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REDUCTION OF SEMIPOLAR SULPHUR LINKAGES WITH CARBODITHIOIC ACIDS AND ADDITION OF CARBODITHIOIC ACIDS TO OLEFINS

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Abstract—Carbodithioic acids react with trivalent sulphur compounds bearing semipolar linkages (sulphoxides, sulphonium ylides and sulphilimines), to give the corresponding sulphides and add to olefins to afford dithioesters. The orientation of olefin addition is controlled by the olefin nature. Michael type addition takes place with olefins bearing an electron-withdrawing group α to the double bond while Markownikoff addition occurs with olefins bearing an electron-donating group. With vinyl and allyl sulphoxides, both addition and reduction took place simultaneously, and new dithioesters were obtained.

XANTHIC ($ROCS_2H$), dithiocarbamic (R_2NCS_2H) and carbodithioic (RCS_2H) acids all belong to the dithioic acid family. The two former dithioic acids have been widely used in industry but carbodithioic acids are not popular because of their extreme unpleasantness and limited stability. However, carbodithioic acids, analogous to both thiols and carboxylic acids, are of interest because of their strongly acidic nature, i.e. they are more acidic than the corresponding carboxylic acids and thiols. (*pKa*: 2·55 for CH_3CS_2H, 4·75 for AcOH,[1] 7·47 for PhSH[2]) Except for the reaction with amines, e.g. ammonia gives thioamides,[3] there has been practically no work reported on carbodithioic acids.

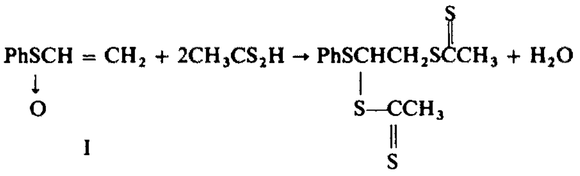
$$RCS_2H + NH_3 \rightarrow RCSNH_2 + H_2S$$

It is well known that thiols or their sodium salts react readily with olefins to form adducts by either radical or nucleophilic reaction, though electrophilic addition of thiols to olefins is rather rare because of the weakly acidic nature of most thiols.[4] However, a strongly acidic organic acid such as trichloroacetic acid will react with a cyclic enamine to form a somewhat unstable trichloromethyl derivative with evolution of CO_2.[5] Therefore, carbodithioic acids, being fairly strong, should show interesting chemical reactions with olefins or other nucleophilic substrates. Thus, we investigated the reduction of trivalent sulphur compounds, i.e., sulphoxides, sulphonium ylides and sulphilimines to the corresponding sulphides with carbodithioic acids and the addition of the acids to olefins giving the corresponding dithioesters, and found the reactions to go very smoothly probably because of the facile protonation by carbodithioic acids. This paper describes a detailed account of the investigation.

RESULTS AND DISCUSSION

Reaction of dithioacetic acid with phenyl vinyl sulphoxide and allyl phenyl sulphoxide

When phenyl vinyl sulphoxide (I) (1 mole) was added to dithioacetic acid (2 mole) at room temperature, an exothermic reaction occurred and 1,2-bis(dithioacetoxy)-ethyl phenyl sulphide (II) was obtained nearly quantitatively.



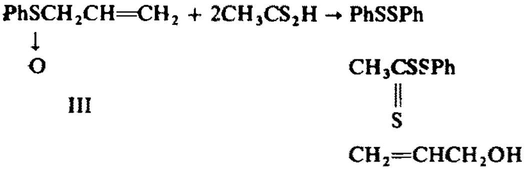
$$\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{PhSCH}} = \mathrm{CH_2} + 2\mathrm{CH_3CS_2H} \rightarrow \mathrm{PhS}\underset{\substack{|\\ \mathrm{S{-}CCH_3}\\ \|\\ \mathrm{S}}}{\mathrm{CH}}\mathrm{CH_2S}\overset{\substack{\mathrm{S}\\ \|}}{\mathrm{C}}\mathrm{CH_3} + \mathrm{H_2O}$$

I

II

This product is formally a reduction–addition product from phenyl vinyl sulphoxide and dithioacetic acid. However, in the reaction of allyl phenyl sulphoxide (III) with dithioacetic acid, allyl phenyl sulphide (IV), the reduction product of sulphoxide (III), was obtained with minor products such as diphenyl disulphide (V), phenyl trithioperacetate (VI) and allyl alcohol (VII).

$\mathrm{PhSCH_2CH{=}CH_2}$ IV



$$\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{PhSCH_2CH{=}CH_2}} + 2\mathrm{CH_3CS_2H} \rightarrow \mathrm{PhSSPh}$$

$$\mathrm{CH_3}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{SSPh}$$

$$\mathrm{CH_2{=}CHCH_2OH}$$

III

V

VI

VII

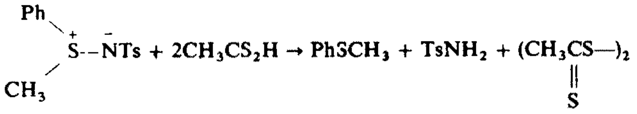
These observations show clearly that dithioacetic acid behaves as a reducing agent for sulphoxides and also adds to unsaturated bonds. In order to study the nature of these reactions in detail and also the relative ease of the reduction of sulphoxides and the addition of carbodithioic acids to olefins, we carried out both the reduction of trivalent sulphur compounds and the addition to various olefins with both dithiobenzoic and dithioacetic acids.

Reduction of sulphoxides, sulphilimines and sulphonium ylides

The general formula for the reaction is

$$\mathrm{R_2\overset{+}{S}{-}\overset{-}{X}} + \mathrm{CH_3CS_2H} \rightarrow \mathrm{R{-}S{-}R} \quad \mathrm{X} = \mathrm{{-}O, {-}NTs, {-}C(COOCH_3)_2}$$

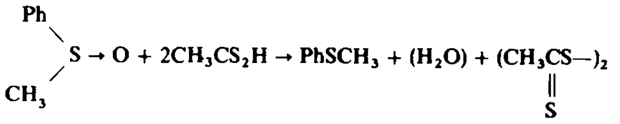
When methyl phenyl N-tolylsulphonylsulphilimine (1 mole) was added to dithioacetic acid (2 mole) at room temp, an exothermic reaction took place, and methyl phenyl sulphide and *p*-toluenesulphonamide were obtained nearly quantitatively together with a minute amount of reddish oil.



$$\begin{matrix}\mathrm{Ph}\diagdown\\ \\ \mathrm{CH_3}\diagup\end{matrix}\mathrm{\overset{+}{S}{-}\overset{-}{N}Ts} + 2\mathrm{CH_3CS_2H} \rightarrow \mathrm{PhSCH_3} + \mathrm{TsNH_2} + (\mathrm{CH_3}\underset{\substack{\|\\ \mathrm{S}}}{\mathrm{C}}\mathrm{S{-}})_2$$

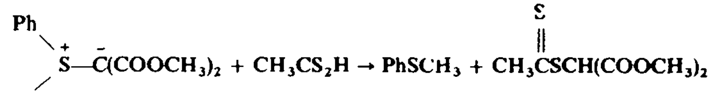
VIII

Similarly, the reduction of sulphoxides proceeded smoothly, giving the corresponding sulphides in good yields although dimethyl sulphone was not reduced at all.



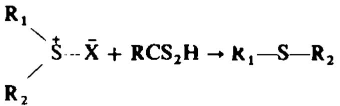
VIII

Methyl phenyl sulphonium bis(methoxycarbonyl)methylide (1 mole) was also reduced readily by dithioacetic acid (1 mole) giving good yields of phenyl methyl sulphide and dimethyl dithioacetoxymalonate (IX). (Table 1).



IX

TABLE 1. REDUCTION OF SULPHOXIDES, SULPHILIMINES AND SULPHONIUM YLIDES TO THE CORRESPONDING SULPHIDES BY CARBODITHIOIC ACIDS

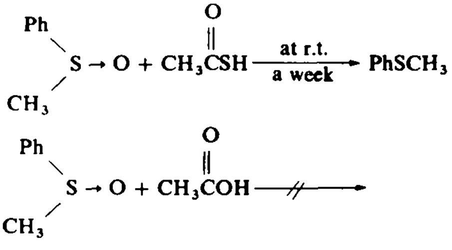


$X = —O, —NTs, —C(COOCH_3)_2$

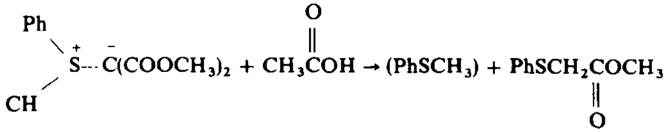
R_1	R_2	Product*	Yield
CH_3	CH_3	CH_3SCH_3	quantitatively
CH_3	Ph	CH_3SPh	quantitatively
CH_3	Et	CH_3SEt	quantitatively
Ph	Et	PhSEt	quantitatively
Ph	CH_2Ph	$PhSCH_2Ph$	quantitatively
Ph	Ph	PhSPh	quantitatively

* Other products (H_2O), $(CH_3CSS—)_2$ for $X = —O$
$TsNH_2$, $(CH_3CSS—)_2$ for $X = —NTs$
$CH_3CSSCH(COOCH_3)_2$ for $X = —C(COOCH_3)_2$
H_2O and $(CH_3CSS—)_2$ were not identified. The latter has not been characterized

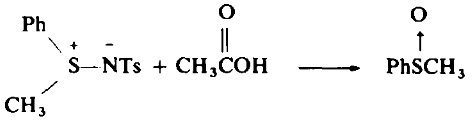
In the reactions of sulphilimines and sulphoxides with CH_3CSSH, dithioacetyl disulphide (VIII) has to be formed initially but under these conditions was not isolated. (experimental) Reduction rate was markedly affected by the groups present on the sulphur atom, e.g. dimethyl sulphoxide was reduced more readily than methyl phenyl sulphoxide, which reacted more readily than diphenyl sulphoxide. Under the same conditions reduction of sulphoxides to the corresponding sulphides with thiolacetic acid took about a week[6] while AcOH did not react at all.[7]



In the reaction of methyl phenyl sulphonium bis(methoxycarbonyl)methylide with AcOH, no reduction product was formed but methyl phenylmercaptoacetate[8] obtained, while methyl phenyl sulphilimine gave the corresponding sulphoxide.[9]

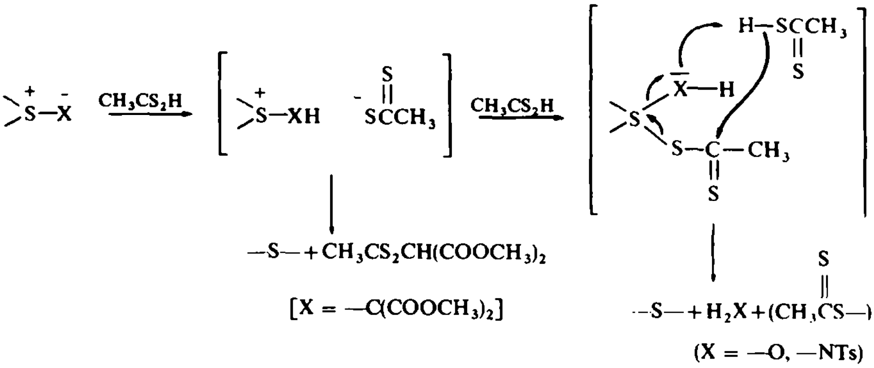


$$\mathrm{Ph(CH)\overset{+}{S}\text{—}\overset{-}{C}(COOCH_3)_2 + CH_3\overset{\overset{O}{\|}}{C}OH \rightarrow (PhSCH_3) + PhSCH_2\underset{\underset{O}{\|}}{C}OCH_3}$$

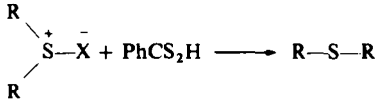


$$\mathrm{Ph(CH_3)\overset{+}{S}\text{—}\overset{-}{N}Ts + CH_3\overset{\overset{O}{\|}}{C}OH \longrightarrow Ph\overset{\overset{O}{\uparrow}}{S}CH_3}$$

Thus, dithioacetic acid displays different chemical behaviour from those of AcOH and thiolacetic acid. The initial step of the reaction is undoubtedly the protonation of the terminal x group by dithioic acid to give a sulphonium salt, which upon reaction with another molecule of dithioic acid eventually collapses to form products *via* somewhat different paths that vary with the nature of group x.



Dithiobenzoic acid also reduces trivalent sulphur compounds to the corresponding sulphides in high yields.



$$\mathrm{R_2\overset{+}{S}\text{—}\overset{-}{X} + PhCS_2H \longrightarrow R\text{—}S\text{—}R}$$

Thus, these carbodithioic acids are mild reducing agents for sulphoxides, sulphilimines and sulphonium ylides.

Addition reaction to olefins

The formation of the addition product in the reaction of phenyl vinyl sulphoxide implies that dithioacetic acid can easily add to olefins as in the reaction of thiols with unsaturated compounds. Dithioic acids are usually much stronger acids than commonly known thiols while a terminal mercapto group is quite nucleophilic. Therefore, it is expected that dithioic acids will behave both as good nucleophiles adding to electrophilic olefins such as acrylonitrile and vinylpyridine and also as electrophiles undergoing electrophilic addition to such nucleophilic olefins as styrene and vinyl ether. In fact, all these addition reactions of dithioacetic acid with several different olefins went smoothly without any acid or base even with electrophilic olefins that undergo Michael type additions.

With vinyl ether, vinyl thioether and 2-vinylpyridine the reaction proceeded exothermically, with the other olefins it was necessary to heat the mixture in CCl_4.

The results of the additions in Tables II and III are divided into two classes, namely, the Markownikoff and the Michael type additions.

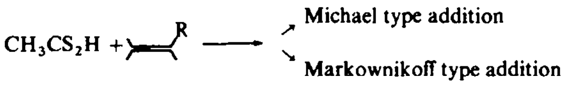


TABLE 2. MARKOWNIKOFF TYPE ADDITION PRODUCTS

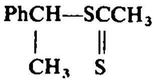
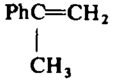
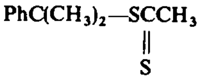
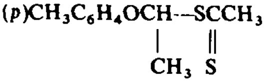
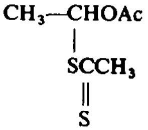
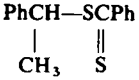
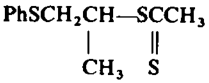
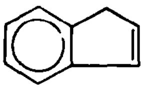
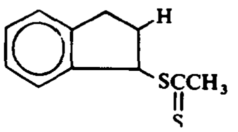
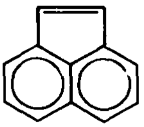
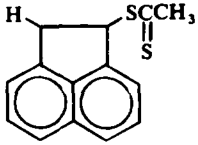
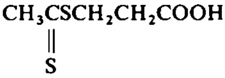
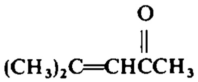
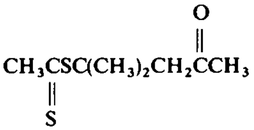
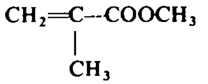
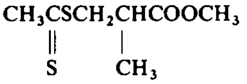
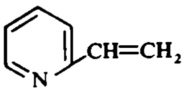
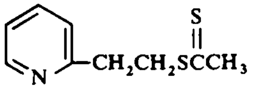
Olefin	Adduct
$PhCH{=}CH_2$	 $\underset{\underset{CH_3}{\vert}}{PhCH}-S\underset{\underset{S}{\Vert}}{C}CH_3$
 $Ph\underset{\underset{CH_3}{\vert}}{C}{=}CH_2$	 $PhC(CH_3)_2-S\underset{\underset{S}{\Vert}}{C}CH_3$
$(p)CH_3C_6H_4OCH{=}CH_2$	 $(p)CH_3C_6H_4O\underset{\underset{CH_3}{\vert}}{CH}-S\underset{\underset{S}{\Vert}}{C}CH_3$
$CH_2{=}CHOAc$	 $CH_3-\underset{\underset{S\underset{\underset{S}{\Vert}}{C}CH_3}{\vert}}{C}HOAc$
$PhCH{=}CH_2$	 $\underset{\underset{CH_3}{\vert}}{PhCH}-S\underset{\underset{S}{\Vert}}{C}Ph$
$PhSCH_2CH{=}CH_2$	 $PhSCH_2\underset{\underset{CH_3}{\vert}}{CH}-S\underset{\underset{S}{\Vert}}{C}CH_3$
	
	

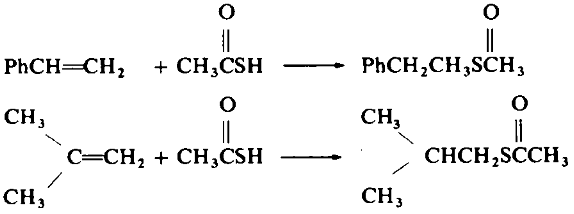
TABLE 3. MICHAEL TYPE ADDITION PRODUCTS

Olefin	Adduct
$CH_2{=}CHCN$	 $CH_3\underset{\underset{S}{\|}}{C}SCH_2CH_2CN$
$CH_2{=}CHCOOH$	 $CH_3\underset{\underset{S}{\|}}{C}SCH_2CH_2COOH$
 $(CH_3)_2C{=}CH\overset{\overset{O}{\|}}{C}CH_3$	 $CH_3\underset{\underset{S}{\|}}{C}SC(CH_3)_2CH_2\overset{\overset{O}{\|}}{C}CH_3$
 $CH_2{=}\underset{\underset{CH_3}{\mid}}{C}{-}COOCH_3$	 $CH_3\underset{\underset{S}{\|}}{C}SCH_2\underset{\underset{CH_3}{\mid}}{CH}COOCH_3$
	

The ease of Markownikoff addition is influenced apparently by the ability of the substituents to stabilize the carbonium ion formed by initial protonation. This is supported qualitatively by the observation that the rates of addition reactions of vinyl ether, styrene and allyl ether with CH_3CS_2H appear to fall in the order:

$$ROCH = CH_2 \approx RSCH = CH_2 \gg PhCH = CH_2 \approx ROCH_2{-}CH = CH_2$$

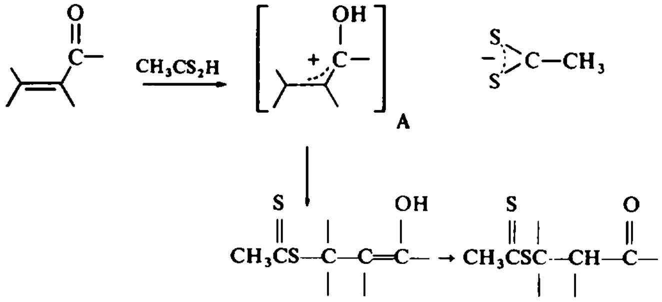
This mode of addition is quite different from that of thiolacetic acid, which usually adds to styrene[10] and isobutene[11] in a Michael type manner, apparently *via* a free radical chain process.



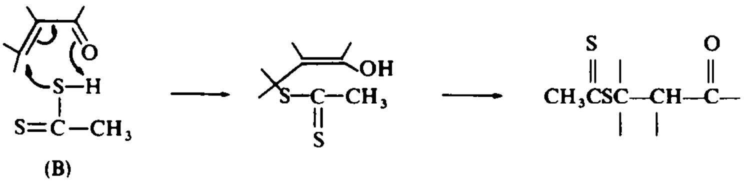
$$PhCH{=}CH_2 + CH_3\overset{\overset{O}{\|}}{C}SH \longrightarrow PhCH_2CH_3S\overset{\overset{O}{\|}}{C}H_3$$

$$\begin{array}{l}CH_3\\ \quad\diagdown\\ \quad\;C{=}CH_2\\ \quad\diagup\\ CH_3\end{array} + CH_3\overset{\overset{O}{\|}}{C}SH \longrightarrow \begin{array}{l}CH_3\\ \quad\diagdown\\ \quad\;CHCH_2S\overset{\overset{O}{\|}}{C}CH_3\\ \quad\diagup\\ CH_3\end{array}$$

Whereas Markownikoff addition prevails with dithioacetic acid without any radical scavenger, the data in Table III reveals that dithioacetic acid can add to electrophilic olefins. The following two mechanisms are considered for the Michael type addition. One is that fast protonation of an electro-negative group forms an intermediate of type A which eventually collapses to final product (eq. 1), the other mechanism is a concerted addition B (eq. 2).



(eq. 1)

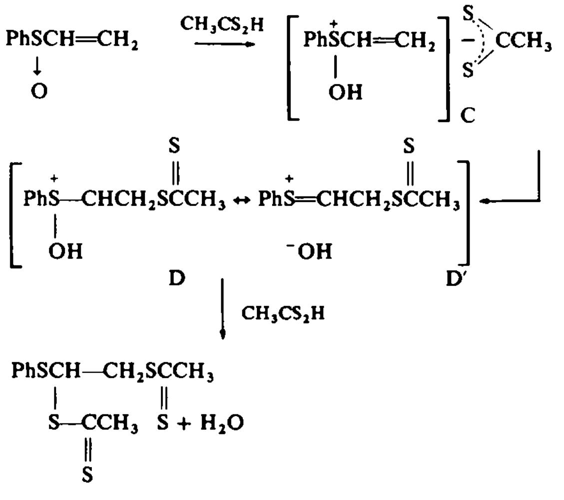


(eq. 2)

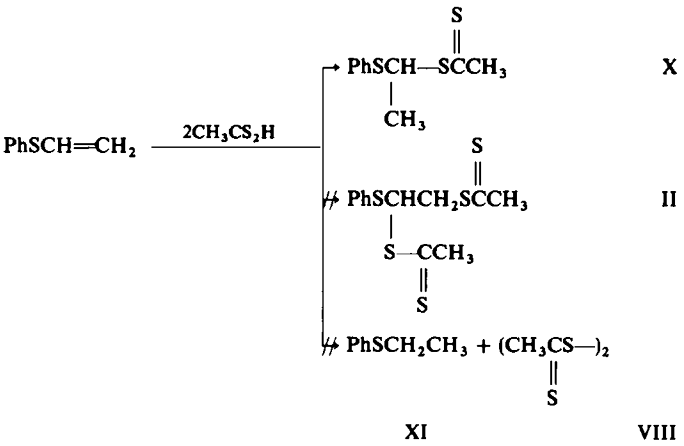
Choice between the two possibilities is not easy, but, in the case of 2-vinylpyridine, the former may be favoured because protonation on nitrogen would be very fast.

Mechanism of the reaction of phenyl vinyl and allyl phenyl sulphoxides with dithioacetic acid

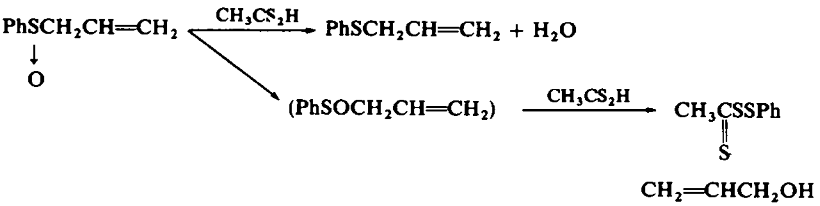
In view of the fact that carbodithioic acids can reduce sulphoxides and add to olefins, reduction of phenyl vinyl sulphoxide with dithioacetic acid seems to proceed *via* protonation on the sulphoxide oxygen, to form a sulphonium salt (C), followed by addition of dithioacetate to form (D) or (D′) which is eventually attacked by another molecule of dithioacetic acid to form the final product.



In order to examine other possibilities, we carried out the reaction of phenyl vinyl sulphoxide (1 mole) and dithioacetic acid (2 mole), and obtained (1-methyl-1-dithioacetoxy) methyl phenyl sulphide (X) as the only product and no 1,2-bis(dithioacetoxy)-ethyl phenyl sulphide (II) or ethyl phenyl sulphide (XI).



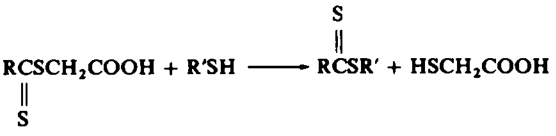
Allyl phenyl sulphoxide was reduced like other simple sulphoxides probably because a sulphinyl group was not directly attached to the olefinic group. Minor products (diphenyl disulphide, phenyl dithioacetyl disulphide and allyl alcohol) encountered are considered to be formed by the initial rearrangement to a sulphenate[12] which upon further nucleophilic attack of either thiophenolate or dithioacetate would lead to final products. The apparently facile rearrangement seems to be due to initial protonation on the sulphoxide oxygen to facilitate heterolysis of the C—S bond.



The synthetic utility

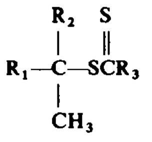
For the preparation of dithiocarboxylic esters, several procedures have been reported.[1, 3] One of the most popular is alkylation of a salt of a carbodithioic acid and many simple dithioesters have been prepared by this method (eq. 3). Another important procedure is an ester exchange reaction between carboxymethyl dithiocarboxylates and thiols.[13] By this procedure, a somewhat complicated ester, such as an aryl ester, can be obtained in a few steps (eq. 4).

$$\mathrm{RX + Na\overset{\overset{S}{\|}}{SC}R' \longrightarrow R\overset{\overset{S}{\|}}{SC}R' + NaX} \qquad \text{(eq. 3)}$$

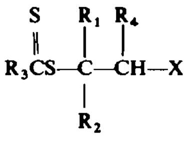


$$\mathrm{R\underset{\underset{S}{\|}}{C}SCH_2COOH + R'SH \longrightarrow R\overset{\overset{S}{\|}}{C}SR' + HSCH_2COOH} \qquad \text{(eq. 4)}$$

In the addition of dithioic acids to olefins, however, dithioesters can be obtained nearly quantitatively simply by mixing the reactants and practically all kinds of dithioesters bearing complicated skeletons like E or F can be prepared.


$R_1-\underset{CH_3}{\overset{R_2}{C}}-\overset{S}{\overset{\|}{S}}CR_3$

or


$R_3\overset{S}{\overset{\|}{C}}S-\underset{R_2}{\overset{R_1}{C}}-\overset{R_4}{CH}-X$

E F

X: electron-withdrawing group

Thus, even the 1,2-bis-dithioester shown below can be prepared.

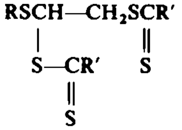

$RS\underset{S\underset{S}{\underset{\|}{C}}R'}{CH}-CH_2S\underset{S}{\underset{\|}{C}}R'$

TABLE 4

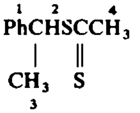
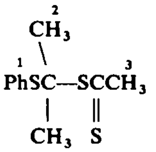
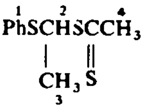
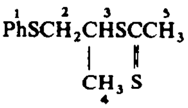
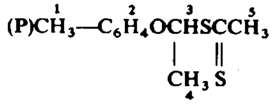
Dithioester		NMR	IR (cm^{-1}) (C=S)		Elemental Analysis (%)
 $\overset{1}{Ph}\underset{\underset{3}{CH_3}}{\overset{2}{CH}}S\underset{S}{\underset{\|}{C}}\overset{4}{CH_3}$	1	7·17 (s, 5H)			$C_{10}H_{12}S_2$
	2	5·01 (q, 1H)			Calc C, 61·22
					H, 6·12
	3	1·69 (s, 3H)	1196	862	Found C, 59·82
	4	2·77 (s, 3H)			H, 5·87
 $\overset{1}{Ph}S\underset{CH_3}{\overset{\overset{2}{CH_3}}{C}}-S\underset{S}{\underset{\|}{C}}\overset{3}{CH_3}$	1	7·30 (m, 5H)			$C_{11}H_{14}S_2$
	2	1·90 (s, 6H)	1200	861	Calc. C, 62·86
	3	2·62 (s, 3H)			H, 6·67
					Found C, 61·22
					H, 6·60
 $\overset{1}{Ph}S\underset{\underset{3}{CH_3}}{\overset{2}{CH}}S\underset{S}{\underset{\|}{C}}\overset{4}{CH_3}$	1	7·30 (m, 5H)			$C_{10}H_{12}S_3$
	2	5·15 (q, 1H)	1190	860	Calc. C, 52·63
	3	1·70 (d, 3H)			H, 5·26
	4	2·74 (s, 3H)			Found C, 51·69
					H, 5·29
 $\overset{1}{Ph}S\overset{2}{CH_2}\underset{\underset{4}{CH_3}}{\overset{3}{CH}}S\underset{S}{\underset{\|}{C}}\overset{5}{CH_3}$	1	7·35 (m, 5H)			$C_{11}H_{14}S_3$
	2	3·35 (t, 2H)	1190	860	Calc. C, 54·54
	3	4·00 (m, 1H)			H, 5·78
	4	1·52 (d, 3H)			Found C, 52·71
	5	2·79 (s, 3H)			H, 5·34
 $(P)\overset{1}{CH_3}-\overset{2}{C_6H_4}O\underset{\underset{4}{CH_3}}{\overset{3}{CH}}S\underset{S}{\underset{\|}{C}}\overset{5}{CH_3}$	1	2·31 (s, 3H)			$C_{11}H_{14}OS_2$
	2	6·92 (m, 4H)	1190	861	Calc. C, 58·89
	3	6·12 (q, 1H)			H, 6·32
	4	1·85 (d, 3H)			Found C, 57·10
	5	2·80 (s, 3H)			H, 6·30

Table 4—*continued*

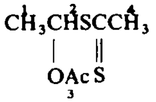
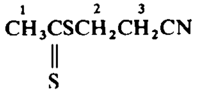
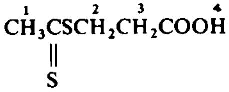
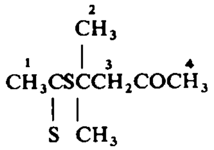
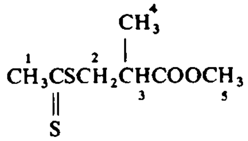
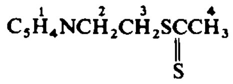
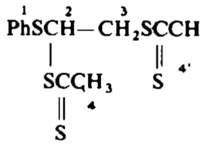
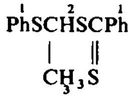
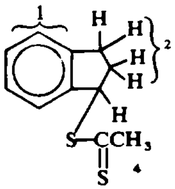
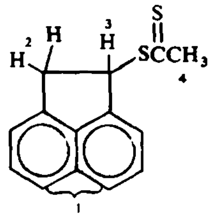
Dithioester	NMR	IR (cm^{-1}) (C=S)	Elemental Analysis (%)
 $CH_3CH(OAc)SC(=S)CH_3$	1 1·62 (d, 3H)		$C_6H_{10}O_2S_2$
	2 6·43 (q, 1H)	1220 856	Calc. C, 40·45
	3 2·08 (s, 3H)	1220 (C=O)	H, 5·62
	4 2·75 (s, 3H)		Found C, 39·05
			H, 5·40
 $CH_3C(=S)SCH_2CH_2CN$	1 2·88 (s, 3H)	1199 860	$C_5H_7NS_2$
	2 3·50 (t, 2H)		Calc. C 41·37
	3 2·72 (t, 2H)	2260 (CN)	H, 4·83
			Found C, 40·8
			H, 5·2
 $CH_3C(=S)SCH_2CH_2COOH$	1 2·83 (s, 3H)		$C_5H_8O_2S_2$
	2 3·47 (t, 2H)	1194 860	Calc. C, 36·58
	3 2·76 (t, 2H)		H, 4·88
	4 11·38 (s, 1H)	1700 (C=O)	Found C, 35·49
			H, 4·63
 $CH_3C(=S)SC(CH_3)_2CH_2COCH_3$	1 2·70 (s, 3H)		$C_8H_{14}OS_2$
	2 1·61 (s, 6H)	1185 865	Calc. C, 50·53
	3 3·36 (s, 2H)	1710 (C=O)	H, 7·37
	4 2·08 (s, 3H)		Found C, 48·82
			H, 7·09
 $CH_3C(=S)SCH_2CH(CH_3)COOCH_3$	1 2·80 (s, 3H)		$C_7H_{12}O_2S_2$
	2 3·38 (d, 2H)	1192 856	Calc. C, 43·75
	3 2·84 (m, 1H)	1730 (C=O)	H, 6·25
	4 1·28 (d, 3H)		Found C, 41·96
	5 3·67 (s, 3H)		H, 5·90
 $C_5H_4NCH_2CH_2SC(=S)CH_3$	1 8·48–8·10 (m, 4H)		$C_9H_{11}NS_2$
	2 3·08 (t, 2H)	1192 862	Calc. C, 54·82
	3 3·60 (t, 2H)		H, 5·59
	4 2·76 (s, 3H)		N, 7·11
			S, 32·48
 $PhSCH(SC(=S)CH_3)-CH_2SC(=S)CH_3$	1 7·34 (m, 5H)	1194 856	Found C, 52·5
	2 5·35 (t, 1H)		H, 5·6
	3 3·76 (d, 2H)		N, 6·9
	4 or 4′ 2·82, 2·77 (s, 6H)		S, 29·6
 $PhSCH(CH_3)SC(=S)Ph$	1 or 1′ 7·52, 8·15 (m, 10H)		$C_{15}H_{14}S_3$
	2 5·54 (q, 1H)	1196 858	Calc. C, 62·02
	3 1·32 (d, 3H)		H, 4·82
			Found C, 61·89
			H, 5·01
	1 7·14 (m, 4H)	1200 860	$C_{11}H_{11}S_2$
	2 2·60–1·62 (m, 4H)		Calc. C, 63·77
	3 5·30 (t, 1H)		H, 5·31
	4 2·28 (s, 3H)		Found C, 61·17
			H, 5·65

Table 4—*continued*

Dithioester	NMR	IR (cm^{-1}) (C=S)		Elemental Analysis (%)
	1 7·35 (m, 6H) 2 4·27–3·02 (m, 2H) 3 5·15 (m, 1H) 4 2·78 (s, 3H)	1200	860	$C_{14}H_{12}S_2$ Calc. C, 68·85 H, 4·83 Found C, 66·41 H, 4·83

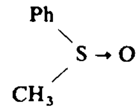
EXPERIMENTAL

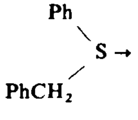
IR spectra were determined with a SG-25 instrument, Japan spectroscopic Co. Ltd., in CCl_4, KBr disk or neat. NMR spectra were recorded on a Hitachi R-20 spectrometer using CCl_4 or $CDCl_3$ containing TMS as internal standard. Chemical shifts are reported in ppm downfield from TMS.

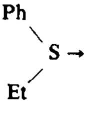
Dithioacetic acid was prepared by the method described by Houben.[14] The fraction boiling at 35–40°/20 mm was collected (yield 15%). Dithiobenzoic acid was prepared by the method of Becke[15] and used without further purification.

Phenyl vinyl sulphoxide and allyl phenyl sulphoxide were prepared by oxidation of the corresponding sulphides with H_2O_2. b.p. 133–134°/6 mm (132–133°/7 mm)[17] 51% yield; b.p. 113–115°/1 mm (103–104°/0·36 mm[17]) 60% yield. Research grade reagents of olefins were used without further purification.

Preparation of sulphoxides, sulphilimines and sulphonium ylides. The sulphoxides listed below were prepared by oxidation of the corresponding sulphides by Br, in the presence of pyridine in AcOH and water, according to the usual procedure.[18]

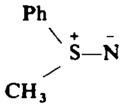

$\mathrm{Ph(CH_3)S \rightarrow O}$ b.p. 110°/1–2 mm (lit.[18] b.p. 84°/0·25 mm)

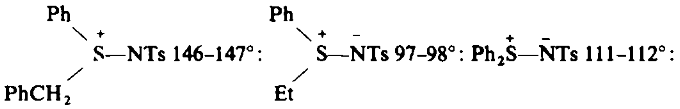

$\mathrm{Ph(PhCH_2)S \rightarrow O}$ m.p. 127° (lit.[19] m.p. 127°)


$\mathrm{Ph(Et)S \rightarrow O}$ b.p. 101·5–102^{c}/2 mm (lit.[19] b.p. 101–102°/1 mm)

DMSO was purified by repeated vacuum distillation from NaH, b.p. 81–82°/20 mm (lit.[21] b.p. 86°/25 mm). Diphenyl sulphoxide was prepared by the reaction of $SOCl_3$, benzene and $AlCl_3$, m.p. 70–71° (lit.[22] m.p. 71°).

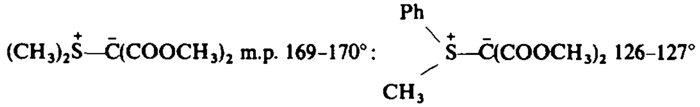
Sulfilimines were prepared by the reaction of the corresponding sulphides and chloramine-T as described.[23]

$(CH_3)_2\overset{+}{S}—\overset{-}{N}Ts$ m.p. 157–157·5°:

$\mathrm{Ph(CH_3)\overset{+}{S}—\overset{-}{N}Ts}$ 129–130°:

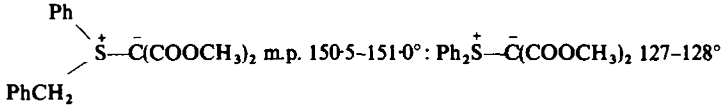


$PhCH_2(Ph)\overset{+}{S}\text{—}\overset{-}{N}Ts$ 146–147°: $Ph(Et)\overset{+}{S}\text{—}\overset{-}{N}Ts$ 97–98°: $Ph_2\overset{+}{S}\text{—}\overset{-}{N}Ts$ 111–112°:

Sulphonium ylides were prepared by the reaction of the corresponding sulphides and dimethyldiazomalonate in the presence of copper salt by a literature procedure.[24]



$(CH_3)_2\overset{+}{S}\text{—}\overset{-}{C}(COOCH_3)_2$ m.p. 169–170°: $Ph(CH_3)\overset{+}{S}\text{—}\overset{-}{C}(COOCH_3)_2$ 126–127°



$PhCH_2(Ph)\overset{+}{S}\text{—}\overset{-}{C}(COOCH_3)_2$ m.p. 150·5–151·0°: $Ph_2\overset{+}{S}\text{—}\overset{-}{C}(COOCH_3)_2$ 127–128°

Phenyl vinyl sulphoxide I *with dithioacetic acid.* When phenyl vinyl sulphoxide (I) (0·42 g, 0·0027 mole) and dithioacetic acid (0·55 g, 0·006 mole) were mixed, an exothermic reaction occurred. The reaction product was separated by chromatography through a silica gel column with benzene–hexane and 0·18 g of wine coloured 1,2-bis(dithioacetoxy)ethyl phenyl sulfide (II) was obtained (90%) IR and NMR spectra are in Table 4. (Calc. for $C_{12}H_{14}S_5$: C, 45·24%, H, 4·42. Found: C, 44·98; H, 4·21%).

Allyl phenyl sulphoxide III *with dithioacetic acid.* A CCl_4 solution of allyl phenyl sulphoxide (III) (2·0 g, 0·012 mole) and dithioacetic acid (2·4 g, 0·026 mole) was heated at 70° for 4 hr. After evaporation of CCl_4, the products were separated by column chromatography (silica gel, benzene–hexane) and allyl phenyl sulphide (IV) (0·9 g, 52%) was obtained as main product together with diphenyl disulphide (V) (0·2 g, 8%), phenyl trithioperacetate (VI) as a reddish oily product (0·12 g, 5%) and allyl alcohol (VII) (trace). IV, V and VII were identified by IR and NMR comparison with those of authentic samples. VI was identified by IR, NMR and elemental analysis.

(VI): IR (cm^{-1}) 1210 (C=S) 850: NMR 2·87 (s, 3H. —$SCSCH_3$) 7·41 (s. 5H. —Ph). (Calc. for $C_8H_8S_3$: C, 50·74; H, 4·43. Found: C, 48·00; H, 4·00%).

Dithioacetic acid with phenyl vinyl sulphide. When dithioacetic acid (0·18 g, 0·002 mole) was added to phenyl vinyl sulphide (0·14 g, 0·001 mole) a vigorous exothermic reaction occurred. After separation of mixture by column chromatography (benzene-hexane) an only product obtained quantitatively was found to be α-dithioacetoxyethyl sulfide, a simple addition product of dithioacetic acid to phenyl vinyl sulfide together with a minute amount of an oily reddish material.

Reduction of sulphoxides, sulphilimines and sulphonium ylides with dithioacetic acid and dithiobenzoic acid. When methyl phenyl sulphoxide (0·84 g, 0·006 mole) was added to dithioacetic acid (1·2 g, 0·013 mole) at room temp, an exothermic reaction occurred. The products were separated by chromatography through a silica gel column with benzene–hexane as solvent or collected by GLC (SE-30, 5%, 2 m, H_2 as a carrier gas). Methyl phenyl sulphide (0·70 g, 95%) was identified by IR and NMR comparison with an authentic sample. The reddish oily product was obtained together with a trace of water but could not be purified. The IR spectrum of the product showed a strong band at 1200 cm^{-1} due partly to dithioacetyl disulphide (VIII), prepared by the KI–I_2 oxidation of dithioacetic acid. Other sulphoxides were similarly reduced to the corresponding sulphides. With diphenyl sulphoxide the reaction proceeded rather slowly but gave the corresponding sulphide quantitatively.

Similarly, the reduction of N-*p*-toluenesulphonyl sulphilimines proceeded smoothly giving the corresponding sulphides and *p*-toluenesulphonamide in good yields. This amide was identified by IR comparison with an authentic sample. IR (cm^{-1}) 906, 1155, 1330, 1093, m.p. 137°.

When an equimolar amount of methyl phenyl sulphonium bis(methoxycarbonyl)methylide and dithioacetic acid was mixed, an exothermic reaction occurred to form phenyl methyl sulphide and dimethyl dithioacetoxymalonate (IX), respectively. IX was readily prepared from the reaction of dimethyl bromomalonate with sodium dithioacetate. In the case of dithiobenzoic acid, dimethyl dithiobenzoyloxymalonate was obtained as a reddish oil.

$CH_3\overset{\overset{S}{\|}}{C}SCH(COOCH_3)_2$ IR (cm^{-1}) 1195 (C=S), 864: 1738 (C=O, broad); NMR 5·51 (S, 1H, $>$CH), 3·84 (S, 6H, —$COOCH_3$), 2·89 (S, 3H, —$SCSCH_3$).

$PhC(=S)CH(COOCH_3)_2$ IR (cm^{-1}) 1201 (C=S), 868: 1742 (C=O, broad); NMR 8·25, 7·71 (m, 5H, —Ph), 3·94 (S, 6H, —$COOCH_3$), 5·89 (S, 1H, $>$CH).

Addition reaction of carbodithioic acids with olefins. All addition reactions were carried out in CCl_4 or neat without degassing in sealed tubes and the products separated by column chromatography (silica gel, benzene-hexane) and identified by IR, NMR and elemental analysis (Table 4). All products were red-coloured. A CCl_4 solution of styrene and carbodithioic acid was sealed in a degassed tube which was heated at 70°. The resulting product was almost the same as the product of the reaction carried out without degassing.

(i) *Markownikoff type addition.* In the case of vinyl sulphoxide and vinyl ether, an exothermic reaction took place immediately upon mixing with the olefins, while in the case of other olefins a CCl_4 solution of an equimolar mixture of an carbodithioic acid and an olefin was heated at 70° for 4 hr. The products listed in Table 2 were obtained quantitatively.

(ii) *Michael type addition.* Except 2-vinylpyridine, other electrophilic olefins were mixed with carbodithioic acids in CCl_4 and heated at 70° for 20–30 hr. When 2-vinylpyridine was mixed with carbodithioic acids, a vigorous exothermic reaction occurred and the adduct was quantitatively formed. Products obtained are shown in Table 3.

Competitive reaction between olefin and sulphonium ylide toward dithioacetic acid. A half mole of dithioacetic acid was added to a $CHCl_3$ solution of an equimolar mixture of methyl phenyl sulphonium bis(methoxycarbonyl)methylide and olefin in the NMR sample tube and the mixture was heated gently until the S—H absorption (6·02 ppm) in the NMR spectrum had disappeared. The relative intensities of the signals of methyl group (2·4 ppm) of the resulting methyl phenyl sulphide and that (about 1·7 ppm) of the resulting adducts in the NMR spectrum were measured. The results are shown below.

Olefin	Ylide/Olefin
$PhSCH{=}CH_2$	~1
$CH_3{-}C_6H_4OCH{=}CH_2$	~1
$PhCH{=}CH_2$	*
$PhSCH_2CH{=}CH_2$	*
$PhOCH_2CH{=}CH_2$	*

* Too slow for olefin to be observed

REFERENCES

[1] S. Patai, *The Chemistry of Carboxylic Acids and Esters*. Interscience. Chapter 15 (1969)
[2] W. H. Fletcher, *J. Am. Chem. Soc.* **68**, 2726 (1946)
[3] E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. IV, Chapter 1 (1962)
[4] S. Oae, *Organo Sulphur Chemistry* Kagaku Dojin Chapter 3 (1968)
[5] G. H. Alt and A. J. Speziale, *J. Org. Chem.* **31**, 1340 (1960)
[6] M. Mikolajczyk, *Angew. Chem. Int. Ed.* **5**, 419 (1966)
[7] T. Yagihara and S. Oae (unpublished data)
[8] W. Ando, H. Matsuyama, S. Nakaido and T. Migita, *Tetrahedron Letters* 3825 (1969)
[9] T. Yoshimura, N. Furukawa and S. Oae (unpublished data)
[10] K. Aktiebolag, *Chem. Abs.* **33**, 5870
[11] V. N. Ipatiefe and B. S. Friedman, *J. Am. Chem. Soc.* **61**, 71 (1939)
[12] P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller and K. Mislow, *Ibid.* **90**, 4869 (1968)
[13] N. H. Leon and R. S. Asquith, *Tetrahedron* **26**, 1719 (1970)
[14] J. Houben and H. Pohl, *Ber. Dtsch. Chem. Ges.* **40**, 1303 (1907)
[15] F. Beck and H. Hagen, *Ann.* **729**, 146 (1969)
[16] E. N. Prilezhaeva, L. V. Tsymbal, O. N. Domina, T. N. Shkrina and M. F. Shostakovski, *Chem. Abs* **54**, 22323 (1960)

[17] A. C. Cope, D. E. Morrison and L. Field, *J. Am. Chem. Soc.* **72**, 59 (1950)

[18] S. Oae, Y. Ohnishi, S. Kozuka and W. Tagaki, *Bull. Chem. Soc. Japan* **39**, 364 (1964)

[19] N. Nishio and I. Ito, *Chem. Pharm. Bull.* **13**, 1392 (1965)

[20] A. G. Erniani, G. Modena and P. Todesco, *Grazz. Chem. Ital.* **90**, 3 (1960)

[21] D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.* **63**, 2939 (1941)

[22] G. Modena, *Grazz. Chem. Ital.* **89**, 834 (1959)

[23] K. Tsujihara, N. Furukawa, K. Oae and S. Oae, *Bull. Chem. Soc. Jap.* **42**, 2631 (1969)

[24] W. Ando, T. Yagihara, S. Tozune, S. Nakaido and T. Migita, *Tetrahedron Letters* 1979 (1969)