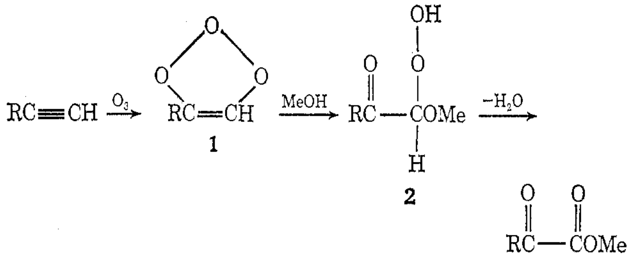
TABLE I

Registry no.	Starting material	Registry no.	α-Keto ester obtained[a]	Bp, °C (mm)	Yield, %
1119-64-8	$C_4H_9C\equiv CBr$	6395-83-1	$C_4H_9COCOOMe$	48–52 (12)	40
38761-67-0	$C_6H_{13}C\equiv CBr$	41172-04-7	$C_6H_{13}COCOOMe$	82–85 (5)	50
932-87-6	$PhC\equiv CBr$	15206-55-0	$PhCOCOOMe$	87–90 (2)	50

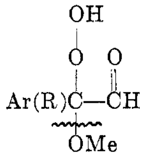
[a] The ir, pmr, and mass spectra are identical with those of authentic specimens.

SCHEME I



1-Hexyne, 1-octyne, and phenylacetylene were used as starting materials. The ozonation reaction was carried out in dry methanol, and $SOCl_2$ was used for the dehydration.

The corresponding α-keto methyl esters were prepared in 10–20% yield. The reason for the low yield is probably because the cleavage of the unstable intermediate **1** is controlled by resonance and inductive effects which promote the formation of α-hydroperoxy-α-methoxy aldehydes such as **3**;[3] dehydration of these compounds does not give α-keto esters.



3

The above reaction was then modified using 1-bromoacetylenes, which are readily available from terminal acetylenes by treatment with alkaline aqueous solutions of sodium or potassium hypobromite,[4] as starting materials. The bromine atom was introduced assuming that it would facilitate zwitterion formation on the terminal carbon atom, while zwitterion formation on the "internal" carbon atom should give an acylic bromine easily esterified by methanolic acylation.

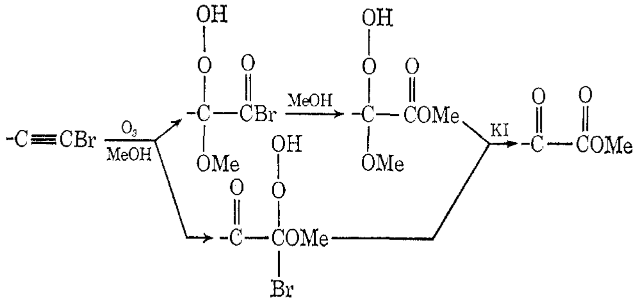
Finally, the ozonolysis of 1-bromoacetylenes in methanol solution should give two peroxides, both of which can be converted to α-keto esters by reduction with potassium iodide (Scheme II).

By this route, 1-bromohexyne,[5] 1-bromooctyne,[6] and bromophenylacetylene[7] were converted to the corresponding α-keto esters in 40–50% yields (Table I).

In both reactions considerable amounts of the carboxylic acid methyl esters were obtained as side products from the decomposition of the intermediate hydroperoxides in methanolic solution.[3,8]

The present work opens a new route to this important class of α-keto esters. Work is in progress on generalization of the method and on improving the yields.

SCHEME II



Experimental Section

α-Keto Methyl Esters from 1-Acetylenes. General Procedure.—An ozone–oxygen stream was passed through a solution of 0.04 mol of the terminal acetylene in 100 ml of dry methanol at −30°, until 90–95% of the starting material had reacted (determined by glc). The solvent was removed at low temperature under reduced pressure. Then 50 ml of cold, dry chloroform was added and a cold mixture of 7.3 ml (0.1 mol) of $SOCl_2$ and 16.1 ml (0.2 mol) of dry pyridine in 9 ml of dry chloroform was added dropwise with stirring at about −10°. The resulting mixture was allowed to warm to room temperature, added to water, and extracted with chloroform. The chloroform extract was neutralized with a saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Fractional distillation of the yellow-brown oil under reduced pressure gave the α-keto esters.

α-Keto Methyl Esters from 1-Bromoacetylenes. General Procedure.—An ozone–oxygen stream was passed through a solution of 0.04 mol of the 1-bromoacetylene in 100 ml of dry methanol at −30° until 90–95% of the starting material had reacted (determined by glc). Dry nitrogen was passed through the solution to remove excess ozone. Then 33.2 g (0.2 mol) of potassium iodide was added portionwise at about −30° with stirring. The reaction mixture was allowed to stand at room temperature for about 30 min and then 0.1 *N* aqueous sodium thiosulfate was added to neutralize the liberated iodine. The solution was extracted with ether, and the extract was dried over anhydrous sodium sulfate and evaporated under reduced pressure. Fractional distillation of the yellow-brown oil under reduced pressure gave the α-keto esters.

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[4] R. G. Viehe, "Chemistry of Acetylenes," Marcel Dekker, New York, N. Y., 1969, p 680.

[5] W. Chodkiewicz, *Ann. Chim. (Paris)*, **2**, 819 (1957).

[6] G. Eglington and W. McCrae, *J. Chem. Soc.*, 2295 (1963).

[7] S. I. Miller, G. R. Ziegler, and R. Wieleseck, *Org. Syn.*, **45**, 86 (1965).

[8] P. S. Bailey and Y.-G. Chang, *J. Org. Chem.*, **27**, 1192 (1962).

The Preparation of Diacyl Dithiosulfites

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Although esters of sulfurous acid, $(RO)_2SO$, are readily prepared from alcohols and thionyl chloride,[1] thio esters of sulfurous acid, $(RS)_2SO$, have not been reported.

Mercaptans react with thionyl chloride to give the corresponding disulfides and trisulfides instead of the thio esters.[2] On the other hand, Tommasi reported

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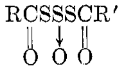
[1] W. E. Bessinger and F. E. Kung, *J. Amer. Chem. Soc.*, **69**, 2158 (1947).

[2] B. Holmberg, *Justus Liebigs Ann. Chem.*, **359**, 81 (1908); B. Holmberg, *Ber.*, **43**, 226 (1910); S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Petrol. Technol.*, **39**, 206 (1953).

TABLE I[a]

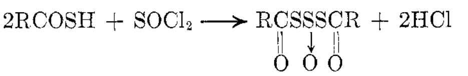

$\mathrm{R\underset{\underset{O}{\|}}{C}S\underset{\underset{O}{\downarrow}}{S}S\underset{\underset{O}{\|}}{C}R'}$

Compd	R	R′	Mp, °C	Yield, %	Ir (KBr), cm^{-1} C=O	Ir (KBr), cm^{-1} S→O
1a[b]	CH_3	CH_3	76–78	79	1705	1140
1b	CH_2Cl	CH_2Cl	66–67	30	1700	1150
1c	C_6H_5	C_6H_5	108–109	93	1675	1145
1d	p-ClC_6H_4	p-ClC_6H_4	130–131	94	1680	1145
1e	p-$O_2NC_6H_4$	p-$O_2NC_6H_4$	152–153	96	1680	1145
1f	o-$CH_3OC_6H_4$	o-$CH_3OC_6H_4$	95–96	84	1640	1120
3a	C_6H_5	p-ClC_6H_4	111–112	86	1675, 1600	1140
3b	C_6H_5	p-$O_2NC_6H_4$	130–131	90	1675, 1660	1145
3c	C_6H_5	o-$CH_3OC_6H_4$	106–107	85	1675, 1630	1130
3d	o-$CH_3OC_6H_4$	p-ClC_6H_4	110–111	73	1670, 1630	1135
3e	o-$CH_3OC_6H_4$	p-$O_2NC_6H_4$	115–116	92	1670, 1640	1130

[a] Satisfactory analytical data (±0.4% for C, H, and S) were reported for all new compounds listed in the table: Ed. [b] This compound was recrystallized from chloroform-petroleum ether (bp 30–70°) and analyzed; however, the melting point was not determined accurately for its instability.

the formation of diacetyl sulfite (acetic sulfurous anhydride) in the reaction of acetyl chloride with lead sulfite.[3] However, no attempt to prepare diacyl dithiosulfites (**1** or **3**), the sulfur analog of diacyl sulfites, has been reported. In this paper, the preparation of **1** and **3** by the reaction of thiocarboxylic acid with thionyl chloride is described.

The reaction of 2 mol of thiocarboxylic acid with 1 mol of thionyl chloride proceeded readily in ether under cooling, and symmetrical diacyl dithiosulfites (**1a–f**) were prepared in good yields (Table I). The

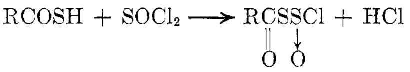

$$2RCOSH + SOCl_2 \longrightarrow \mathrm{R\underset{\underset{O}{\|}}{C}S\underset{\underset{O}{\downarrow}}{S}S\underset{\underset{O}{\|}}{C}R} + 2HCl$$

1

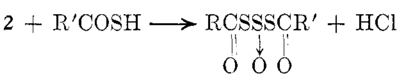
ir, nmr, and analytical values were in accord with the expected structure for **1a–f**. The ir of **1a–e** showed the carbonyl and sulfinyl absorptions in the region of 1705–1675 and 1150–1140 cm^{-1}, respectively, whereas **1f** showed the both absorptions at 1640 and 1120 cm^{-1} (Table I). **1c–f** were relatively stable and could be stored in a refrigerator for several months.

By the decomposition of **1a** or **1c** at the melting point, carboxylic anhydride and elementary sulfur were formed.

When the reaction mixture of 1 mol of thiocarboxylic acid and 1 mol of thionyl chloride was treated successively with 1 mol of another thiocarboxylic acid, unsymmetrical diacyl dithiosulfites (**3a–e**) were prepared (Table I). The sulfinyl absorption in ir of


$$RCOSH + SOCl_2 \longrightarrow \mathrm{R\underset{\underset{O}{\|}}{C}S\underset{\underset{O}{\downarrow}}{S}Cl} + HCl$$

2


$$\mathbf{2} + R'COSH \longrightarrow \mathrm{R\underset{\underset{O}{\|}}{C}S\underset{\underset{O}{\downarrow}}{S}S\underset{\underset{O}{\|}}{C}R'} + HCl$$

3

3c (1130 cm^{-1}) appeared in the region between those of **1c** (1145) and **1f** (1120). Similar results were also observed for **3d** and **3e**. The preparation of **3a–e** suggested the possibility of the formation of acyl thiochlorosulfinates (**2**) as interesting intermediates in the reaction.

Actually, when the reaction of thiobenzoic acid with thionyl chloride was carried out in concentrated solution, benzoyl thiochlorosulfinate (**2a**, R = Ph) was isolated. On standing at room temperature, **2a** decomposed in half a day to benzoic anhydride, benzoyl chloride, and sulfur. When **2a** was immediately allowed to react with p-nitrothiobenzoic acid, **3b** was obtained in a good yield.

Experimental Section

Materials.—Thioacetic acid and thiobenzoic acid were obtained commercially. Chlorothioacetic acid[4] and p-nitrothiobenzoic acid[5] were prepared by the methods of the literature. p-Chlorothiobenzoic acid, mp 70–71°, and o-methoxythiobenzoic acid, bp 101–103° (2 mm), were prepared in a way similar to the preparation of p-nitrothiobenzoic acid.

Symmetrical Diacyl Dithiosulfites (1a–f).—To a solution of 0.10 mol of thiocarboxylic acid in 150 ml of ether, 0.05 mol of thionyl chloride in 10 ml of ether was added dropwise over 0.5-hr period at −60 to −40°. The stirring was continued for additional 2 hr and then the temperature of the mixture was allowed to rise to −20 to −10°. The precipitated material was collected by filtration, washed with ether, and dried to obtain **1a–f**. The results are shown in Table I.

Decomposition of 1a.—**1a** (20.0 g, 0.11 mol) was heated at 75–80° for 1 hr under nitrogen atmosphere. On standing at room temperature, the mass turned to a yellow liquid mixed with elementary sulfur. Distillation of the liquid gave 6.5 g of acetic anhydride, bp 58–59° (39 mm).

Decomposition of 1c.—**1c** (19.2 g, 0.06 mol) was heated at 110–115° for 1 hr under nitrogen atmosphere. On standing at room temperature, the mass turned to a yellow liquid mixed with elementary sulfur. Distillation of the liquid gave 5.2 g of benzoic anhydride, bp 160–163° (1.5 mm).

Unsymmetrical Diacyl Dithiosulfites (3a–e).—To a solution of 0.02 mol of thionyl chloride in 60 ml of ether, 0.02 mol of thiocarboxylic acid in 20 ml of ether was added dropwise over 0.5-hr period at −40°. After the stirring was continued for additional 0.5 hr at −40°, 0.02 mol of another thiocarboxylic acid in a mixture of 10 ml of ether and 10 ml of THF[6] was added dropwise for 1 hr at −40°. The stirring was continued for additional 2 hr and then the temperature of the mixture was allowed to rise to −5°. The precipitated material was collected by filtration, washed with ether, and dried to obtain **3a–e**. The results are shown in Table I.

Benzoyl Thiochlorosulfinate (2a).—To a solution of 19.0 g (0.16 mol) of thionyl chloride in 30 ml of ether, 11.0 g (0.08 mol) of thiobenzoic acid in 10 ml of ether was added dropwise for 0.5 hr at −40°. The stirring was continued for additional 1 hr and

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(3) D. Tommasi, *Ber.*, **7**, 826 (1874).

(4) F. Arndt and N. Bekir, *Ber.*, **63**, 2390 (1930).

(5) A. M. Khaletskii and A. M. Yanovitskaya, *Zh. Obshch. Khim.*, **19**, 1193 (1949).

(6) o-Methoxythiobenzoic acid was dissolved in 20 ml of ether.

then the temperature of the mixture was allowed to rise to −20°. The precipitated material was collected by filtration, washed with petroleum ether, and dried to obtain 8.0 g (45%) of **2a** as white solid: mp 39–42°; ir (CS_2) 1665 (C=O), 1215 cm^{-1} (S → O).

Anal. Calcd for $C_7H_5ClO_2S_2$: C, 38.10; H, 2.28. Found: C, 38.68; H, 2.55.

Decomposition of 2a.—When 19.0 g (0.086 mol) of **2a** was allowed to stand at room temperature for 1 day, the mass turned to a yellow liquid mixed with elementary sulfur. Fractional distillation of the liquid gave 3.0 g of benzoyl chloride, bp 55–56° (4 mm), and 5.5 g of benzoic anhydride, bp 160–165° (1.5 mm).

Benzoyl *p*-Nitrobenzoyl Dithiosulfite (3b).—This sulfite was prepared by the reaction of 4.41 g (0.02 mol) of **2a** in 60 ml of ether with 3.66 g (0.02 mol) of *p*-nitrothiobenzoic acid in a mixture of 10 ml of ether and 10 ml of THF at −40°. The precipitated material was collected by filtration to obtain 6.79 g (93%) of **3b**, mp 129–130°.

Registry No.—**1a**, 41118-48-3; **1b**, 41118-49-4; **1c**, 41118-50-7; **1d**, 41118-51-8; **1e**, 41118-52-9; **1f**, 41118-53-0; **2a**, 41118-54-1; **2d**, 41118-55-2; **3a**, 41118-56-3; **3b**, 41118-57-4; **3c**, 41118-58-5; **3d**, 41118-59-6; **3e**, 41118-60-9; RCOSH (R = CH_3), 507-09-5; RCOSH (R = $ClCH_2$), 867-49-2; RCOSH (R = C_6H_5), 98-91-9; RCOSH (R = *p*-ClC_6H_4), 31143-03-0; RCOSH (R = *p*-$O_2NC_6H_4$), 39923-99-4; RCOSH (R = *o*-$CH_3OC_6H_4$), 41118-62-1; thionyl chloride, 7719-09-7; acetic anhydride, 108-24-7; benzoic anhydride, 93-97-0; benzoyl chloride, 98-88-4.

The Reaction of Phenyllithium with Cinnamyl Chloride

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The reaction of phenyllithium with cinnamyl chloride has been found to form the following mixture of hydrocarbons in the per cent yields indicated based on the cinnamyl chloride used: 3,3-diphenyl-1-propene (**1**) (0.2), *cis*-1,3-diphenylpropene (**2**) (0.2), *trans*-1,3-diphenylpropene (**3**) (23.1), *cis*-1,2-diphenylcyclopropane (**4**) (0.8), *trans*-1,2-diphenylcyclopropane (**5**) (12.8), 1,1-diphenyl-1-propene (**6**) (1.2), 1,6-diphenyl-1,5-hexadiene (**7**) (5.2), 1,6-diphenyl-1,3,5-hexatriene (**8**) (5.6), and benzylacetylene (**9**) (35.7). Identification of the various compounds was made by comparing their retention times and ir and nmr spectra with those of authentic samples.

The first five compounds are similar to those formed in the reaction of phenyllithium with 1-halo-2-butenes[2] and result by either displacement reactions of phenyllithium on cinnamyl chloride (**1**, **2**, **3**)[3] or through an intermediate carbene followed by cyclization to phenylcyclopropene that reacts further with phenyllithium and forms **4** and **5**.[4] The ratio (94.1:5.9) of *trans*-1,2-diphenylcyclopropane (**5**) to *cis*-1,2-diphenylcyclopropane (**4**) found was similar to that (94:6) found for the 1-methyl-2-phenylcyclopropanes[2] and substantiated such a reaction.

The formation of the other products isolated can be rationalized in the following manner. 1,1-Diphenyl-1-propene (**6**) is formed by the isomerization of **1** by phenyllithium or by heat. 1,6-Diphenyl-1,5-hexadiene (**7**) is produced by the chlorine–lithium exchange

$$C_6H_5CH{=}CHCH_2Cl \xrightarrow{C_6H_5Li} C_6H_5CH{=}CHCH_2Li \xrightarrow{C_6H_5CH{=}CHCH_2Cl} \mathbf{7}$$

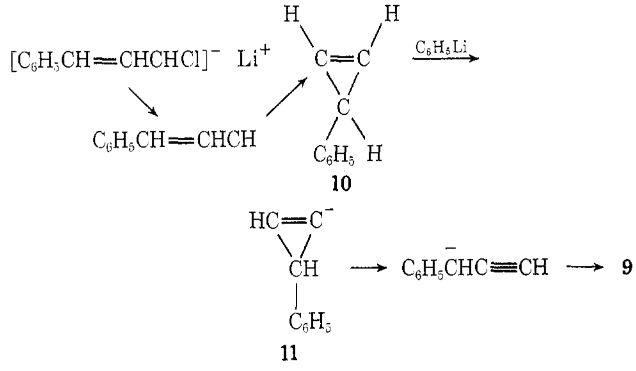
of cinnamyl chloride followed by coupling with another molecule of cinnamyl chloride.

1,6-Diphenyl-1,3,5-hexatriene (**8**) is probably formed by the dimerization of the intermediate carbene. Evidence for its presence in the crude reaction mixture was obtained by ultraviolet spectroscopy; a curve was obtained with three shoulders corresponding to the absorption peaks for the triene at 372, 353, and 336 nm. These peaks were better developed in the uv examination of the fraction boiling at 115–140° obtained by distillation of the mixture at reduced pressure (0.8 mm). This temperature is below that required to isomerize the diolefin **7** to the triene.[5]

Benzylacetylene (**9**) is probably formed by an elimination of hydrogen chloride from cinnamyl chloride with the formation of phenylallene, which would be isomerized by phenyllithium to **9**.

A second possible source of **9** is the intermediate phenylcyclopropene (**10**) formed by the action of phenyllithium on cinnamyl chloride.[4]

The vinyl hydrogens in cyclopropenes are acidic[6] enough to react with phenyllithium and form a carbanion (**11**) which would isomerize to **9**. Such a rearrangement of a cyclopropene to an acetylene has thus far been only carried out thermally with cyclopropene and 1-methylcyclopropene.[7]



Attempts to prepare 3-phenylcyclopropene for the verification of this reaction were not successful. The reaction of phenylacetylene with methylene iodide and zinc–copper couple gave methylphenylacetylene. Lead tetraacetate oxidation and electrolytic oxidation of 3-phenylcyclopropane-*cis*-1,2-dicarboxylic acid[8] gave no hydrocarbon products. Thermolysis of 3-phenylcyclopropane-*trans*-1,2-di-*tert*-butyl perester gave acetone, methanol, and polymer.

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[1] Abstracted in part from the Ph.D. Thesis of A. R. Z., 1966.

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[4] J. G. Welch and R. M. Magid, *J. Amer. Chem. Soc.*, **89**, 5300 (1967).

[5] H. P. Koch, *J. Chem. Soc.*, 1111 (1948).

[6] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963).

[7] R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 6250 (1969).

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