-stabilized sulfur ylides are not as long known. In fact, until 1965–1966 these ylides appear to have been unknown as isolable compounds,[12-14] having been prepared and used until then only in situ.[15,16] Isolable carbonyl-stabilized sulfur ylides are prepared usually by the deprotonation of β-ketosulfonium ions with bases such as triethylamine.[17] This method, and direct ones, such as the reactions of Me_2SO and dicyclohexylcarbodiimide (DCC) with activated methylene groups (such as in 1,3-diketones), have been reviewed by Ratts.[18] More recently, reaction of carbonyl-containing carbenes with a sulfide, e.g., in the pho-

tolysis of $(MeCO)_2C{=}N^+{=}N^-$ in the presence of Me_2S, has given some varieties of β-carbonyl sulfur ylides.[19]

Recently we reported an entirely new and different method of preparing β-ketoalkylsulfonium salts of the thianthrene series by reaction of thianthrene cation radical perchlorate (1) with ketones in acetonitrile solution.[20] Reaction with acetone and methyl ketones, MeCOR, in which R does not have an α-H, followed the stoichiometry of eq 1.



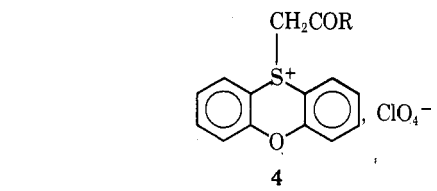
1

2

2a, R = Me; b, R = *t*-Bu; c, R = C_6H_5; d, R = 2-naphthyl

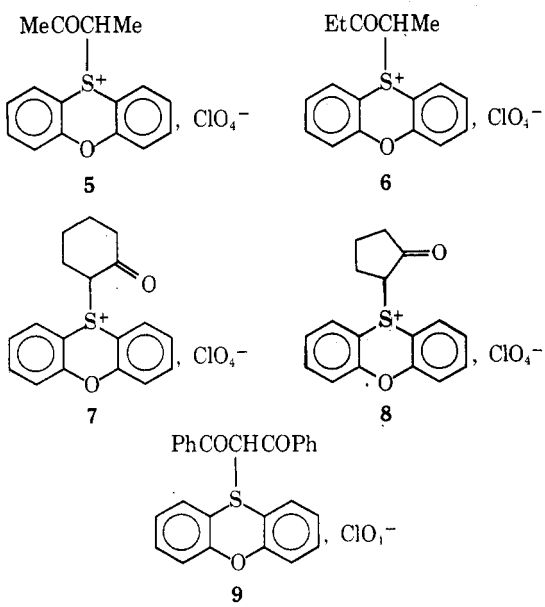
The products, 2, and thianthrene, were obtained in almost quantitative yields, the only other product being a small amount of thianthrene 5-oxide, formed presumably by the reaction of 1 with water in the solvent or liquid ketones. Reactions with butanone, tetralone-1, dimedone, and ethyl benzoylacetate were also described, the last two leading directly to ylides rather than the corresponding sulfonium salts.

We now report some further reactions of 1 with ketones, and analogous reactions of the recently isolated phenoxathiin cation radical perchlorate (3).[1a] Thus, reaction of 3 with a series of methyl ketones has given the sulfonium perchlorates 4a–d. Phenoxathiin was also formed (see eq 1). Reaction with butanone, 3-pentanone, cyclohexanone, cyclopentanone, and dibenzoylmethane gave the products 5, 6, 7, 8, and 9, respectively. Reaction with 1,3-pentanedione led directly to the ylide 10. Reactions of 1 with indanone and 4-*tert*-butylcyclohexanone gave the sulfonium salts 11 and 12. Reaction of 1 with cyclohexanone, cyclopentanone, diisopropyl ketone, and ethyl acetoacetate gave an oil in each case. The oils were not analyzed, but in the cases of diisopropyl ketone and ethyl acetoacetate the structures of the oils were deduced to be β-ketosulfonium perchlorates from their reactions with nucleophiles. These cases and the reactions of 2c and 2d with nucleophiles are discussed below.

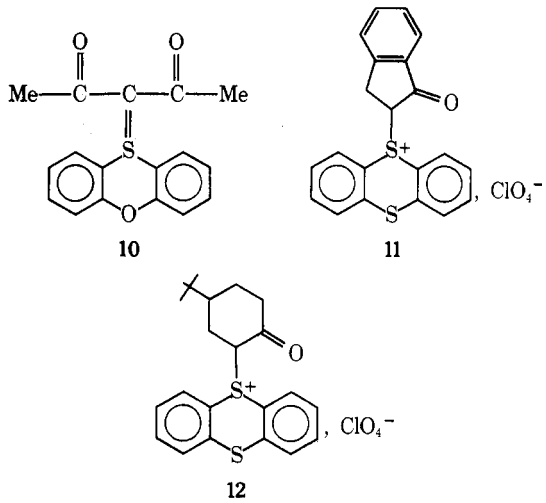


4

a, R = Me; b, R = *t*-Bu; c, R = C_6H_5; d, R = 2-naphthyl



5 6 7 8 9



10 11 12

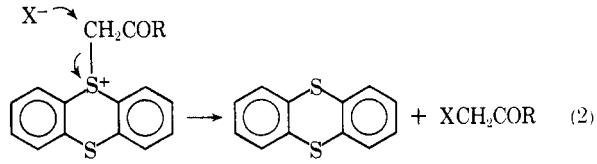
Discussion

As far as we are aware, prior to our first communication[20] the only report in the literature indicating that a cation radical may react with a ketone concerns the cyclization of the 6-β-ketopropionic ester side chain of a magnesium porphyrin derivative during oxidation by iodine. This reaction is thought to occur within the metalloporphyrin cation radical,[21] but whether or not the cation radical is involved has not been made certain. It is, in fact, uncommon also for organic carbocations of the usual type (i.e., nonradical) to react with ketones. Alkylation of ketones on the carbonyl oxygen occurs in reaction with trialkyloxonium salts. For example, triethyloxonium fluoroborate leads to salts of the type $R_2C{=}O^+Et\ BF_4^-$.[22] Corresponding ions, i.e., $Me_2C{=}OR^+$, have been implicated in certain solvolyses in acetone in which acetone is believed to behave as a nucleophile.[23,24]

In the cation radical reactions we have reported, we believe that the carbonyl compound behaves as a nucleophile also, but that reaction occurs at the α-carbon atom rather than at the carbonyl oxygen atom.

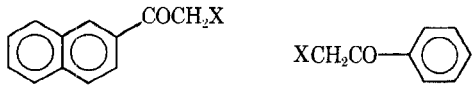
These reactions are viewed as electrophilic substitutions involving the enol, but a full discussion of mechanism must await the results of kinetic studies in progress.

Most of our reactions led to sulfonium salts. The sulfonium salts are nicely susceptible to reactions with strong nucleophiles. Displacement of the heterocycle occurs and an α-substituted carbonyl compound is formed (eq 2). We have carried out such reactions mostly with 2c and 2d.



In most cases the products XCH_2COR which were obtained were already known, and we carried out the reactions to find how easily α-substituted carbonyl compounds

may be made by this method. In some cases, the products were new. That is, the ketones **13** and **14** were obtained

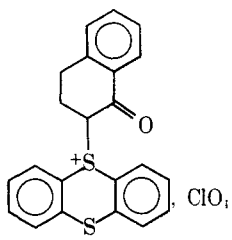


13 **14**

a, X = p-$MeC_6H_4SO_2$; b, X = $EtOCS_2$

from reactions with sodium p-toluenesulfinate and potassium ethyl xanthate, and appear to be new. Ketone **14a** was made more easily by reaction of phenacyl bromide with sodium p-toluenesulfinate, but we were unable to obtain **14b** from reaction of phenacyl bromide with potassium ethyl xanthate. Our conclusion is that this displacement method (eq 2) may be useful for making α-substituted ketones which are not as readily accessible by more conventional routes.

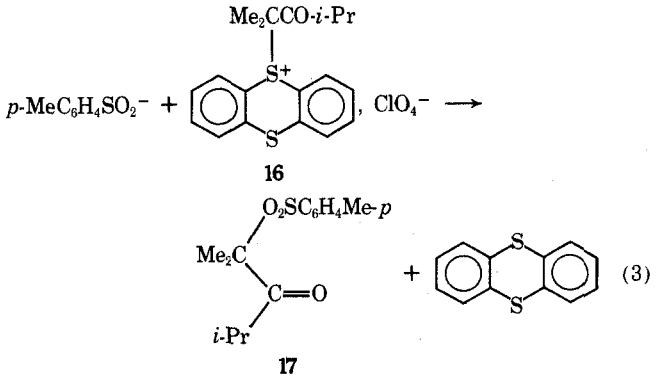
The displacement method may have wider implications, however, in reactions with conformationally stable ketoalkylsulfonium ions. The ^1H NMR spectra of **12** and **15** indi-



15

cate that the proton in the 2 position of each cyclohexyl ring is in the axial configuration. For **12** we obtain two well-resolved doublets centered at δ 5.42 with J = 7 and 13 Hz, while for **15** we obtain two very sharp doublets centered at δ 5.68 with J = 7 and 14 Hz. The peak-to-peak width of the doublets is 19 and 20 Hz, respectively, and the data are indicative of an axial 2 proton coupling with an adjacent axial–equatorial methylene group.[25] SN2 displacement reactions of **12** and **15** with nucleophiles, therefore, may give α-substituted ketones in which the nucleophile is in the axial and the 2 proton in the equatorial configuration, provided that epimerization does not occur after substitution. Exploration of these features of the displacement reaction is being undertaken.

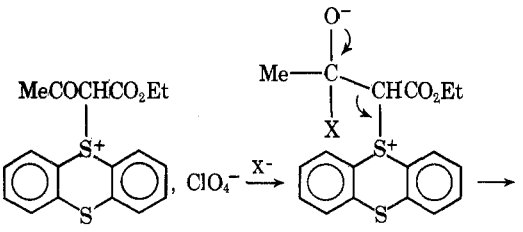
The sulfonium salt (**16**) obtained by reaction of **1** with diisopropyl ketone was a solid which appeared to decompose during attempts at recrystallization. Elemental analysis was waived, therefore. ^1H NMR and infrared (ClO_4^- band) indicated that **16** had the anticipated structure, and this was confirmed by reaction with sodium p-toluenesulfinate. Thianthrene (103%) and the ketone **17** (33%) were obtained (eq 3).



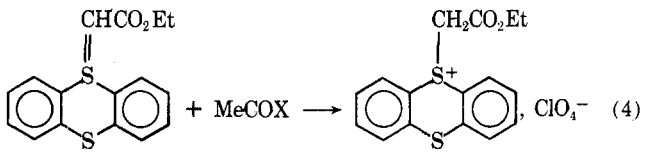
16

17 (3)

Ethyl acetoacetate reacted with **1** to give thianthrene and an oil (assumed to be **18**). The oil was treated with sodium p-toluenesulfinate and in this case thianthrene was not obtained; i.e., reaction did not follow eq 3. Instead, a sulfonium perchlorate was obtained which, from ^1H NMR and elemental analysis, appears to be **20**. Reaction of **18** with p-toluenesulfinate ion (X^-) appears to have followed the path in eq 4. Protonation of the ylide **19** in situ would



18

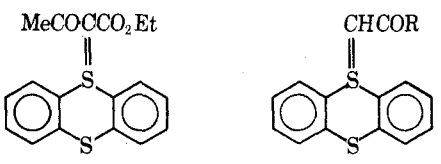


(4)

19 **20**

lead to the isolated product (**20**). Attempts to make **20** by direct reaction of **1** with ethyl acetate failed. A dimer of **1** was formed, instead, whose nature, and that of analogous dimers, will be discussed in a later publication. We failed also to obtain **20** by reaction of thianthrene with ethyl α-bromoacetate both in the absence and presence of silver perchlorate. Thianthrene was recovered quantitatively in each case.

Confirmation that **18** had been formed in reaction of **1** with ethyl acetoacetate was obtained by treating the oil produced with triethylamine, whereupon the ylide **21** was obtained.



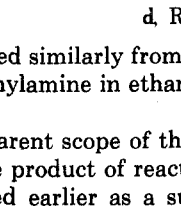
21 **22**

22b, R = t-Bu

d, R = 2-naphthyl

Ylides were obtained similarly from treating other sulfonium salts with triethylamine in ethanol; **2b** gave **22b**, and **2d** gave **22d**.

In view of the apparent scope of these ketone reactions, it is possible that the product of reaction of **1** with cyanoacetamide, formulated earlier as a sulfilimine derivative, namely 5-[(cyanoacetyl)imino]-5,5-dihydrothianthrene,[26] may be instead an ylide (**23**) analogous to **10**. This possibil-



23

ity and reactions with analogous activated amides is being investigated.

Experimental Section

Thianthrene cation radical perchlorate (**1**) was prepared as described earlier.[27] *Attention is called to the warning of explosive hazard.*[27] Phenoxathiin cation radical perchlorate was prepared by a modification of this procedure.[1a] Acetonitrile was Eastman anhydrous grade and was stored over molecular sieve in a septum-

capped bottle. Acetone, reagent grade, was boiled with $KMnO_4$ for 2 hr and distilled over 3 Å molecular sieve. All other carbonyl compounds were either distilled at atmospheric or reduced pressure as appropriate or recrystallized, except methyl 2-naphthyl ketone (J. T. Baker, photosensitizer grade, mp 53–54°) and dimedone (Aldrich, 99%), which were used without further treatment. Nucleophilic reactants were from standard sources except potassium ethyl xanthate, which was prepared by the standard route.[28] Sodium *p*-toluenesulfinate dihydrate was from Aldrich. Me_2SO was reagent grade (J. T. Baker) and hydriodic acid was Eastman, 50%.

Reactions of 1 and 3 with Carbonyl Compounds. General Procedure. Between 1 and 3 mmol of the cation radical perchlorate was dissolved in about 30 ml of acetonitrile and to this was added an excess of the carbonyl compound (50–200%). Stirring was continued for a variable period, since some reactions were rapid and others were quite slow as judged by the disappearance of the purple color of **1** and **3**. The solutions were usually colored at the end of the reaction. In the cases of reactions of **1** the colors varied from light purple to red, while in most reactions of **3** the final color of the solution was yellow. In most cases the solution was concentrated to small volume and placed on a column of silica gel (Merck No. 7733). In the cases of **1**, elution with benzene gave thianthrene, while elution next with ether gave thianthrene 5-oxide. The oxide was always formed in small amounts. Finally, elution with acetone gave the β-ketosulfonium perchlorate. The products of reactions of **3** were similarly separated by chromatography with the exception of some cases in which the β-ketosulfonium salt was precipitated before chromatographic separation of the phenoxathiin and phenoxathiin 5-oxide. Also, after use of benzene to remove phenoxathiin, the column was first treated with chloroform to begin the downward separation of phenoxathiin 5-oxide and this was then removed more quickly with ether. Data for individual reactions are given below.

Reaction of 1 with Indanone-1. Formation of 11. The sulfonium perchlorate (**11**) had mp 156–157° (ethanol–MeCN); λ_{max} (MeCN) (10^{-4} ϵ) 255 nm (4.13), 243 (2.50), and 291 br, (0.41); ^1H NMR (acetone-d_6) δ 7.9 (m, 12 H, aromatic), 5.2 (t, 1 H, J = 6 Hz, –CH–), and 3.1, 3.2 (2 d, 2 H, J = 6 Hz, $-CH_2-$).

Anal. Calcd for $C_{21}H_{15}S_2ClO_5$: C, 56.4; H, 3.38; S, 14.3; Cl, 7.93. Found: C, 56.6; H, 3.40; S, 14.6; Cl, 7.76.

Reaction of 1 with 4-*tert*-Butylcyclohexanone. Formation of 12. The sulfonium perchlorate (**12**) was isolated from the column as an oil. This was dissolved in a small amount of acetonitrile and diluted with a large volume of ether. An oil precipitated which solidified overnight in the refrigerator. Reprecipitation from acetonitrile with ether gave a white, crystalline solid: mp 122.5–123°; λ_{max} (MeCN) (10^{-4} ϵ) 225 nm (4.48), 255 (2.38), 290–312 br (0.95); ^1H NMR (CD_3CN) δ 7.98 (m, 8 H, aromatic), 5.42 (2 d, 1 H, C_2H), 2.48 (m, 2 H, $-CH_2-$), 1.60 (m, 5 H), 0.76, (9 H, *t*-Bu).

Anal. Calcd for $C_{22}H_{25}S_2ClO_5$: C, 56.3; H, 5.37; S, 13.7; Cl, 7.55. Found: C, 56.2; H, 5.46; S, 13.6; Cl, 7.57.

Reaction of 3 with Acetone. Formation of 4a. To a solution of 807 mg (2.69 mmol) of **3** in 30 ml of acetonitrile was added 2 ml of acetone. The purple color became brown after 1 hr of stirring. The solution was evaporated and the residue was dissolved in acetone, to which solution petroleum ether (bp 30–60°) was added to cause turbidity, and crude, white **4a** (444 mg, 1.24 mmol, 99%) crystallized out: mp 179–180° dec (aqueous Me_2SO); λ_{max} (MeCN) (10^{-3} ϵ) 235 nm (14.6), 287 (4.7); ^1H NMR (Me_2SO-d_6) δ 8.2–7.0 (m, 8 H, aromatic), 5.15 (s, 2 H, $-CH_2-$), and 2.15 (s, 3 H, Me).

Anal. Calcd for $C_{15}H_{13}SClO_6$: C, 50.5; H, 3.68; S, 8.97; Cl, 9.94. Found: C, 50.6; H, 3.66; S, 9.22; Cl, 9.99.

The filtrate from **4a** precipitation was concentrated and chromatographed to give 269 mg (1.35 mmol, 100%) of phenoxathiin and 21 mg (0.096 mmol, 7.1%) of phenoxathiin 5-oxide.

Reaction of 3 with Pinacolone. Formation of 4b. Reaction as above was carried out with 745 mg (2.48 mmol) of **3** and overnight stirring. After evaporation of the mixture and washing with water to remove excess of pinacolone, the residue was dissolved in a small amount of acetone and chromatographed, giving phenoxathiin (100%), phenoxathiin 5-oxide (7.8%), and 479 mg (1.21 mmol, 105%) of crude **4b:** mp 192–193° dec (acetone–ether); λ_{max} (MeCN) 287 nm (ϵ 4.85 × 10^3); ^1H NMR (Me_2SO-d_6) δ 7.4–8.3 (m, 8 H, aromatic), 5.45 (s, 2 H, $-CH_2-$), and 0.95 (s, 9 H, *t*-Bu).

Anal. Calcd for $C_{18}H_{19}SClO_6$: C, 54.2; H, 4.80; S, 8.04; Cl, 8.89. Found: C, 54.5; H, 4.97; S, 7.87; Cl, 8.99.

Reaction of 3 with Acetophenone. Formation of 4c. Reaction with 603 mg (2.01 mmol) of **3** for 3 hr and work-up as above (see **4b**), without water wash, gave 98% of phenoxathiin, 5.6% of phenoxathiin 5-oxide, and 410 mg (0.98 mmol, 103%) of crude **4c:** mp 165–166° dec (acetone–ether); λ_{max} (MeCN) (10^{-3} ϵ) 287 nm (6.26), 252 sh (37.9), and 241 (23.3); ^1H NMR (Me_2SO-d_6) δ 7.5–8.8 (m, 13 H, aromatic) and 5.1 (s, 2 H, $-CH_2-$).

Anal. Calcd for $C_{20}H_{15}SClO_6$: C, 57.4; H, 3.61; S, 7.66; Cl, 8.47. Found: C, 57.3; H, 3.67; S, 7.89; Cl, 8.49.

Reaction of 3 with 2-Acetonaphthone. Formation of 4d. Reaction of 1.05 g (3.5 mmol) of **3** for 30 min and work-up as above gave 100% of phenoxathiin, 4.3% of phenoxathiin 5-oxide, and 741 mg (1.58 mmol, 90%), of crude **4d:** mp 154–154.5° dec (ethanol); λ_{max} (MeCN) (10^{-3} ϵ) 292 nm (11.6), 252 sh (34.8), and 245 (39.7); ^1H NMR (Me_2SO-d_6) δ 8.5–7.0 (m, 15 H, aromatic), 5.9 (s, 2 H, $-CH_2-$).

Anal. Calcd for $C_{24}H_{17}SClO_6$: C, 61.5; H, 3.66; S, 6.84; Cl, 7.56. Found: C, 61.4; H, 3.90; S, 6.60; Cl, 7.24.

Reaction of 3 with Butanone. Formation of 5. After reaction of 1.12 g (3.73 mmol) of **3** for 20 min, ether was added to the medium to give a precipitate of crude **5**. The filtrate was evaporated and the residue was washed with water and chromatographed, giving 101% of phenoxathiin, 4% of phenoxathiin oxide, and a further portion of **5**, amounting to a total of 525 mg (1.42 mmol, 76%): mp 149° dec (acetone–ether); λ_{max} (MeCN) (10^{-3} ϵ) 289 nm (5.17) and 234 (18.4); ^1H NMR (Me_2SO-d_6) δ 6.9–8.1 (m, 8 H, aromatic), 5.05 (q, 1 H, –CH–), 2.2 (s, 3 H, Me), and 1.3 (d, 3 H, Me).

Anal. Calcd for $C_{16}H_{15}SClO_6$: C, 51.8; H, 4.08; S, 8.63; Cl, 9.56. Found: C, 51.6; H, 4.03; S, 8.53; Cl, 9.33.

Reaction of 3 with Pentan-3-one. Formation of 6. Reaction of 724 mg (2.41 mmol) of **3** for 1 hr was followed by evaporation to small volume and addition of ether. The precipitate of **6** was filtered and the filtrate was chromatographed to give 105% of phenoxathiin, 19% of phenoxathiin 5-oxide, and a further small amount of **6**. The combined portions of crude **6** amounted to 252 mg (0.66 mmol, 55%): mp 122° dec (acetone–ether); λ_{max} (MeCN) (10^{-3} ϵ) 291 nm (4.86) and 234 (19.9); ^1H NMR (Me_2SO-d_6) δ 6.95 (m, 8 H, aromatic), 5.1 (q, 1 H, –CH–), 1.35 (d, 3 H, Me), 0.91 (t, 3 H, Me). The $-CH_2-$ group signal was obscured by a solvent peak.

Anal. Calcd for $C_{17}H_{17}SClO_6$: C, 53.0; H, 4.46; S, 8.32; Cl, 9.22. Found: C, 52.8; H, 4.30; S, 8.27; Cl, 9.08.

Reaction of 3 with Cyclohexanone. Formation of 7. Reaction of 712 mg (2.37 mmol) of **3** for 5 min and addition of ether to the medium gave 277 mg of crude **7**. Chromatography gave 95% of phenoxathiin, 9.5% of phenoxathiin 5-oxide, and 83 mg of crude **7**, totaling 0.91 mmol (76%): mp 121–122° dec (acetone–ether); λ_{max} (MeCN) 291 nm (ϵ 5.05 × 10^3); ^1H NMR (Me_2SO-d_6) δ 6.8–8.1 (m, 8 H, aromatic), 5.1 (t, 1 H, α-CH), and 1.5 [br s, 8 H, $-(CH_2)_4-$].

Anal. Calcd for $C_{18}H_{17}SClO_6$: C, 54.5; H, 4.32; S, 8.08; Cl, 8.93. Found: C, 54.7; H, 4.30; S, 8.28; Cl, 8.89.

Reaction of 3 with Cyclopentanone. Formation of 8. Reaction of 762 mg (2.54 mmol) of **3** for 10 min and addition of ether gave 225 mg of crude **8**. Chromatography gave 91% of phenoxathiin, 11% of phenoxathiin 5-oxide, and 132 mg of crude **8**, totaling 0.95 mmol (75%), mp 96.0–96.5° (acetone–ether).

Anal. Calcd for $C_{17}H_{15}SClO_6$: C, 53.3; H, 3.95; S, 8.37; Cl, 9.26. Found: C, 53.3; H, 4.20; S, 8.50; Cl, 8.98.

Reaction of 3 with Dibenzoylmethane. Formation of 9. After reaction of 771 mg (2.57 mmol) of **3** for 15 min the solvent was removed and the residue was dissolved in a small amount of acetone. Addition of ether gave 556 mg (1.1 mmol, 85%) of crude **9:** mp 186° dec (acetone–ether); λ_{max} (MeCN) (10^{-3} ϵ) 319 nm (4.73), 277 (15.3), and 241 (40.5).

Anal. Calcd for $C_{27}H_{19}SClO_7$: C, 62.0; H, 3.66; S, 6.13; Cl, 6.78. Found: C, 61.7; H, 3.60; S, 6.09; Cl, 6.69.

Reaction of 3 with 2,4-Pentanedione. Formation of Ylide 10. After reaction of 843 mg (2.8 mmol) of **3** for 15 min the solvent was removed and the residue was washed with water to remove excess of ketone. The residue was treated as above (see **9**) to give 309 mg of crude **10:** mp 236° (acetone); λ_{max} (MeCN) (10^{-3} ϵ) 301 (5.73), 256 (19.7), and 227 (32.4); ^1H NMR ($CDCl_3$) δ 7.3 (m, 8 H, aromatic), 2.45 (s, 6 H, Me).

Anal. Calcd for $C_{17}H_{14}SO_3$: C, 68.4; H, 4.73; S, 10.75. Found: C, 68.2; H, 4.81; S, 11.0.

Reactions of 2d with Nucleophiles. Formation of α-Substituted Methyl 2-Naphthyl Ketones (13). Approximately 150–250 mg (0.3–0.5 mmol) of **2d** was dissolved in 10–15 ml of acetonitrile and to the stirred solution was added a severalfold excess of the nucleophile and approximately 1 ml of water. The mixture was stirred for an additional period of time depending on the nucleophile. TLC was carried out to monitor the reaction and when two spots (thianthrene and an unknown one) appeared only or predominantly, the solvent was evaporated under vacuum at room temperature. The times of stirring are given in parentheses, and

they may or may not be significant. After evaporation of the solvent the residue was chromatographed on a column of silica gel (Merck 7733). Elution with benzene gave thianthrene and elution with ether gave the α-substituted methyl 2-naphthyl ketone (**13**). The results of reactions which led to known compounds are listed in abbreviated form [reagent (time), % yield of thianthrene, X in XCH_2CO-2-naphthyl, % yield, mp (lit. mp)]: KCN (24 hr), 98, -CN, 98, 126–127° (126.6–128.2°);[29] NaSCN (2 hr), 95, -SCN, 94, 105–106° (109–110°);[29] NaN_3 (1.5 hr), 99, $-N_3$, 100, 63–64° (66–67°);[30] Me_4NCl (30 min), 92, -Cl, 97, 64–65° (65–66°);[31] Bu_4NI (2 min), 101, -I, 97, 90–91° (91–91.5°);[32] $AgNO_2$ (10 min), 94, -OH, 96, 114° (114°);[33] $NaNO_2$ (20 min), 90, -OH, 54, 114°; $AgNO_3$ (16 hr), 93, -OH, 63, 114°; $NaNO_3$ (11 hr), 47, -OH, 73, 105–112°; Me_2SO (2 hr), 99, -OH, 98, 109–110°; concentrated HCl (16 hr), 111, -Cl, 81, 61–62°; concentrated HBr (30 min), 97, -Br, 96, 78–80° (80–82°);[33] 50% HI (5 hr), 103, -I, 87, 90–91°.

Reaction of 2d with Sodium *p*-Toluenesulfinate Dihydrate. Formation of 13a. Reaction carried out as above (15 hr) gave 99% of thianthrene and 78% of α-(*p*-toluenesulfinyl)methyl 2-naphthyl ketone (**13a**): mp 149–150° (methanol); λ_{max} (MeCN) (10^{-4} ε) 228 nm (2.15), 253 (4.04), 285 (1.00), and 294 (1.05); ^1H NMR ($CDCl_3$) δ 7.67 (m, 11 H, aromatic), 4.86 (s, 2 H, $-CH_2-$), 2.39 (s, 3 H, Me).

Anal. Calcd for $C_{19}H_{16}O_3S$: C, 70.3; H, 4.97; S, 9.88. Found: C, 70.2; H, 5.19; S, 10.1.

Reaction of 2d with Potassium Ethyl Xanthate. Formation of 13b. Reaction gave 85% of thianthrene and 86% of the ethyl ester of *S*-(2-naphthoyl)methylxanthic acid (**13b**) (X = $EtOCS_2^-$): mp 92–93° (aqueous methanol); λ_{max} (MeCN) (10^{-4} ε) 243 nm (4.63), 248 (5.20), and 282 (2.05); ^1H NMR ($CDCl_3$) δ 7.7 (m, 7 H, aromatic), 4.81 (s, 2 H, $-CH_2-$), 4.65 (q, 2 H, $-CH_2-$), 1.37 (t, 3 H, Me).

Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.0; H, 4.85; S, 22.1. Found: C, 62.2; H, 4.93; S, 22.2.

Reactions of 2c with Nucleophiles. Formation of α-Substituted Acetophenones (14). The same procedure was used as with **2d** except that cyclohexane instead of benzene was used to elute thianthrene from the column. Known phenacyl compounds, $XCH_2COC_6H_5$ (**14**), were formed: Me_4NCl (1 min), 104, -Cl, 99, 54–55° (55–56°);[34] Me_4NBr (2 min), 95, -Br, 100, 48–49° (50°);[34] Bu_4NI (17 min), 99, -I, 81, oil (34.4°);[34] NaSCN (10 min), 100, -SCN, 103, 71–72° (74.1–74.6°);[29] NaN_3 (75 min), 101, $-N_3$, 101, oil (17°).[35]

Reaction of 2c with Sodium *p*-Toluenesulfinate Dihydrate. Formation of 14a. Reaction gave 99% of thianthrene and 99% of α-(*p*-toluenesulfinyl)acetophenone (**14a**): mp 106.5–107.5° (aqueous methanol); λ_{max} (MeCN) (10^{-4} ε) 228 nm (1.25), 251 (1.42); ^1H NMR ($CDCl_3$) δ 7.57 (m, 9 H, aromatic), 4.70 (s, 2 H, $-CH_2-$), 2.40 (s, 3 H, Me).

Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.7; H, 5.14; S, 11.7. Found: C, 65.8; H, 5.25; S, 12.3.

Reaction of 2c with Potassium Ethyl Xanthate. Formation of 14b. Reaction gave 100% of thianthrene and 97% of the ethyl ester of phenacylxanthic acid (**14b**): mp 32–32.5° (aqueous ethanol); λ_{max} (MeCN) (10^{-4} ε) 241 nm (0.29), 277 (0.26); ^1H NMR ($CDCl_3$) δ 8.12 (m, 3 H, aromatic), 7.63 (m, 2 H, aromatic), 4.71 (s, 2 H, $-COCH_2-$), 4.64 (q, 2 H, $-CH_2-$), 1.40 (t, 3 H, Me).

Anal. Calcd for $C_{11}H_{12}O_2S_2$: C, 55.0; H, 5.03; S, 26.7. Found: C, 54.9; H, 5.29; S, 27.0.

Reaction of 1 with Diisopropyl Ketone. Formation of 2,4-Dimethyl-2-(*p*-toluenesulfinyl)pentan-3-one (17). Reaction of **1** with 2,4-dimethylpentanone followed by column chromatography gave 86% of thianthrene and a yellow oil from which trituration with ethyl acetate gave 164 mg (37%) of a white solid which we believe to be the anticipated β-ketoalkylsulfonium perchlorate (**16**), mp 93° dec, infrared ClO_4^- band. Attempts to recrystallize this solid from common solvents (ethyl acetate, methanol, ethanol, Me_2SO) caused its decomposition. Therefore, the solid was treated in acetoritrile with sodium *p*-toluenesulfinate dihydrate and gave on column chromatography with cyclohexane 103% of anticipated thianthrene and 33% of the anticipated **17**: mp 76–77°; λ_{max} (MeCN) (10^{-4} ε) 227 nm (1.83); ^1H NMR ($CDCl_3$) δ 7.37 (2 d, 4 H, aromatic), 3.45 (heptet, 1 H, -CH-), 2.44 (s, 3 H, Me), 1.54 (s, 6 H, Me), 1.15 (d, 6 H, Me).

Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.7; H, 7.51; S, 11.9. Found: C, 62.8; H, 7.45; S, 12.1.

Reaction of 1 with Ethyl Acetoacetate. A. Formation of 5-(Ethoxycarbonylmethyl)thianthreniumyl Perchlorate (20). Reaction of **1** with ethyl acetoacetate was carried out and the yellow oil (**18**) was obtained as in B below. A solution of 814 mg of this in 10 ml of acetonitrile was stirred for 1 min with 323 mg of sodium *p*-toluenesulfinate dihydrate. Work-up and column chromatography gave no thianthrene (cyclohexane elution). Acetone elution gave a yellow oil from which trituration with methanol gave 132 mg (39%) of what we believe to be **20**: mp 169.5–170.5° (methanol); λ_{max} (MeCN) (10^{-4} ε) 227 nm (1.39), 255 (1.73), 291 (0.38); ^1H NMR (Me_2SO-d_6) δ 7.86 (m, 8 H, aromatic), 4.94 (s, 2 H, $-CH_2-$), 4.18 (q, 2 H, $-CH_2-$), 1.19 (t, 3 H, Me).

Anal. Calcd for $C_{16}H_{15}S_2ClO_6$: C, 47.7; H, 3.75; S, 15.9; Cl, 8.80. Found: C, 47.3; H, 3.68; S, 15.7; Cl, 8.56.

Attempts to make **20** by direct reaction of **1** with ethyl acetate failed. The only product was from the dimerization of **1**.[36] Attempts to prepare **20** by reaction of thianthrene with ethyl α-bromoacetate, both in the presence and absence of silver perchlorate, also failed. Thianthrene was recovered quantitatively.

Reactions of β-Ketoalkylsulfonium Perchlorates with Triethylamine. Formation of Ylides 21 and 22. 1. Reaction of 1 with Ethyl Acetoacetate (B). Use of 1.1 g (3.51 mmol) of **1** and an excess of ethyl acetoacetate followed by column chromatography, as described earlier, gave a brownish-yellow oil, assumed to be the anticipated β-ketoalkylsulfonium perchlorate. However, in that case the yield (1.42 g, 3.19 mmol) is far too high. The oil could not be rendered crystalline, and it was treated with 1.6 ml of triethylamine in 10 ml of acetonitrile. The solvent was removed after 20 hr and the residue was chromatographed on silica. Elution with benzene gave 327 mg of thianthrene, while elution with ether gave 542 mg (1.57 mmol) of what we deduce to be the ylide **21**: mp 179–180° (petroleum ether–CCl_4); λ_{max} (MeCN) (10^{-4} ε) 236 nm (2.77); ^1H NMR ($CDCl_3$) δ 7.47 (m, 8 H, aromatic), 4.14 (q, 2 H, $-CH_2$), 2.70 (s, 3 H, Me), and 1.03 (t, 3 H, Me).

Anal. Calcd for $C_{18}H_{16}O_3S_2$: C, 62.8; H, 4.68; S, 18.6. Found: C, 62.7; H, 4.73; S, 18.6.

Elution of the column with acetone gave 749 mg of a reddish-yellow gum which has not been identified.

2. To a solution of 214 mg (0.51 mmol) of **2b** in 10 ml of ethanol was added 1 ml (ca. 7.2 mmol) of triethylamine. After stirring for 14 hr TLC showed only very weak spots corresponding to thianthrene and **2b**, but a large spot of an unknown. The solvent was removed under vacuum and the white residue was chromatographed on a column of silica. Elution with benzene gave 3 mg of thianthrene and 77 mg (0.24 mmol, 47%) of the ylide **22b**: mp 189–190° (petroleum ether–CCl_4); λ_{max} (MeCN) (10^{-4} ε) 238 nm (0.52) 249 (0.47), 286 (0.21); ^1H NMR ($CDCl_3$) δ 7.44 (m, 8 H, aromatic), 4.06 (s, 1 H, =CH-), 1.35 (s, 9 H, *t*-Bu).

Anal. Calcd for $C_{18}H_{18}OS_2$: C, 68.7; H, 5.53; S, 20.39. Found: C, 68.9; H, 5.83; S, 20.43.

3. A similar reaction with **2d** gave the ylide **22d**: mp 81–86° (from petroleum ether–CCl_4); ^1H NMR ($CDCl_3$) δ 7.86 (m, 15 H, aromatic), 4.76 (s, 1 H, =CH-).

Registry No.—**1**, 21299-20-7; **2b**, 55116-86-4; **2c**, 55116-88-6; **2d**, 55116-90-0; **3**, 56817-58-4; **4a**, 56817-60-8; **4b**, 56817-62-0; **4c**, 56817-64-2; **4d**, 56817-66-4; **5**, 56817-68-6; **6**, 56817-70-0; **7**, 56817-72-2; **8**, 56817-74-4; **9**, 56817-76-6; **10**, 56817-77-7; **11**, 56817-79-9; **12**, 56817-81-3; **13a**, 56817-82-4; **13b**, 56817-83-5; **14a**, 31378-03-7; **14b**, 56817-84-6; **17**, 56817-85-7; **20**, 56817-87-9; **21**, 56817-88-0; **22b**, 55116-97-7; **22d**, 55116-98-8; indanone-1, 83-33-0; 4-*tert*-butylcyclohexanone, 98-53-3; acetone, 67-64-1; pinacolone, 75-97-8; acetophenone, 98-86-2; 2-acetonaphthone, 93-08-3; butanone, 78-93-3; pentan-3-one, 96-22-0; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; dibenzoylmethane, 120-46-7; 2,4-pentanedione, 123-54-6; sodium *p*-toluenesulfinate, 824-79-3; potassium ethyl xanthate, 140-89-6; diisopropyl ketone, 565-80-0; ethyl acetoacetate, 141-97-9.

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Different Reactivities of 5-Bromo-2′-deoxyuridine and 5-Bromouracil in the Bisulfite-Mediated Debromination

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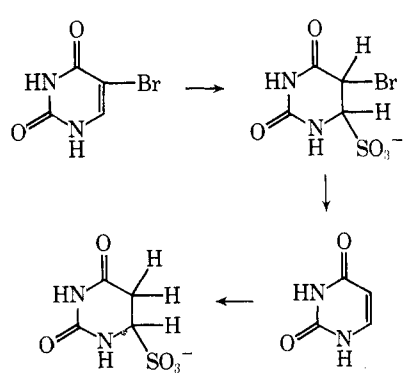
Sodium bisulfite mediated debromination of 5-bromo-2′-deoxyuridine, 1-methyl-5-bromouracil, and 5-bromouracil was studied. Spectroscopic determination of the velocity at pH 7.0 and 17° showed that 5-bromo-2′-deoxyuridine undergoes debromination two orders of magnitude more slowly than 5-bromouracil. The debromination of 1-methyl-5-bromouracil in this system was also slow, only several times faster than that of 5-bromo-2′-deoxyuridine. The optimum pH for the debromination of both 5-bromo-2′-deoxyuridine and 5-bromouracil was about 7. In the debromination of 5-bromo-2′-deoxyuridine, the existence of the intermediate 5,6-dihydro-5-bromo-2′-deoxyuridine 6-sulfonate was proved by NMR and by the reversal to 5-bromo-2′-deoxyuridine upon dilution of the reaction mixture. The formation of the intermediate from 5-bromo-2′-deoxyuridine was a rapid process, whereas the subsequent debromination was a slow process which was the rate-limiting step of the overall reaction. The facile debromination of 5,6-dihydro-5-bromouracil 6-sulfonate, in contrast to its N^1-substituted derivatives, was explained in terms of participation of an intermediate formed by elimination of HSO_3^- from the N^1–C^6 linkage of this dihydro compound.

Recent research in several laboratories has shown that sulfur nucleophiles, such as bisulfite and cysteine, bring about dehalogenation of 5-halogenouracil derivatives under mild conditions in aqueous solution.[1-4] Sander and coworkers[1a,b] reported that the bisulfite-mediated decomposition of 5-bromouracil proceeds as illustrated in Scheme I,

Scheme I



which involves addition of bisulfite across the 5,6 double bond of the pyrimidine ring followed by elimination of bromonium and sulfite ions to give uracil. The uracil in turn produces 5,6-dihydrouracil 6-sulfonate upon reaction with bisulfite.

The formation of the intermediate, 5,6-dihydro-5-bromouracil 6-sulfonate, was assumed by the analogy to the well-established 5,6-dihydrouracil 6-sulfonate formation from uracil and bisulfite.[5,6] This assumption was supported by the fact that in the case of the reaction between 5-fluorouracil and bisulfite, the formation of 5,6-dihydro-5-fluorouracil 6-sulfonate was demonstrated both by NMR studies and by reversal to 5-fluorouracil.[1a] However, since the bisulfite adduct of 5-bromouracil cannot be observed as a discrete species, it was not possible to determine whether the rate-determining step of the bisulfite-promoted debromination was the addition of bisulfite to 5-bromouracil or the subsequent dehalogenation.

Although Fourrey[2] reported that 5-bromouridine can also be converted to 5,6-dihydrouridine 6-sulfonate by treatment with sodium bisulfite, the study was not performed under kinetically controlled conditions. When we compared reactivities of 5-bromouracil, 1-methyl-5-bromouracil, and 5-bromo-2′-deoxyuridine toward bisulfite under defined conditions, a great difference was observed between these substrates; the N^1-substituted substrates react much more slowly than 5-bromouracil, and the intermediate 5,6-dihydro-5-bromo-2′-deoxyuridine 6-sulfonate can be detected as a discrete species. This paper reports the results of these studies, which show that in the bisulfite-promoted debromination of 5-bromo-2′-deoxyuridine the rate-determining step is the debromination reaction