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Reactions of Sulfur Dichloride with Active Methylene Compounds. A New Synthesis of 1,3-Dithietanes

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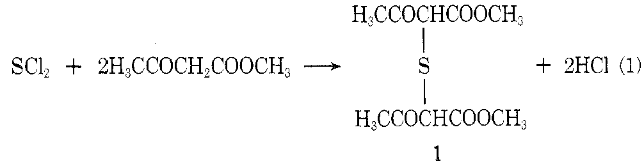
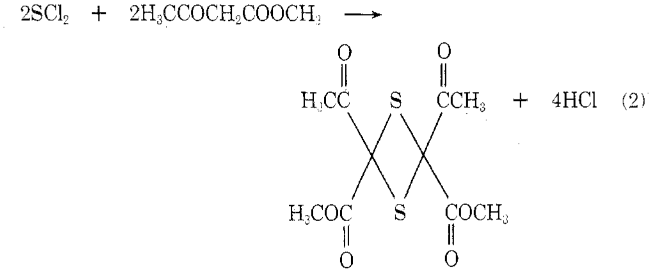
Sulfur dichloride (SCl_2) reacts with active methylene compounds under mild conditions to give sulfurated products in good yields. The course of product formation was dependent upon the reactivity of the active methylene moiety and the stoichiometry of the reaction. For example, sulfides 1 were produced with sulfur dichloride and a β-keto ester in a 1:2 ratio (eq 1).



$$SCl_2 + 2H_3CCOCH_2COOCH_3 \longrightarrow \begin{array}{c} H_3CCOCHCOOCH_3 \\ | \\ S \\ | \\ H_3CCOCHCOOCH_3 \end{array} + 2HCl \quad (1)$$

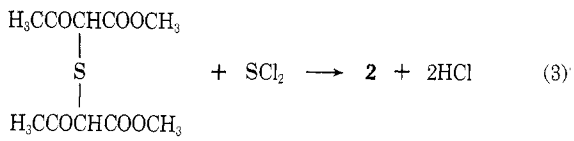
1

However, 1,3-dithietanes (2) were obtained when the stoichiometry of this reaction was changed according to eq 2.



2

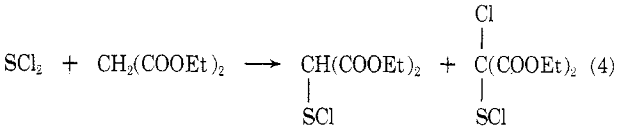
1,3-Dithietanes (2) were also synthesized by the reaction of sulfur dichloride with sulfides 1 (eq 3).



$$\begin{array}{c} H_3CCOCHCOOCH_3 \\ | \\ S \\ | \\ H_3CCOCHCOOCH_3 \end{array} + SCl_2 \longrightarrow 2 + 2HCl \quad (3)$$

1

Diethyl malonate, in sharp contrast to the results on the reaction of β-diketones and β-keto esters with SCl_2, reacted with sulfur dichloride according to eq 4.

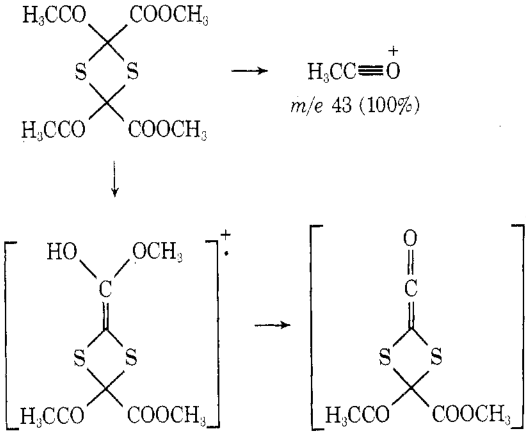


$$SCl_2 + CH_2(COOEt)_2 \longrightarrow \begin{array}{c} CH(COOEt)_2 \\ | \\ SCl \end{array} + \begin{array}{c} Cl \\ | \\ C(COOEt)_2 \\ | \\ SCl \end{array} \quad (4)$$

The representative examples of the reactions of sulfur dichloride with active methylene compounds and the characterization data of the resultant products are summarized in Table I.[1]

A noteworthy feature of the reactions of sulfur dichloride reported here is the ready synthesis of 1,3-dithietanes (2) from β-diketones and β-keto esters. The structure of these 1,3-dithietanes is based on their nmr (absence of active methylene or methine hydrogens) and C, H, S analytical data. In addition to this, the mass spectral fragmentation pattern of 2 was similar to that expected for disubstituted β-keto esters (Scheme I),[2] and their desulfurization with Raney nickel regenerated the corresponding β-keto ester starting material.

Scheme I



m/e 43 (100%)

m/e 250 (M−42)

m/e 218

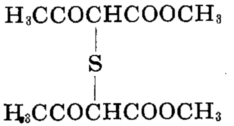
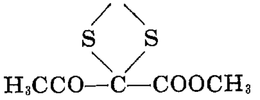
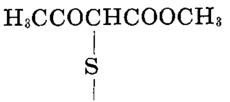
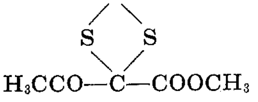
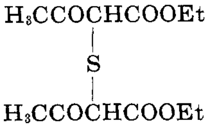
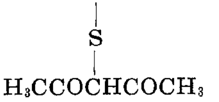
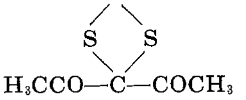
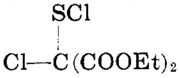
The sulfides 1 are capable of existence in meso or *dl*-pair configuration. The 1,3-dithietanes of type 2, on the other hand, may involve cis-trans isomerism. Assignments in this regard have not been established and are beyond the scope of our current interests in this area.

Although the reactions of sulfenyl halides with various organic compounds are well known,[3] it is surprising that only few reactions of sulfur dichloride with organic compounds have so far been explored. These examples include the addition of SCl_2 to olefins,[3,4] dienes,[3,5] and carbon suboxide,[6] and the brief report on the reaction of SCl_2 with ethyl acetoacetate[7] and β-diethylaminoacrolein.[8] The present sequence of reactions thus opens a new area in organosulfur chemistry with many mechanistic and synthetic possibilities.

Experimental Section[9]

Reaction of Sulfur Dichloride with Active Methylene Compounds in a 1:2 Ratio. Bis(α-carbomethoxyacetonyl) Sulfide (1). A solution of 29.03 g (250 mmol) of methyl acetoacetate in 100 ml of ethyl acetate was cooled to 10° and then 14.4 g (125 mmol) of sulfur dichloride was added to it in 10 min with efficient stirring. The stirring was continued for an additional 1 hr at 25° and the

Table I
Reactions of Sulfur Dichloride with Active Methylene Compounds to Give Sulfurated Products[a]

Active methylene compound, reacted (registry no.)	SCl_2/active methylene ratio	Product isolated (registry no.)	Yield,[b] %	Mp, °C	Nmr[c]	Mol wt[d]
$H_3CCOCH_2COOCH_3$ (105-45-3)	0.5	 $H_3CCOCHCOOCH_3$ S $H_3CCOCHCOOCH_3$	65	141–143	2.41 (s, 3 H), 3.76 (s, 3 H), and 13.33 (s, 1 H)	262
	1	 (51270-70-3)	25	125–126	2.60 (s, 1) and 3.85 (s, 1)	292 (294)
 $H_3CCOCHCOOCH_3$ S $H_3CCOCHCOOCH_3$ (51270-69-0)	1.1		50	125–126	2.60 (s, 1) and 3.85 (s, 1)	292
H_3CCOCH_2COOEt (141-97-9)	0.5	 $H_3CCOCHCOOEt$ S $H_3CCOCHCOOEt$ (51270-71-4)	70	123–124[e]	1.28 (t, 3 H, J = 6.5 Hz), 2.41 (s, 3 H), 4.24 (q, 2 H, J = 6.5 Hz), and 13.45 (s, 1 H)	290
$H_3CCOCH_2COCH_3$ (123-54-6)	0.5	 $H_3CCOCHCOCH_3$ S $H_3CCOCHCOCH_3$ (31655-65-9)	70	104.5–105.5	2.35 (s, 6 H) and 16.9 (s, 1 H)	230
	1	 (51270-72-5)	30	165–166.5	2.4 (s)	262 (257)
$EtOCOCH_2COOEt$ (105-53-3)	2.5	$ClCH(COOEt)_2$ + (14064-10-9)  SCl $Cl—C(COOEt)_2$[f] (51270-73-6)		91–108[g] (0.3 mm)		

[a] Satisfactory analytical values (±0.3% for C, H, S) were reported for all compounds in table. Ed. [b] By isolation. [c] In $CDCl_3$ using TMS as internal standard at 0 ppm. [d] By mass spectrometry. The values in parentheses are by osmometry (benzene). [e] Lit.[8] mp 83–85.5°. [f] The mixture of products isolated by distillation was identified by glpc [$ClCH(COOEt)_2$] and mass spectrometry [$ClCSCl(COOEt)_2$]. [g] Boiling point of the mixture of two products.

reaction mixture was then cooled to 0°. The solid thus precipitated was filtered and washed with 10 ml of cold ethyl acetate to give 21.2 g (65%) of the desired product, mp 140–142°. Recrystallization from hot ethyl acetate provided the pure substance: mp 141–143°; mass spectrum (70 eV) *m/e* (rel intensity) 262 (0.08), 188 (0.1), 156 (0.09), 116 (0.09), 85 (0.11), 69 (0.07), 59 (0.08), 43 (100).

Reaction of Sulfur Dichloride with Active Methylene Compounds in a 1:1 Ratio. 2,4-Bis(acetyl)-2,4-bis(carbomethoxy)-1,3-dithietane (2). Methyl acetoacetate (29.03 g, 250 mmol) was dissolved in 50 ml of chloroform and then sulfur dichloride (28.8 g, 250 mmol) was added to it at 25° to 28° in 1.25 hr. The resulting yellow solution was stirred at 25° for 16 hr. The solvent was then removed under vacuum and the oil (43.6 g) crystallized upon cooling. The compound was triturated with diethyl ether (50 ml) and filtered. The solid thus obtained (15.6 g) was recrystallized from hot ethyl acetate to give the product as cubic crystals; yield 9.1 g (25%); mp 125–126°; mass spectrum (70 eV) *m/e* (rel intensity) 292 (0.001), 250 (0.04), 233 (0.2), 218 (0.31), 191 (0.22), 175 (0.05), 104 (0.07), 103 (0.07), 43 (100).

Reaction of Bis(α-carbomethoxyacetonyl) Sulfide (1) with Sulfur Dichloride. The sulfide 1 (2.62 g, 10 mmol) was dissolved in 10 ml of chloroform and then a solution of sulfur dichloride (1.1 g, 11 mmol) in chloroform (5 ml) was added to it at 10°. The resulting yellow solution was stirred for 16 hr at 25°. The solvent was then removed and the residue upon trituration with diethyl ether (10 ml) gave **2** as a crystalline product, yield 2.0 g. Recrystallization from ethyl acetate afforded 1.41 g (50%) of pure substance, mp 124–126°.

Reaction of Diethyl Malonate with Sulfur Dichloride. Diethyl malonate (40 g, 250 mmol) was added to sulfur dichloride (65.3 g, 625 mmol) at 10° in 0.5 hr. After the resulting yellow solution was stirred at 25° for 16 hr, the solvent was removed *in vacuo* to give an oil. The distillation provided 23.7 g of a yellow liquid, bp 91–108° (0.3 mm). Glpc analysis indicated it to be a mixture of two compounds (Table I).

Desulfurization of 2,4-Bis(acetyl)-2,4-bis(carbomethoxy)-1,3-dithietane (2) with Raney Nickel.[5] A mixture of **2** (2.92 g, 10 mmol) and 10 g of Raney nickel in 50 ml of ethanol was refluxed under nitrogen for 6 hr. Glpc analysis indicated the presence of methyl acetoacetate in the reaction mixture.

Acknowledgments. The author wishes to thank Dr. R. K. Blackwood for discussions and Mr. H. J. Slater for technical assistance.

Registry No.—Sulfur dichloride, 10545-99-0.

References and Notes

(1) Unless specified otherwise, all compounds in Table I with yields given are new.

(2) J. H. Bowie, S.-O. Lawesson, G. Schroll, and D. H. Williams, *J.*

Amer. Chem. Soc., **87**, 5742 (1965). For a recent synthesis of certain 1,3-dithietanes, see J. J. Worman, M. Shew, and P. C. Nichols, *Can. J. Chem.*, **50**, 3923 (1972).

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(7) A. Delisle, *Ber.*, **22**, 306 (1889). For a related reaction of a bissulfenyl halide with a β-keto ester, see C. M. Leir, *J. Org. Chem.*, **37**, 887 (1972).

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(9) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Glpc analyses were performed on a DC-550, 5% on Chromosorb W, 5 ft × 0.25 in. column. Sulfur dichloride was freshly distilled and stored at 0° before use. Microanalyses were performed by Mr. T. Toolan and Miss A. McLellan of the Analytical Research Department.

7(S)-Acetoxy-2(S)-methoxy-1(S)-3,6,8-trioxabicyclo[3.2.1]octane.[1] Characterization of the Product from Periodic Acid Oxidation of Methyl β-L-Arabinopyranoside in Methyl Sulfoxide[3]

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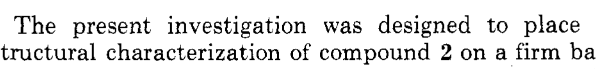
It was shown by Yu and Bishop[2] that methyl β-L-arabinopyranoside (1) in methyl sulfoxide containing excess periodic acid consumes only one mole per mole of oxidant, presumably through C-3–C-4 glycol cleavage, as borohydride reduction and subsequent acid hydrolysis of the product gave a volatile compound chromatographically indistinguishable from ethylene glycol. The lack of further oxidation was attributed to rapid internal cyclization of the initial dialdehyde to afford a tricyclic product containing no group labile to the glycol-cleavage oxidant. Acetylation of the oxidized **1** gave a mixture from which was isolated a 38% yield of a crystalline monoacetate **2**, mp 89–90°, $[\alpha]^{22}{}_{D}$ +44° (chloroform). Based on the presumption of C-3–C-4 cleavage in **1**, a structure of type A was assigned.[2] However, the modest yield of **2** leaves open the conceivable possibility that it could have arisen *via* C-2–C-3 cleavage in **1**, to generate an acetate having a structure of type B.

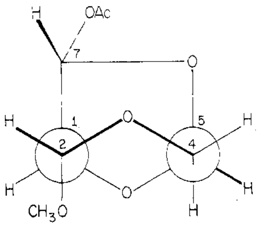


The present investigation was designed to place the structural characterization of compound **2** on a firm basis. Such products are useful matrices in which to examine, with dioxolane and 1,4-dioxane ring systems, the types of anomeric equilibria and polar anomeric effects that have already been studied extensively in this laboratory with respect to polysubstituted tetrahydropyran ring systems derived from sugars.[5] Related equilibria have also been investigated by one of us in racemic tricyclic analogs obtained from glycerol and dicarbonyl compounds.[6]

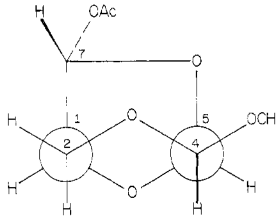
Mass spectral data for **2** include a weak (0.3% of the base peak) molecular ion (m/e 204) consistent with a formulation of $C_8H_{12}O_6$, relatively small fragments corresponding to the loss of $CH_3O\cdot$ at m/e 173 (0.3%) and of $CH_3CO_2\cdot$ at m/e 145 (4.7%), more prominent fragments at m/e 43 (100%), 103 (21%), and 145 (4.7%) characteristic of acetate groups, and a metastable-verified elimination of ketene at m/e 129–87 (m*, 58.8). These data accord with the formulation of a monomeric, monoacetylated, methyl acetal structure for **2**.

Also consistent with the formulation $CH_3O(C_5H_6O_3)OCOCH_3$ for compound **2** is the 22.3-MHz ^{13}C nmr spectrum in chloroform-*d*, which exhibits eight separate resonances assignable, respectively, to the acetate methyl group [δ^{C} (Me_4Si) +27.0], the *O*-methyl group (61.4), singly oxygenated methylene (69.1) and methine (85.8) carbon atoms, three doubly oxygenated carbon atoms (100.3, 101.5, and 109.0), and an acetate carbonyl carbon atom (176.7). Lacking appropriate reference compounds, specific assignments of the three acetal carbon atoms must be deferred. The shift of the methylene carbon atom corresponds fairly closely to the shifts (66.7–66.8) measured[7] for the resonance of the analogous methylene carbon atoms in some 4-alkoxy-5-methyl-3,6,8-trioxabicyclo[3.2.1]octanes in which the alkoxyl group has been shown[6] to adopt the axial disposition.

Four pairs of diastereoisomers could, in principle, exist for structure A, and a similar number for B. In actuality, however, a number of these possibilities may be excluded because the stereochemistry at the anomeric carbon atom of 1 and at the hydroxylated carbon atom that is *not* oxidized is retained in the final product; furthermore, the stereochemistry at the bridgehead acetal carbon atom is determined by the orientation of the unoxidized alcoholic center. These considerations decrease the possibilities to two pairs of compounds epimeric at C-7. In each pair the endo isomer would presumably experience sufficient destabilization due to repulsive interactions with O-3 to preclude the formation of this isomer. This conclusion is supported by the earlier observation that the resonance of H-7 in this molecule gives rise to a very narrow singlet, an observation consistent only with the location of this proton in the endo orientation[2] because of the ~90° dihedral relationship between the bond to the adjacent bridgehead proton (H-1) and the 7 endo bond.



A′



B′

Only two structural possibilities remain for **2**, namely, A′ and B′. Specific evidence permitting selection between these two structures is suggested in the 60-MHz ^1H nmr spectrum of **2** published by Yu and Bishop,[2] although the resolution in that spectrum is insufficient to permit extraction of the necessary coupling information. The ^1H nmr spectrum of **2** in chloroform-*d* was redetermined at 100 MHz with a sample that had been deoxygenated with a stream of nitrogen. Well-separated signals are observed for each of the six ring protons, permitting[8] extraction of a complete set of reliable, first-order coupling constants for this molecule. These values, which were measured from 100-Hz sweeps, were verified by double-irradiation experiments. As with other examples[9,10] of bicyclo[3.2.1]octane derivatives, long-range coupling interactions of the "W" and extended-"W" type[8] abound. See Table I.

A closely related compound, (racemic) 1,4,4-trimethyl-3,6,8-trioxabicyclo[3.2.1]octane (3), exhibits[10] two long-range couplings whose presence or absence can be used to