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ION RADICALS. XXXI. REACTION OF THIANTHRENE CATION RADICAL PERCHLORATE WITH KETONES. FORMATION OF β-KETOALKYLSULFONIUM PERCHLORATES AND YLIDES[1]

Kyongtae Kim and Henry J. Shine*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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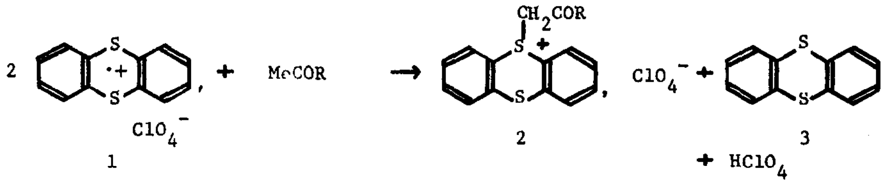
β-Ketoalkylsulfonium salts are ordinarily made by reaction of an α-halogenoketone with an organic sulfide. Phenacyl bromide is often used (eq. 1); α-bromoesters (e.g., methyl bromoacetate) are also used.[2] This method is quite old, having been used, for example, by Clarke to measure the relative reactivities of sulfides without isolation of the sulfonium salts.[3] Alternatively, a β-ketoalkyl sulfide can be alkylated, for example, with trimethyloxonium fluoroborate (eq. 2).[4]

$$R_2S + BrCH_2COC_6H_5 \rightarrow R_2\overset{+}{S}CH_2COC_6H_5\overset{-}{Br} \qquad (1)$$

$$RSCH_2COC_6H_5 + Me_3\overset{+}{O}\overset{-}{BF_4} \rightarrow R(Me)\overset{+}{S}CH_2COC_6H_5BF_4^- + Me_2O \qquad (2)$$

β-Ketosulfonium ylides are not so long known, the first examples having been prepared in the late 1960's.[2] The ylides are usually made by treatment of β-ketoalkylsulfonium ions with base, such as triethylamine or even hydride ion. More recently some varieties of β-carbonylsulfonium ylides have been made by reaction of a carbonyl-containing carbene with a sulfide, for example, from the photolysis of $(MeCO)_2C=\overset{+}{N}=\overset{-}{N}$ in the presence of dimethyl sulfide.[5]

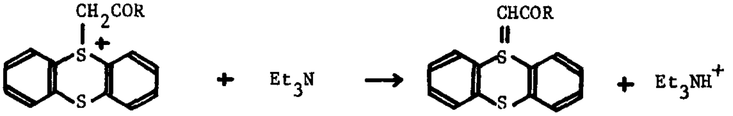
We have now found that thianthrene cation radical perchlorate (1) reacts smoothly with a variety of ketones to give either a β-ketoalkylsulfonium perchlorate or a β-ketosulfonium ylide, depending on the ketone used. The reactions are carried out in acetonitrile solution at room temperature, and the products are separated either by column or thin-layer chromatography, using silica gel. Acetone and methyl ketones, MeCOR, in which R does not have an α-H, react as in eq. 3. The product (2) and thianthrene (3) were obtained in almost quantitative yields, the only other organic product being a small amount of thianthrene 5-oxide.



(3)

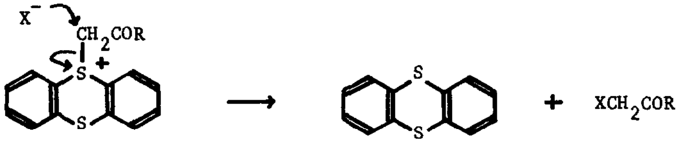
R = a, Me; b, *tert*-Bu; c, C_6H_5; d, 2-naphthyl

The products **2** are crystalline compounds with sharp melting points: **2a**, 180-1° (dec) (from ethanol); **2b**, 193-4° (dec) (from ethyl acetate); **2c**, 149-50° (dec) (from ethanol); and **2d**, 164-5° (dec) (from ethanol). The structure of the products **2** is inferred from elemental analyses, nmr spectra (in DMSO-d_6), infrared (broad perchlorate band at 9.1 μ), rapid exchange of the methylene protons of **2c** with D_2O and consequent disappearance of the methylene pmr signal, conversion of **2a** and **2d** to the corresponding ylides (eq. 4) and from reactions of **2d** with nucleophiles which led to excellent yields of α-substituted methyl 2-naphthyl ketones and thianthrene (eq. 5). A representative preparation (of **2a**) is given.



(4)

R = *tert*-Bu and 2-naphthyl



(5)

2d

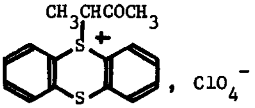
X = Br, I, CN, N_3, SCN

Preparation of **2a**.- Acetonitrile was Eastman's anhydrous grade, stored over molecular sieve in a septum capped bottle. Acetone was reagent grade, refluxed over potassium permanganate, dried over anhydrous potassium carbonate, distilled and stored over molecular sieve. To a solution of 522 mg (1.65 mmol) of **1**[6] in 15 ml of acetonitrile was added 1 ml of acetone.

The solution was stirred at room temperature and became colorless in 17 min. After stirring further for 10 min the solvent was removed under vacuum, and the pale yellow residue was chromatographed on silica gel (Merck No. 7733, 27 x 2.4 cm column). Elution with benzene gave 177 mg (0.82 mmol, 99%) of crude thianthrene. Elution with ether gave 6.6 mg (0.028 mmol, 3.4%) of thianthrene 5-oxide. Elution with acetone gave 321 mg (0.82 mmol, 99%) of crude 2a, which was crystallized from ethanol, mp 180-1° (dec), λ_{max} (acetonitrile) 224, 255 and 291-307 (broad) nm.

Anal. Calcd. for $C_{15}H_{13}S_2ClO_5 \cdot H_2O$ (2a): C, 46.09; H, 3.86; S, 16.40; Cl, 9.06. Found: C, 46.03; H, 3.51; S, 16.62; Cl, 8.66. Nmr, δ_H, 1.97 (s, 3H), 4.91 (s, 2H) and 7.65 (m, 8H).

Reaction of 1 with methyl ethyl ketone and tetralone-1 gave, analogously, and in good yields, thianthrene and, respectively, according to elemental analyses and nmr data, 4 (mp 142-3°, dec) and 5 (mp 162-3°, dec). In contrast, but nevertheless in analogy with eq. 3, dimedone and ethyl benzoylacetate gave the ylides 6 (mp 249-250°) and 7 (mp 193-194°), respectively. It is evident that ylide formation in the last two reactions is facilitated by delocalization of the ylide's negative charge into the two carbonyl groups.



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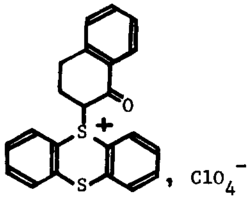

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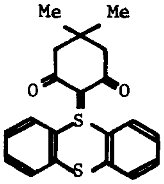

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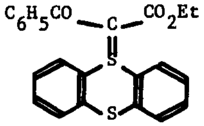

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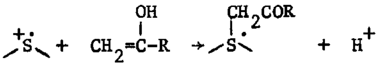
Anal. Calcd. for $C_{20}H_{18}S_2O_2$ (6): C, 67.77; H, 5.12; S, 18.08. Found: C, 67.73; H, 5.29; S, 18.61.

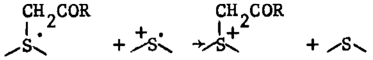
Anal. Calcd. for $C_{23}H_{18}S_2O_3$ (7): C, 67.98; H, 4.45; S, 15.74. Found: C, 68.04; H, 4.37; S, 15.32.

To our knowledge reaction of cation radicals with ketones has not been reported before.

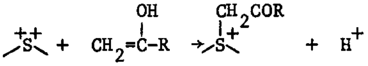
The most probable pathway for these new reactions is the addition of the cation radical (eq. 6 and 7) or the dication (eq. 8) formed in disproportionation of the cation radical,[6] to the enol. We are in the process of testing these pathways kinetically.



$$\overset{+\cdot}{S} + CH_2{=}\overset{OH}{\overset{|}{C}}-R \rightarrow \overset{CH_2COR}{\overset{|}{\dot{S}}} + H^+ \quad (6)$$



$$\overset{CH_2COR}{\overset{|}{\dot{S}}} + \overset{+\cdot}{S} \rightarrow \overset{CH_2COR}{\overset{|}{S^+}} + S \quad (7)$$



$$\overset{++}{S} + CH_2{=}\overset{OH}{\overset{|}{C}}-R \rightarrow \overset{CH_2COR}{\overset{|}{S^+}} + H^+ \quad (8)$$

Although it is our practice to use solutions of previously isolated, solid **1** for these reactions, we have also prepared **2a** by anodic oxidation of thianthrene in acetone solution using tetra-*n*-butylammonium perchlorate as electrolyte.[7] We anticipate that such anodic oxidations will make the synthesis of sulfonium salts such as **2** and sulfonium ylides wider in scope than available by use of isolated organosulfur cation radical perchlorates. Further details of reactions of **1** and some analogues will be published.

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1. Supported by the National Science Foundation, Grant No. GP-25989X.
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7. Dr. B. K. Bandlish, unpublished work.