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Reactions Involving the Addition of Dithio-acids to Unsaturated Compounds

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Data on the reactions involving the addition of dithiocarboxylic, dithiocarbamic, and other heterosubstituted dithio-acids to compounds with a multiple bond are surveyed. It is shown that the character of the addition depends on the nature of the dithio-acid: dithiocarbamic and xanthic acids add via an ionic mechanism, while for dithiocarboxylic acids there is a possibility also of radical addition as well as cycloaddition together with the ionic addition.
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I. INTRODUCTION

In contrast to the reactions involving the addition of carboxylic acids to multiple bonds, which have been investigated in detail, those of the sulphur analogues (dithio-acids) have attracted the attention of investigators relatively recently. The interest in these reactions is associated both with the active development of the chemistry of organosulphur compounds and with the practical application of dithio-acid esters—the products of the interaction of unsaturated compounds and dithio-acids.

Divinyl sulphide and its derivatives have been obtained by reactions of dithio-acid salts.[1-4] The vinyl esters of various dithio-acids have found applications in the synthesis of polymeric materials.[5-9] The products of the interaction of dithio-acids with unsaturated compounds have a fairly broad spectrum of biological activity. Thus dithiocarbamic acid esters exhibit insecticidal, acaricidal, nematocidal, and fungicidal activities.[10-13] A wide variety of heterocyclic sulphur derivatives have been obtained from the products of the interaction of dithio-acids with unsaturated compounds. For example, one may note the synthesis of sulphur analogues of pyrimidine derivatives which form part of the composition of nucleic acids—uracil and thymine,[14] as well as the synthesis of derivatives of tetrathiafulvalene, which are used to obtain "organic metals"—radical-ion salts with conducting properties.[15]

In connection with the undoubted practical value of dithio-acid esters, their properties and the methods of their synthesis have been considered in fair detail in a series of books, monographs, and reviews.[1-4,16-19] However, the reactions involving the addition of dithio-acid to unsaturated compounds have not been described in these publications.

The present review is devoted to the consideration of the characteristic features of reactions involving the addition of dithio-acids to the multiple bonds of a wide variety of unsaturated compounds.

II. DITHIOCARBAMIC AND XANTHIC ACIDS

1. The Addition of Dithiocarbamic and Xanthic Acids to Double Bonds

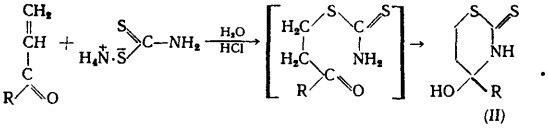
The first reactions of dithio-acids with unsaturated compounds were carried out in relation to the interaction of unsubstituted and *N*-monosubstituted dithiocarbamic acid with alkenes activated by electron-accepting substituents. The regioselectivity of the reaction and the fact that the reactions are carried out in polar solvents (water, alcohol) permit the claim that all cases involve the ionic addition of dithiocarbamic acid with formation of dithio-esters (I) in high yields (60–90%):[20-26]

$$R^1NHCS_2H + R^2R^3C{=}R^4Z \rightarrow R^1NHC(S)SCR^2R^3CHR^4Z \quad (I)$$

$R^1 = H, Alk; R^2, R^4 = H, Alk; R^3 = H, Alk, Ar, CCl_3;$
$Z = CHO, CONAlk_2, COAlk, CO_2Alk, CN.$

The exclusively ionic character of the addition can probably be accounted for by the fact that the unsubstituted and *N*-monosubstituted dithiocarbamic acids, generated by treating ammonium salts with HCl, can behave as the inner salts $R\overset{+}{N}H_2C(S)S^-$ under the reaction conditions.

The dithio-esters (I), obtained by condensing dithiocarbamic or *N*-alkyldithiocarbamic acids with αβ-ethylenic carbonyl compounds, have been converted by intramolecular cyclisation into the corresponding 1,3-thiazines (II),[21,23,24] sometimes without isolating compounds (I):[22]



(II)

In the reactions of dithiocarbamic acids with substituted divinyl ketones, the attack is directed to the less substituted double bond:[26]

$$Me_2C{=}CHCOCH{=}CH_2 \xrightarrow[-5^\circ C, HCl]{RR^1NCS_2^-N^+H_4(Na^+)} Me_2C{=}CHCOCH_2CH_2SC(S)NR^1R;$$
$R = H, Alk, R^1 = Alk, Ar, PhCH_2.$

The reactions of salts of dithiocarbamic acids with alkenes, activated by electron-accepting substituents, also lead to the dithio-esters (I):[13,27-35]

$$R^1R^2NCS_2^-Kat^+ + R^3R^4C{=}CR^5Z \xrightarrow{H_2O} R^1R^2NC(S)SCR^3R^4CHR^5Z \quad (I)$$

$R^1, R^2 = H, Alk, (CH_2)_n; R^3, R^4, R^5 = H, Me, Ph; Z = COAlk,$
$CO_2Alk, CONH_2, CN, NO_2, SO_2Alk; Kat = K, Na, NH_4, AlkNH_3, Alk_2NH_2, Alk_3NH.$

It has been noted in a number of studies[29,30] that, together with the dithio-esters (I), the reaction mixture contains considerable amounts of the sulphides $(ZCHRCHR)_2S$ (III), the sulphide becoming the main product in the presence of an

excess of the base. A possible mechanism of the formation of these compounds has been put forward:

$$RNHCS_2^-Na^+ + H_2C{=}CHCN \xrightarrow{H_2O} (I) + NaOH\,,$$
$$(I) \xrightarrow{OH^-} RN{=}C{=}S + HSCH_2CH_2CN\,;$$
$$HSCH_2CH_2CN + H_2C{=}CHCN \rightarrow (NCCH_2CH)_2S\,.$$

However, the possibility that the sulphide ion is generated in the rearrangement of the dithiocarbamate anion to isothiocyanate under the influence of the base is not ruled out:

$$RNHCS_2^- \rightleftarrows RN{=}C\begin{matrix}S^-\\SH\end{matrix} \xrightarrow{OH^-} RN{=}C{=}S + S^{2-} + H_2O\,;$$
$$S^{2-} + 2H_2C{=}CHCN \xrightarrow{H_2O} (NCCH_2CH_2)_2S\,.$$

In order to increase the yield of compound (I), it has been suggested that the reaction be carried out in the presence of acetic acid and with cooling (at 0 °C).[30]

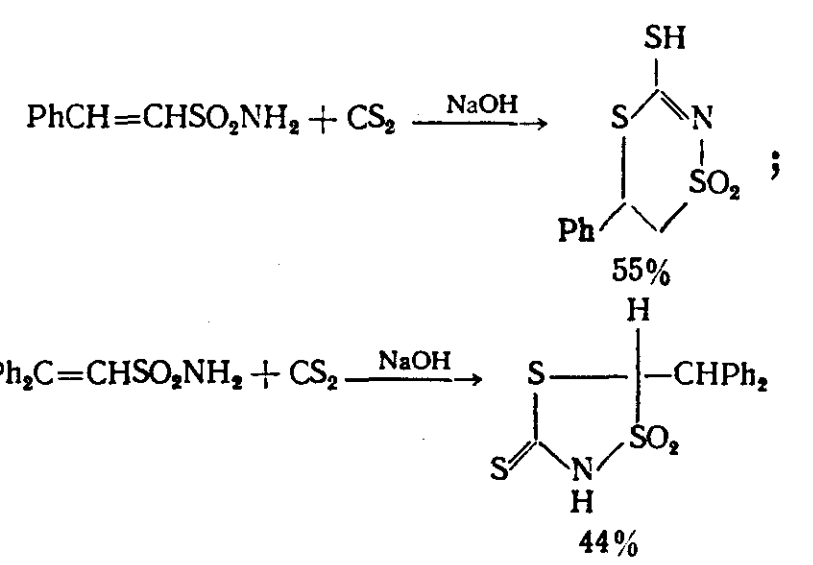
Reactions of dithiocarbamic salts with activated alkenes are reversible and are accompanied by the isomerisation of the alkenes:[10,31,34,36–38] in the reaction of triethylammonium *NN*-diethyldithiocarbamate with dimethyl fumarate, the equilibrium is attained when 82% of the reaction product (I) has accumulated in the mixture.[39]

The reaction of perfluoropropene with sodium *NN*-dialkyldithiocarbamate in an effectively solvating solvent [dimethylformamide (DMF)] affords, together with the expected product (I) of the addition of the dithiocarbamate anion to the double bond, also the product (IV) of the substitution of the fluorine atom at the double bond by the dithiocarbamate group:[40]

$$CF_3CF{=}CF_2 + R_2NCS_2^-Na^+ \rightarrow \underset{(I)}{CF_3CFHCF_2SC(S)NR_2} + \underset{(IV)}{CF_3CF{=}CFSC(S)NR_2}\,.$$

However, it has been shown[40] that a mixture of the (*Z*)- and (*E*)-isomers of compound (IV) is formed when hydrogen fluoride is eliminated from the dithio-ester (I) under the reaction conditions.

The reaction, described by Hasegawa et al.,[41,42] can be classified as an example of intramolecular nucleophilic addition of the dithiocarbamate anion to the double bond:



In the presence of electron-donating substituents in the *para*-position in the benzene ring, the yields increase to 95%.

The reactions of organyldithiocarbamic acids, formed from carbon disulphide and a secondary amine, with alkyl vinyl ethers and sulphides has been investigated recently; in the general case, the reaction proceeds as electrophilic addition, leading to 1-alkoxy- and 1-alkylthio-1-(organyldithiocarbamoyl)ethanes in yields ranging from 77% to quantitative:[43,44]

$$2R_2^1NH + CS_2 \rightarrow R_2^1NCS_2^-\overset{+}{N}H_2R_2^1 \overset{CS_2}{\rightleftarrows} 2R_2^1NCS_2H \xrightarrow{R^2XCH=CH_2} R_2^1NC(S)SCH(XR^2)CH_3\,;$$

X = O, S.

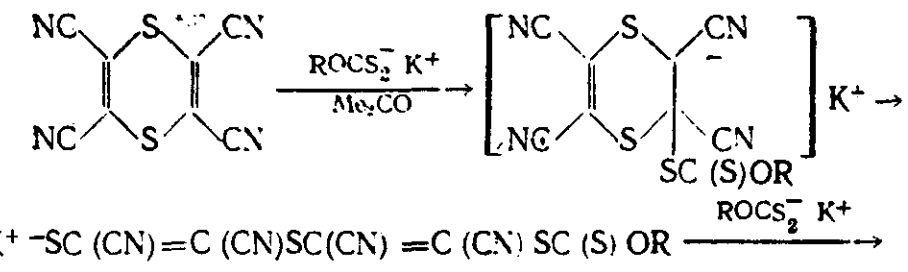
As expected, alkyl vinyl ethers proved to be more reactive in the reaction investigated than alkyl vinyl sulphides: the former react at 45–55 °C and the latter at 100 °C.

Numerous examples of the ionic addition of *O*-alkylxanthic acids to activated alkenes are known:[45–47]

$$R^1OCS_2H + R^2R^3{=}CHZ \rightarrow R^1OC(S)SCR^2R^3CH_2Z\,;$$
$$R^1 = Me, Et, n\text{-}Pr, iso\text{-}Pr, iso\text{-}Bu;\ R^2 = H, Me, Ph;\ R^3 = H, Me;$$
$$Z = COAlk, COAr, CO_2H, CONH_2, Ac\,.$$

Free xanthic acids are generated by treating the potassium salts with H_2SO_4.[45]

The reaction of potassium *O*-alkylxanthate with tetracyano-1,4-dithiine and tetracyanothiophen has been investigated.[48] Nucleophilic attack on the double bond is in this case always accompanied by ring opening with formation of compounds (V) and (VI):



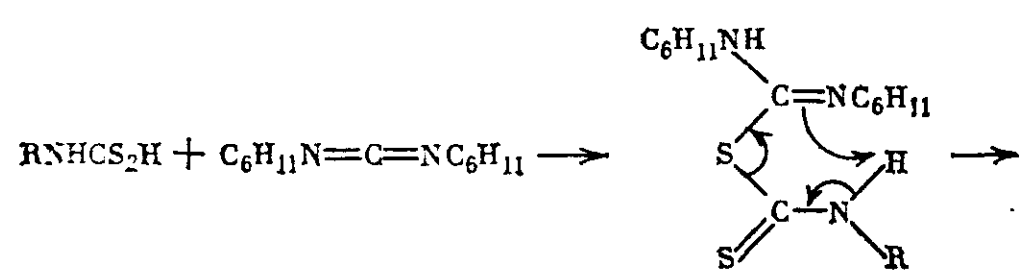
$$\rightarrow K^+\,{}^-SC(CN){=}C(CN)SC(CN){=}C(CN)SC(S)OR \xrightarrow{ROCS_2^-K^+}$$
$$\rightarrow \underset{(V)}{(Z,E)\text{-}[K^+\,{}^-SC(CN){=}C(CN)]_2S} + \underset{(VI)}{(ROCS)_2S}\,.$$

Like the reaction of dithiocarbamates, that of triethylammonium xanthate with dimethyl fumarate is reversible;[39] equilibrium is attained when 67% of the adducts (VII) has accumulated in the reaction mixture:

$$EtOCS_2^-\overset{+}{H}NEt_3 + (E)\text{-}MeO_2CCH{=}CHCO_2Me \rightleftarrows$$
$$\rightleftarrows \underset{(VII)}{EtOC(S)SCH(CO_2Me)CH_2CO_2Me} + Et_3N\,.$$

In the case of a heterodouble bond (C=N), the reactions with dithiocarbamic acid proceed in a more complex manner, although here too the initial formation of the product of nucleophilic addition has been postulated.[49] Thus dithiocarbamic acid reacts with dicyclohexylcarbodiimide to form the isothiocyanate (VIII) and *NN'*-dicyclohexylthiourea (IX):

$$RNH_2 + CS_2 \rightarrow RNHCS_2H$$



$$\rightarrow \underset{(VIII)}{RN{=}C{=}S} + \underset{(IX)}{C_6H_{11}NHC(S)NHC_6H_{11}}\,.$$

When dimethyl azodicarboxylate was allowed to react with *O*-alkylxanthic acids, the product (X) of nucleophilic addition to the N=N bond was isolated:[45]

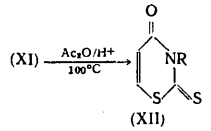
$$ROCS_2H + MeO_2CN{=}NCO_2Me \rightarrow \underset{(X)}{ROC(S)SN(CO_2Me)NHCO_2Me}\,.$$

2. The Addition of Dithiocarbamic and Xanthic Acids to Alkynes and Nitriles

Only alkynes activated by electron-accepting substituents react with dithiocarbamic acids. The reaction is exclusively ionic. Thus free dithiocarbamic acid and its *N*-monoalkyl derivatives, obtained from the ammonium salts *in situ*, add to the triple bond of propiolic acid and its esters at a low temperature with formation of *S*-vinyl esters of dithiocarbamic acid (XI):[14,50,51]

$$RNHCS_2^-\overset{+}{N}H_4 + HC{\equiv}C{-}CO_2R^1 \rightarrow \underset{(XI)}{(Z)\text{-}RNHC(S)SCH{=}CHCO_2R^1}\,;$$
$$R, R^1 = H, Alk\,.$$

All the adducts of type (XI) obtained have the (*Z*)-configuration, cyclising to the corresponding 1,3-thiazines (XII) on heating in acetic anhydride in the presence of H_2SO_4:[14]



(XII)

The reactions of dithiocarbamic acid salts with non-activated alkynes have been widely investigated in recent years. The synthesis of *NN*-dialkyl-*S*-vinyl dithiocarbamates (XII) from acetylene, carbon disulphide, and secondary aliphatic amines in the presence of traces of KOH should probably be regarded as the first example of such reactions: [52,53]

$$HC{\equiv}CH + CS_2 + Alk_2NH \rightarrow \underset{(XIII)}{Alk_2NC(S)SCH{=}CH_2} .$$

It has been noted that the best yields of compound (XIII) (52–60%) are obtained at a pressure of 13–18 atm and 130 °C in DMF or water. [53]

A series of studies by Trofimov and co-workers on the interaction of dithiocarbamate anions with non-activated acetylenes have been a logical continuation of these investigations. [1–4,54] The reaction is carried out in polar aprotic solvents: dimethyl sulphoxide (DMSO), tetrahydrofuran (THF), hexamethylphosphoramide (HMP), and dioxan containing 1–6% of water. The reaction products are the corresponding *S*-vinyl esters of dithiocarbamic acids (XIII) and divinyl sulphides (XIV):

$$R^1_2NCS_2^- M^+ + R^2C{\equiv}CH \xrightarrow{H_2O} \underset{(XIII)}{(Z)\text{-}R^1_2NC(S)SCH{=}CHR^2} + \underset{(XIV)}{+ (Z,Z)\text{-}(R^2CH{=}CH)_2S} ;$$

$$R^1 = Alk;\ R^2 = H, Ph;\ M = Na, K .$$

The divinyl sulphides (XIV) are the products of secondary reactions of the *S*-vinyl esters (XIII): [1–4]

$$(XIII) + OH^- \rightarrow \begin{matrix} H \\ R^2 \end{matrix}\!\!>\!\!=\!\!<\!\!\begin{matrix} H \\ S^- \end{matrix} + [R^1_2NC(O)SH] \xrightarrow{R^2C{\equiv}C\text{-}I}$$

$$\rightarrow \underset{(XIV)}{(Z,Z)\text{-}(R^2CH{=}CH)_2S} + R^1_2NC(O)S^- .$$

The divindyl sulphides (XIV) are formed especially readily in "superbasic media" (DMSO, H_2O, KOH solutions), where they become the main products. The best yields of the dithio-esters (XIII) have been obtained in THF in the presence of an excess of dithiocarbamate anions, at a moderate temperature, and for a long reaction time and also when buffer systems, preventing the accumulation of the base in the reaction mixture, were used. [54]

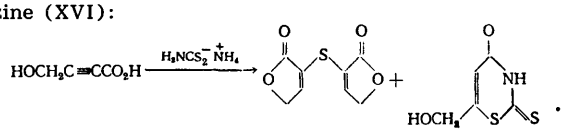
The reaction of the ammonium salts of dialkyldithiocarbamic acids with diacetylene leads to butenyne esters having exlusively the (*Z*)-configuration. [55] The reaction does not stop after the addition of one dithiocarbamate molecule:

$$R^2NCS_2^- \overset{+}{N}H_4 + HC{\equiv}C{-}C{\equiv}CH \xrightarrow{H^+} (Z)\text{-}HC{\equiv}C{-}CH{=}CH{-}SC(S)NR_2$$

$$\xrightarrow{R_2NCS_2^- \overset{+}{N}H_4} (Z,Z)\text{-}(Z,E)\text{-}R_2NC(S)SCH{=}CH{-}CH{=}CHSC(S)NR_2 .$$

Activated aceylenes also interact with dithiocarbamic acid salts. Thus the interaction of propiolic acid with dithiocarbamate anions at room temperature leads to low yields of the dithio-esters (XI), [56] which are also formed from *N*-alkyldithiocarbamic acids *in situ*. [14] All the adducts of type (XI) obtained have the (*Z*)-configuration. On heating in water in the presence of hydrobromic acid, the dithio-esters (XI) are converted into the (*E*)-isomers, while in the case of *N*-monosubstituted dithiocarbamic acids the dithio-esters (XI) cyclise to the 1,3-thiazines (XII). [56]

The main product of the interaction of ammonium dithiocarbamate with 4-hydroxy-2-butynoic acid is the divinyl sulphide (XV) together with a small amount of the 1,3-thiazine (XVI):



(XV), 30% (XVI), 6%

The reaction with the ethyl ester of this acid results in a significant increase in the yield of compound (XVI) (to 64%), but linear adducts have not been isolated in either the former or the latter case. [51]

According to Kishida and Terada, [57] the only products of the reaction of ammonium dithiocarbamate with functional derivatives of substituted and unsubstituted propiolic acid are the divinyl sulphides (XVII):

$$RC{\equiv}CX + H_2NCS_2^- \overset{+}{N}H_4 \rightarrow \underset{(XVII)}{(Z,Z)\text{-}(XCH{=}CR)_2S} ;$$

$$R = H, Me, Ph,\ X = CN, CO_2Et .$$

^1H NMR data demonstrate convincingly that the adducts (XVII) obtained have the (*Z*,*Z*)-configuration. On irradiation with UV light or on heating, the (*Z*,*Z*)-isomers are converted into the (*Z*,*E*)-form. The authors [57] explain the formation of (*Z*,*Z*)-divinyl sulphide (XVII) by the *trans*-nucleophilic addition to the triple bond. This view is shared by almost all investigators. [54–56] However, Cain and Warrener, [14] who carried out similar studies, believe that the configuration of the adducts does not indicate in this instance the preferential *trans*-addition of the sulphur-containing nucleophiles to the triple bond but reflect in reality merely the fact that the (*Z*)-isomer is more stable in the crystalline state.

In the reaction with tertiary propargyl chlorides, the dithiocarbamate anion initially substitutes the chlorine atom and only then adds to the triple bond. [58]

$$R^1_2NCS_2^- Na^+ + ClCR^2R^3C{\equiv}CH \xrightarrow[20°C]{H^+} \underset{(XVIII)}{(Z)\text{-}R^1_2NC(S)SCR^2R^3CH{=}CHSC(S)NR^1_2} ;$$

$$R^1 = Alk,\ R^2 = R^3 = Me;\ R^2 = H,\ R^3 = Me .$$

The product (XVIII) has the (*Z*)-configuration but isomerises on heating to 50 °C.

α-Acetylenic ketones react with *NN*-dialkyldithiocarbamic salts to form the corresponding *S*-vinyl dithio-esters (XIX), which are readily converted on heating into divinyl sulphides (XX): [59,60]

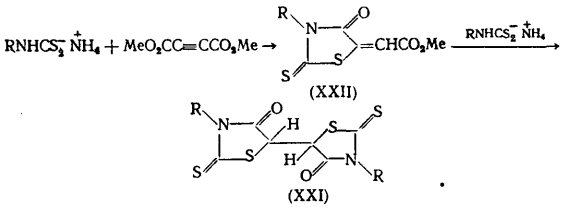
$$R^1_2NCS_2^- Cat^+ + R^2C{\equiv}CCOR^3 \rightarrow \underset{(XIX)}{R^1_2NC(S)SCR^2{=}CHCOR^3} \rightarrow \underset{(XX)}{(R^3COCH{=}CR^2)_2S} ;$$

$$R^1 = Alk;\ R^2, R^3 = H, Me, Ph;\ Cat = Na, K, NH_4 .$$

By carrying out the reaction in a two-phase system (water–diethyl ether), it is possible to avoid the charring of the products (XIX) and the formation of divinyl sulphide (XX). [59] The dithio-esters (XIX) are formed as a mixture of the (*Z*)- and (*E*)-isomers with the (*Z*)-isomer predominating. The appearance of the (*E*)-isomer, formally corresponding to the breakdown of the *trans*-addition rule, is due to the ease of the transition (*Z*) → (*E*). The decrease in the activation barrier to the isomerisation has been explained by the strong through-conjugation of the S–C=C–C=O system, which loosens the C=C bond. [1] When ammonium dithiocarbamate ($R^1 = H$) is introduced into the above reaction, the only product is the divinyl sulphide (XX). [60]

The nature of the products of the reactions of ammonium dithiocarbamates with dimethyl acetylenedicarboxylate (DMAD) depends significantly on the reaction conditions. In the

reaction of DMAD with an excess of ammonium *N*-alkyldithiocarbamate, the bisthiazolidinones (XXI) are formed. On the other hand, when the ammonium salt is added to an excess of DMAD, the reaction products are the thiazolidinones (XXII):[61]



(XXII)

(XXI)

The salts of *NN*-disubstituted dithiocarbamic acids react with acetylenecarboxylic acid esters regiospecifically and stereospecifically with formation of only the linear products (XXIII) (*trans*-nucleophilic addition) regardless of the electronic properties of the substituents at the nitrogen atoms and also of the nature of the cation and the solvent:[39,62,63]

$$R^1_2NCS_2^-Kat^+ + R^2C{\equiv}CCO_2Me \xrightarrow{H^+} (Z)\text{-}R^1_2NC(S)SCR^2{=}CHCO_2Me\ ;$$
(XXIII)

R^1 = Alk, $PhCH_2$; R^2 = H, CO_2Me, Ph; Kat = Na, $HNEt_3$.

In the presence of an excess of the dithiocarbamic salt, the adduct (XXIII) combines with a second dithiocarbamic acid molecule, forming a mixture of the *dl*- and *meso*-forms of the dimethyl esters of 2,3-bis(*NN*-dialkylthiocarbamoylthio)-succinic acid (XXIV):[39]

$$(Z)\text{-}R^1_2NC(S)SCR^2{=}CHCO_2Me + R^1_2NCS_2^-H\overset{+}{N}Et_3 \rightarrow$$
$$\rightarrow R^1_2NC(S)SCHR^2CH(CO_2Me)SC(S)NR^1_2\ ;$$
(XXIV)

R^1 = Et, R^2 = CO_2Me .

The non-stereospecificity of the addition of the second dithiocarbamic acid molecule is probably caused by the partial isomerisation of the adduct (XXIV) to the thermodynamically more stable diastereoisomer in the presence of the base. This hypothesis is confirmed by the results of a study of Angadiyavar et al.:[64] when DMAD was allowed to react with salts of secondary amines and *NN*-dialkyldithiocarbamic acids, only the thermodynamically more stable *erythro*-isomers of α-amino-β-dithiocarbamoylsuccinates (XXV) were found. In the first stage, the triple bond of DMAD is subjected to nucleophilic attack by the dithiocarbamate anion with formation of the monoadduct (XXVI). The formation of the diadduct (XXV) is a consequence of the addition of the secondary amine to compound (XXVI):

$$Alk_2NCS_2^-H_2\overset{+}{N}Alk_2 + MeO_2CC{\equiv}CCO_2Me \rightarrow Alk_2NC(S)SC(CO_2Me){=}$$
(XXVI)

$$={=}CHCO_2Me + HNAlk_2 \rightarrow Alk_2NC(S)SCH(CO_2Me)CH(CO_2Me)NAlk_2\ .$$
(XXV)

Acetylenic and diacetylenic compounds activated by the trifluoromethyl group (a σ-acceptor substituent) also interact with the triethylammonium salts of *NN*-dialkyldithiocarbamic acids regiospecifically and stereospecifically, forming only linear adducts of type (XXVII):[63,65]

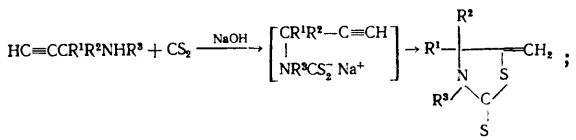
$$Alk_2NCS_2^-H\overset{+}{N}Et_3 + CF_3C{\equiv}CR \rightarrow (Z)\text{-}Alk_2NC(S)SC(R){=}CHCF_3 + NEt_3\ ;$$
(XXVII)

R = H, CF_3 .

The dithiocarbamate anion adds to trifluoromethyldiacetylenes contrary to the Markovnikov rule:[63]

$$Alk_2NCS_2^-H\overset{+}{N}Et_3 + CF_3C{\equiv}CC{\equiv}CR \rightarrow (Z)\text{-}Alk_2NC(S)SC(CF_3){=}$$
$$={=}CHC{\equiv}CR + NEt_3\ .$$

Apart from the intermolecular interaction of dithiocarbamates and acetylenes, there exist examples of the intramolecular nucleophilic addition of these salts to the triple bond:[66–69]



R^1, R^2, R^3 = H, Me, iso-Pr.

The yield is a maximum for R^3 = H.[67]

The addition of xanthic acid salts has been studied in less detail than for dithiocarbamates. Thus it has been noted that, like dithiocarbamates, the ethylxanthate anion interacts with non-activated acetylenes.[70] The main reaction product is the divinyl sulphide (XXIV), although under certain conditions it is possible to isolate the intermediate vinyl ester (XXVIII):

$$EtOCS_2^-\overset{+}{N}a + RC{\equiv}CH \rightarrow \underset{\text{(XXVIII)}}{EtOC(S)SCH{=}CHR} + \underset{\text{(XIV)}}{(Z,Z)\text{-}(RCH{=}CH)_2S}\ .$$

The addition of the xanthate anion to diacetylene in alcoholic solutions leads to the formation of the corrsponding vinyl acetylenic dithio-esters with the (*Z*)-configuration:[71]

$$ROH + CS_2 + HC{\equiv}C{-}C{\equiv}CH \xrightarrow[70^\circ C]{KOH} (Z)\text{-}ROC(S)SCH{=}CHC{\equiv}CH\ ;$$
R = Me, Et, Bu .

Activated acetylenes such as derivatives of acetylenecarboxylic acids also combine with alkylxanthates regiospecifically and stereospecifically to form the corresponding vinyl dithioesters (XXIX):

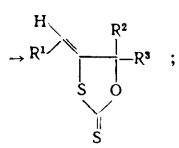
$$R^1OCS_2^-Kat^+ + R^2C{\equiv}CCO_2R^3 \rightarrow \underset{\text{(XXIX)}}{(Z)\text{-}R^1OC(S)SCR^2{=}CHCO_2R^3} \rightarrow$$
$$\xrightarrow{R^1OCS_2^-Cat^+} \underset{\text{(XXX)}}{R^1OC(S)SCHR^2CH(CO_2R^3)SC(S)OR^1}\ ;$$

R^1, R^3 = Alk; R^2 = H, CO_2Alk; Cat = NH_4, $HNEt_3$.

The adduct (XXIX, R^1 = Et, R^2 = CO_2Me) can react with a second xanthate molecule to form a 2 : 1 adduct of type (XXX).[39]

The reactions of carbon disulphide with substituted propargyl alcohols take place via a mechanism involving the intramolecular addition of xanthates to the triple bond:[72,73]

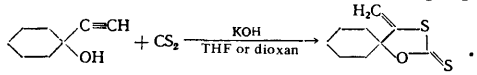
$$R^1C{\equiv}CCR^2R^3OH \xrightarrow{NaH} R^1C{\equiv}CCR^2R^3ONa \xrightarrow{CS_2} \underset{\text{(XXXI)}}{R^1C{\equiv}CCR^2R^3OCS_2Na} \rightarrow$$



(XXXII)

R^1 = H, Me, Ph, R^2, R^3 = H, Me, Et, n-Pr.

The intermediates (XXXI) can be isolated as the methyl esters after alkylation with methyl iodide.[74,75] Other experimental conditions for this reaction have also been proposed:[76]

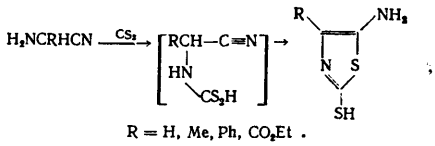


A single example of the interaction of potassium ethyl trithiocarbamate with phenylacetylene has been described in the literature.[77] This results in the formation of a mixture of the "usual" product (XXXIII) and the "anomalous" product (XXXIV) of the addition of the anion:

$$EtSCS_2^-K^+ + HC{\equiv}CPh \xrightarrow[THF/H_2O]{130^\circ C} \underset{\text{(XXXIV)}}{H_2C{\equiv}CPhSEt} + \underset{\text{(XXXIII)}}{(Z)\text{-}PhCH{=}CHSEt}\ .$$

There is also a possibility of intramolecular nucleophilic cyclisation with participation of the carbon–nitrogen triple bond. Thus it has been demonstrated[78–80] that the reaction

of carbon disulphide with α-aminonitriles leads to 5-amino-2-mercaptothiazoles:



R = H, Me, Ph, CO_2Et .

III. DITHIOCARBOXYLIC ACIDS

Derivatives of dithiocarbamic and xanthic acids have found extensive applications in industry. On the other hand, the chemistry of dithiocarboxylic acids RCS_2H, where R = aryl or alkyl, has been studied to a much lesser extent, for a number of reasons, than the chemistry of derivatives of dithiocarbamic and xanthic acids.[16–18] The compounds indicated differ significantly both from the related carboxylic and monothiocarboxylic acids. In the first place, the RCS_2H are stronger acids than the RCOSH and RCO_2H (the pK_a are 2.55, 3.33, and 4.75 respectively for R = Me [81]) and the character of their interaction with saturated compounds may be different.

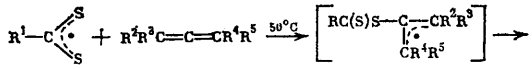
1. The Addition of Dithiocarboxylic Acids to Unsaturated Compounds

Examples of radical addition to unsaturated compounds do not exist for dithiocarbamic and other heterosubstituted dithio-acids. On the other hand, reactions involving radical addition to alkenes, dienes, allenes, and compounds with a strained double bond (norbornadiene) have been investigated in detail for aliphatic dithiocarboxylic acids.[9,82–85] The distinctive features of these reactions are as follows: dithiocarboxylic acids add to the double bonds of alkenes which have not been activated by electron-accepting substituents; the reaction is initiated in the presence of a source of free radicals and leads to the formation of not only the adducts (the corresponding dithio-esters) but also to cycloaddition products (see the next Section).

However, under certain conditions cyclisation may not in fact be observed. Thus the interaction of dithiobenzoic acid with styrene in the presence of azobisisobutyronitrile results in the exclusive formation of α-phenylethyl dithiobenzoate.[84] The introduction of a source of free radicals into the isoprene–dithioisobutyric acid system results in the formation of only a mixture of the dithio-esters (XXXV) and (XXXVI) [83]— the products of the 1,4-addition of the dithiocarboxylic acid to the olefin:

$$CH_2{=}CMeCH{=}CH_2 + \text{iso-Pr}CS_2H \xrightarrow{R^{\cdot}} \underset{\text{(XXXV)}}{\text{iso-Pr}C\,(S)\,SCH_2CMe{=}CHMe} + \underset{\text{(XXXVI)}}{Me_2C{=}CHCH_2SC\,(S)\,Pr\text{-iso}}.$$

The addition of dithio-acids to allenes under mild conditions (40–50 °C) leads to the vinyl dithio-esters (XXVII): [85]



$$\longrightarrow \underset{\text{(XXXVII)}}{R^1C(S)SC(CHR^4R^5){=}CR^2R^3}\ ;$$

R^1 = Me, Et; R^2=R^4=H, R^3R^5=$(CH_2)_6$: R^2=R^3=Me, R^4=R^5=H; R^2=R^3=R^4=H; R^5=Me .

The interaction of dithiocarboxylic acids with alkylacetylenes has been scarcely investigated, but there are data showing that the free-radical addition of dithioacetic acid (DTA) to 3-hexyne leads to a mixture of the (*Z*)- and (*E*)-vinyl dithio-esters (XXXVIII): [83]

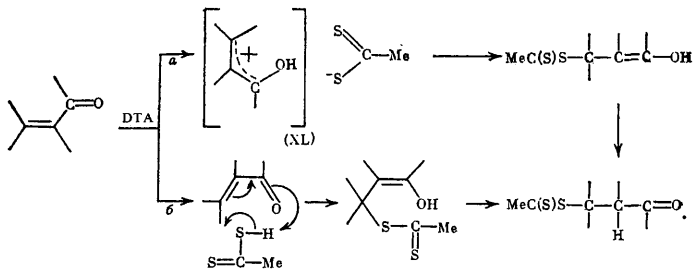
$$EtC{\equiv}CEt \xrightarrow[CCl_4(\text{boil})]{DTA} \underset{\text{(XXXVIII)}}{MeC\,(S)\,SCEt{=}CHEt}.$$

The familiar method of synthesis of dithiocarboxylic acid esters can be regarded as the first example of the thermal interaction of free dithiocarboxylic acids with alkenes activated by electron-accepting substituents: [17,87]

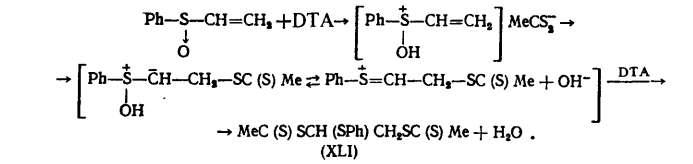
$$R^1CS_2H + R^2R^3C{=}R^4Z \rightarrow \underset{\text{(XXXIX)}}{R^1C\,(S)\,SCR^2R^3CR^4Z}\ ;$$

R^1 = Me, Et; R^2,R^3 = H, Alk, Ar, heteroaryl; R^4 = H, Me; Z = HCO, COR, CO_2H, CO_2Alk, CN, SOAlk, SO_2Alk, NO_2 .

In a study of the mechanism of this reaction, Oae et al.[88] proposed in 1972 two alternative versions, one of which (pathway *a*) presupposes the initial protonation of the electronegative group with formation of the intermediate (XLI) and the subsequent nucleophilic attack by the dithioacetate anion, while the other (pathway *b*) involves concerted addition:



It was found in the same study [88] that DTA can act as a reagent which reduces sulphoxides, sulphonium ylides, and sulphimides to the corresponding sulphides. Thus the reaction of DTA with phenyl vinyl sulphoxide leads to the product (XLI) of addition to the multiple bond with the simultaneous Pummerer rearrangement:



For alkenes with substituents incapable of being protonated with formation of intermediates of type (XL), the interaction with dithiocarboxylic acids leads to adducts in accordance with the Markovnikov rule:

$$CH_2{=}CR^1R^2 \xrightarrow{DTA} MeCR^1R^2SC\,(S)\,Me\ ;$$

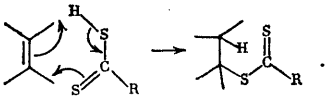
R^1 = H, Me; R^2 = Ph, OAlk, SAlk, OAc .

Vinyl esters and sulphides react much more readily than styrene.

Further studies [9,82–85] showed that the thermal (40–80 °C) addition of dithiocarboxylic acids to alkenes takes place fairly rapidly only when the double bond is activated by a neighbouring aromatic ring, carbonyl group, or heteroatom. In the case of simple alkenes, this is a very slow process even at about 120 °C. The presence of Lewis acids ($BF_3.Et_2O$) induces a faster, compared with a concerted process, ionic addition accompanied by rearrangements usual for reactions of this type, for example: [83]

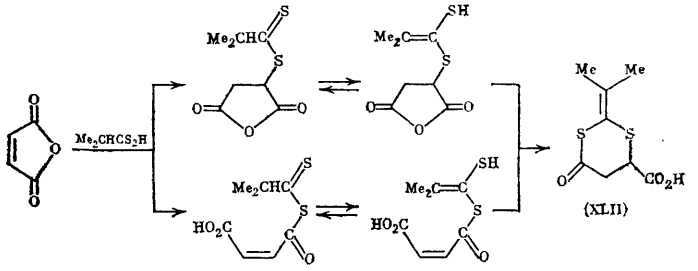
$$Me_2CH{-}CH{=}CH_2 \begin{cases} \xrightarrow{A} MeC\,(S)\,SCH\,(Me)\,CHMe_2\ , \\ \xrightarrow{BF_3Et_2O} MeC\,(S)\,SCMe_2CH_2Me\ . \end{cases}$$

The study of the thermal reaction in relation to deuterio-DTA showed[83] that (*Z*)-addition takes place. According to the authors,[83] the most probable mechanism of the thermal addition of dithiocarboxylic acids to alkenes involves a bimolecular reaction without an ionic or radical intermediate. Such addition may be most conveniently represented as a process occurring as a result of a concerted pericyclic shift (by analogy with "ene syntheses"):



Conjugation in the system increases its reactivity.

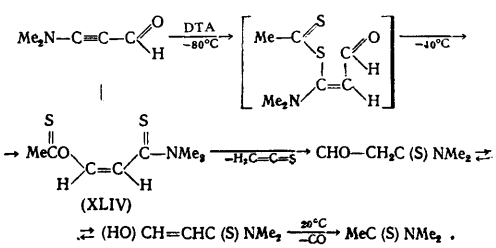
Maleic anhydride reacts with dithioisobutyric acid quantitatively, in the absence of catalysts, affording 1,3-dithiane (XLII). Presumably the addition begins in this case at the C=C bond and is followed by cyclisation via the enethiol form of the diothio-ester; however, Gressier and Levesque[9] do not rule out the possibility of the initial opening of the anhydride ring:



The reaction of DTA with propiolic acid at room temperature leads to a quantitative yield of the product (XLIII) of the Michael addition [a mixture the (*Z*)- and (*E*)-isomers in proportions of 6 : 4]. Methyl propiolate reacts with DTA in boiling CCl_4 and affords a mixture of the (*Z*)- and (*E*)-isomers of compound (XLIII) in proportions of 5 : 95; in the presence of Lewis acids, the isomer ratio is 25 : 75:[86]

$$HC{\equiv}CCO_2R \xrightarrow{DTA} MeC(S)S{-}CH{=}CHCO_2R\ ;$$
(XLIII)
$$R = H, Me\ .$$

The reaction of DTA with "push-pull" acetylene—a substituted ynamide—leads to an extremely unstable adduct, which rearranges to compound (XLIV) already at −40 °C. However, in contrast to the products of the addition of thiocarboxylic acids, the reaction does not stop at this point: on heating to room temperature, initially thioketen and then carbon monoxide are split off; the reaction product is thioacetamide:[89]



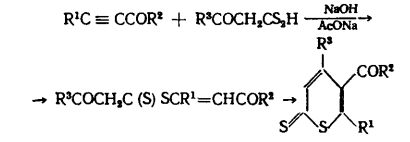
Several examples of the interaction of salts of dithiobenzoic acid with αβ-unsaturated ketones, which proceed with formation of adducts, have been described:[90]

$$PhCS_2MgBr + R^1R^2C{=}CHCOR^3 \rightarrow PhC(S)SCR^1R^2CH_2{-}COR^3\ ;$$
$$R^1, R^2 = H, Me, Ph;\ R^3 = Me, Ph$$

It has been noted that sodium dithiobenzoate is more reactive than the magnesium salt; it also reacts with benzoquinone and 1,2-dihydro-1-methylenenaphthalin-2-one.[90]

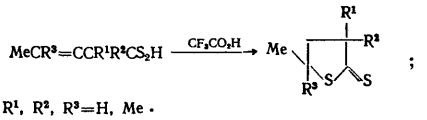
The interaction of triethylammonium dithiobenzoate with methyl propiolate in acetonitrile at −70 °C in the presence of an equimolar amount of acetic acid takes place stereoselectively as *trans*-addition with the preferential (>95%) formation of (*Z*)-PhC(S)−CH=CH.CO_2Me (overall yield 88%).[39]

The condensation of salts of β-ketodithiocarboxylic acids with DMAD [91] and α-acetylenic ketones[92] passes through a stage in which dithiocarboxylic acids add to the triple bond and leads to substituted thiopyrans; in a number of instances, the products of the Michael addition were isolated and characterised:[91]



R^1=CO_2Me, Ph; R^2=Me, OMe, Ph; R^3=Ar .

The reaction of αβ-unsaturated β-chloro-substituted aldehydes and ketones with aliphatic dithiocarboxylic acid apparently proceeds analogously.[92,93] The conversion of unsaturated tithiocarboxylic acids into γ-dithiolactones, described by Schonufts et al.,[94] can be regarded as an example of the intramolecular addition of dithiocarboxylic acids to the double bond:



R^1, R^2, R^3=H, Me .

There exist several examples of the interaction of dithiocarboxylic acids with heterounsaturated compounds. Thus the reactions of aromatic dithiocarboxylic acids with aryl isocyanates lead to the corresponding products of addition to the C=N bond:[95]

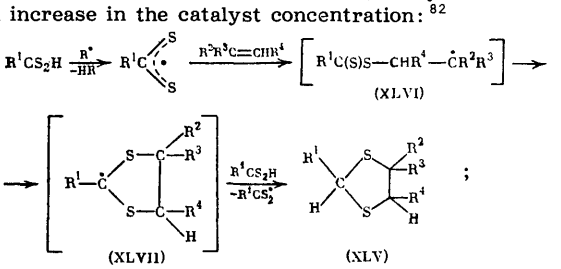
$$R^1CS_2H + R^2N{=}C{=}O \xrightarrow{EtONa} R^1C(S)SC(O)NHR^2\ .$$

Treatment of dicyclohexylcarbodiimide with DTA results in the formation of dicyclohexylthiourea and the unstable DTA anhydride:[49]

$$C_6H_{11}N{=}C{=}NC_6H_{11} \xrightarrow{2DTA} [MeC(S)]_2S + C_6H_{11}NHC(S)NHC_6H_{11}\ .$$

2. Cycloaddition of Dithiocarboxylic Acids to Unsaturated Compounds

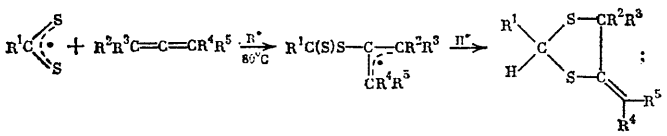
(a). Radical [3 + 2]cycloaddition. As was shown above, many adducts of dithiocarboxylic acids with unsaturated compounds can subsequently give rise to cyclic derivatives. However, in the presence of sources of free radicals, dithiocarboxylic acids can also enter directly into cyclisation reactions involving double bonds. Thus the interaction of DTA with styrene in the presence of azobisisobutyronitrile affords 1,3-dithiolans (XLV) and not dithioesters, the yield increasing with increase in the catalyst concentration:[82]



R^1=Alk; R^2=Ar; R^3=H, Me, Ph; R^4=H, Me .

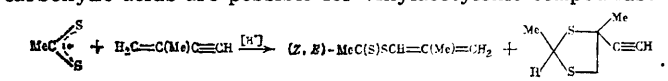
The use of deuterio-DTA in the reaction showed that deuteriation takes place exclusively at the C(2) atom of the dithiolan ring. A more detailed study showed[84] that the dithiolans (XLV) are formed preferentially in the reactions of alkenes having a phenyl substituent with aliphatic dithiocarboxylic acids. The cyclisation reaction (XLVI) → (XLVII) represents a non-trivial instance of thiophilic radical addition to the C=S bond.

The formation of 1,3-dithiolans is observed in the reactions of dithiocarboxylic acids with allenes in the presence of a source of free radicals and on refluxing in benzene:[85]

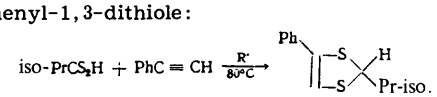


R^1=Me, Et; R^2=R^5=H, R^3R^4=$(CH_2)_6$; R^2=R^3=Me; R^4=R^5=H; R^2=R^3=R^4=H, R=Me.

Both free-radical addition and cycloaddition of dithiocarboxylic acids are possible for vinylacetylenic compounds:[86]

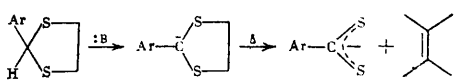


It was found in the same study[86] that the reaction of dithioisobutyric acid with phenylacetylene in the presence of azobisisobutyronitrile (on refluxing in benzene) affords 2-isopropyl-4-phenyl-1,3-dithiole:



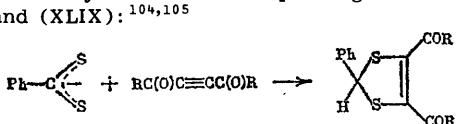
(b) Anionic [3 + 2]cycloaddition of dithioate anions. The anions of dithiocarboxylic acids are isoelectronic analogues of allyl anions. The cycloaddition of allyl anions to unsaturated compounds is known to be symmetry-allowed.[96] Although this reaction could not be achieved for the allyl anion itself, such cycloaddition is known for aza- and diaza-allyl anions[97] and a large group of αβ-unsaturated thioate anions and their selenium and tellurium analogues.[98]

A method of synthesis of aromatic dithiocarboxylic acids from 1,3-dithiolans was proposed in 1979:[99]



During recent years, this method has been used fairly widely to synthesise derivatives of trithiocarbonic acids[100–102] and also for the preparation of aliphatic dithiocarboxylic acids from 2-substituted 1,3-dithiolans.[103] The above syntheses are examples of anionic [3 + 2]cycloelimination. It was logical to suppose that, when the reactants and conditions have been chosen appropriately, it would be possible to achieve also the reverse reaction involving the anionic [3 + 2]cycloaddition of 1,3-dithia-allyl systems to multiple bonds.

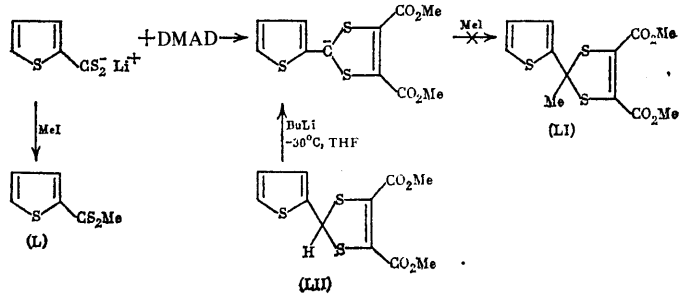
Indeed the reaction of triethylammonium dithiobenzoate with DMAD or dibenzoylacetylene in acetonitrile or methanol at room temperature yielded the corresponding 1,3-dithioles (XLVIII) and (XLIX):[104,105]



R=OMe (XLVIII), Ph (XLIX).

It has been suggested[106,107] that the 1,3-dipole reactivity is a common property of 1,3-dithia-allyl anionic systems. However, it was found unexpectedly that the nature of the group at the central carbon atom of the dithioate group has a decisive influence on the character of the adduct formed:

anions of aromatic or heteroaromatic systems (Ar = phenyl, 1-naphthyl, 2-thienyl, 2-furyl, or *N*-pyrrolyl) enter into the cycloaddition reaction.[39,62,105,106] On the other hand, the salts of dithiocarbamic and xanthic acids react with DMAD to form only the alternative adduct resulting from nucleophilic addition to the triple bond and the reaction proceeds exclusively stereospecifically as *trans*-addition.[39] The reaction depends little on the nature of the solvent, while the nature of the salt cation influences significantly its course. Thus the introduction into the reaction of the magnesium salt of naphthalene-1-dithiocarboxylic acid reduced the yield of the cycloadduct to 3–4% and the lithium salt of thiophen-2-dithiocarboxylic acid does not react at all with DMAD: alkylation with methyl iodide for 1 h leads to the formation of only the methyl ester of thiophen-2-dithiocarboxylic acid (L) and not to the expected 2-methyl derivative of 1,3-dithiole (LI):[63]

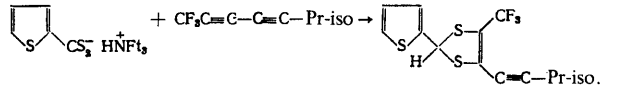


(LII)

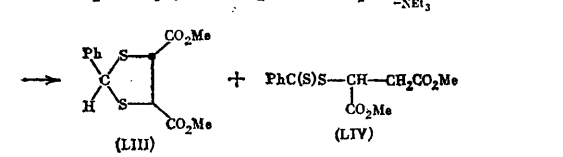
It has been demonstrated convincingly that the intermediate cyclic carbanion in the form of its lithium salt readily undergoes the reverse anionic [3 + 2]cycloelimination reaction; metallation of the 1,3-dithiole (LII) (obtained by the reaction of the triethylammonium salt of thiophen-2-dithiocarboxylic acid with DMAD) by butyl-lithium in THF at −30 °C and subsequent methylation with methyl iodide led to the subsequent detection in the reaction products, as in the previous case, of only the methyl ester of thiophen-2-dithiocarboxylic acid (L).[63]

Acetylenes whose triple bond has been activated on either side by electron-accepting (π or σ) substituents enter into the cycloaddition reaction: these are acetylenedicarboxylic acid esters, dibenzoylacetylene,[105] the methyl ester and nitrile of phenylpropiolic acid,[63] and hexafluorobutyne.[65]

Acetylenes whose triple bond has been activated by only one electron-accepting substituent react with the anions of dithiocarboxylic acids via the mechanism involving the ionic stereoselective *trans*-addition;[39] however, in the reaction of triethylammonium thiophen-2-dithiocarboxylate with trifluoromethylacetylene, the less stable cycloadduct was detected in the reaction medium together with the stable acyclic adduct. Only the cycloadduct was isolated in the reaction of the same salt with isopropyltrifluoromethyldiacetylene:[63]



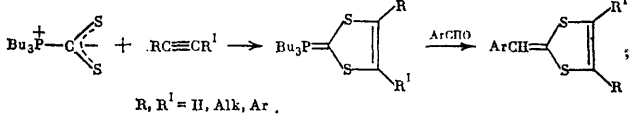
The reaction of triethylammonium dithiobenzoate with dimethyl fumarate takes place via two pathways with formation of both the product (LIII) of anionic [3 + 2]cycloaddition and the product (LIV) of nucleophilic Michael addition to the double bond in proportions of 2 : 1:[105]



Detailed study of the reaction mechanism showed that, under the reaction conditions, the adduct (LIV) cannot be converted into the cycloadduct (LIII) on treatment with a base, by-passing the stage involving decomposition into the initial components; this supports indirectly the concerted mechanism of the cycloaddition reaction.

The betaines formed by the reaction of phosphines with carbon disulphide and also the formamidinium and imidazolidinium dithiocarboxylates, obtained from the corresponding tetra-aminoethylenes and carbon disulphide, constitute unusual 1,3-dithia-allyl systems capable of anionic [3 + 2]-cycloaddition.

The adduct of carbon disulphide and tributylphosphine reacts with acetylene having electron-accepting substituents at temperatures as low as −30–0 °C; arylacetylenes react slowly at room temperature and acetylene itself reacts at temperatures above 100 °C with formation of the corresponding phosphorus ylides:[108,109]

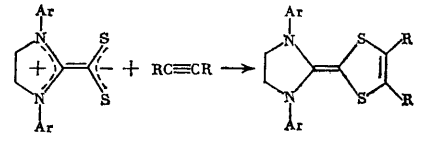


R, R^1 = H, Alk, Ar.

When aromatic aldehydes are introduced into the reaction mixture, the process terminates with the Wittig reaction. It is essential to note that ketones do not enter into this reaction.[109]

The reaction has since been widely used in the synthesis of varied 1,3-dithiole structures—2-substituted 1,3-dithioles [110] and tetrathiafulvalenes.[111,112] A fairly complete survey of the reactions of trialkyl (1,3-dithiolyl)phosponium tetrafluoroborates has been published in two reviews.[113,116]

Formamidinium and imidazolidinium dithiocarboxylates react analogously with doubly activated acetylenes,[117] for example

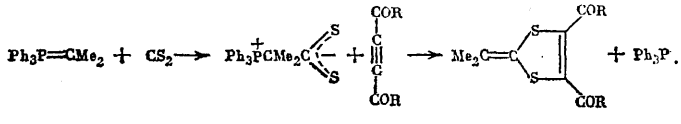


R = CO_2Alk, P(O)Ph_2, COPh; CF_3.

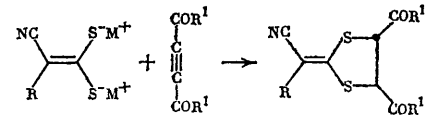
It is of interest that dipolarophile compounds having activated double bonds (tetracyanoethylene, dimethyl dicyanofumarate, dibenzyl azodicarboxylate) do not enter into the reaction.[118]

Betaines in which the 1,3-dithia-allyl system of the anion is separated from the positively charged centre by carbon atoms have been obtained by the reaction of triphenylphosphonium ylides with carbon disulphide.[119–121]

The 1,3-dithia-allyl system in the α-(triphenylphosphonia)-alkanedithiocarboxylates reacts with the triple bond activated on either side by electron-accepting substituents via the anionic [3 + 2]cycloaddition mechanism with formation of 2-alkylidene-1,3-dithioles; the fact which determines this course of the reaction is the subsequent stabilisation of the intermediate cyclic zwitter-ion as a result of the elimination of triphenylphosphine and the formation of an exocyclic double bond:[112,113]



The salts of 1,1-vinylidenedithioles are formed readily in the reactions of carbon disulphide and compounds having an active methylene group in the presence of bases. These salts, which can be regarded as salts of the dianions of the corresponding dithiocarboxylic acids, also react readily with doubly activated acetylenes, affording *trans*-4,5-disubstituted 2-alkylidene-1,3-dithiolans as the reaction products:[124–126]



R = CN, $CONH_2$, CO_2Et; R^1 = Alk, Ph.

The reactions involving the addition of dithio-acids to unsaturated compounds, examined above, are of undoubted interest also from the theoretical point of view apart from their practical and synthetic importance. Frequently a seemingly not very significant change in the details of the structures of the reactants and the reaction conditions leads to striking qualitative transitions from one mechanism to another, which are sometimes not easy to explain from modern theoretical standpoints.

REFERENCES

1. B.A.Trofimov and S.V.Amosova, in "Divinilsul'fid i Ego Proizvodnye" (Divinyl Sulphide and Its Derivatives), Izd.Nauka, Novosibirsk, 1982, p.119.
2. B.A.Trofimov, Sulfur Rep., 1983, 3, 83.
3. B.A.Trofimov and S.V.Amosova, Sulfur Rep., 1984, 3, 323.
4. B.A.Trofimov, Z.Chem., 1986, 26, 41.
5. T.Nakai, K.Shioya, and M.Okawara, Makromol.Chem., 1967, 108, 95.
6. G.Atsushi and Y.Nakagawa [this is probably a reference to Japanese Patent No.52-132 093 cf. Chem., Abs., 88: 74717c (Ed.of Translation)], Japanese Appl. 52-132 093, 1977; Ref.Zhur.Khim., 1978, 19S482.
7. J.Barnes, G.Esslemont, and P.Holt, Makromol.Chem., 1975, 176, 275.
8. W.H.Daly and C.D.Lee, J.Polymer Sci., 1975, 13, 105.
9. J.-C.Gressier and G.Levesque, Bull.Soc.chim.France, 1976, 1151.
10. M.Furdik, V.Konecny, and S.Truchlik, Acta Fac. Rerum.Natur.Univ.Comenianae (Chemia), 1968(13), 45.
11. M.Furdik, V.Konecny, S.Priehradny, and S.Truchlik, Acta Fac.Rerum.Natur.Univer.Comenianae (Chemia), 1968(13), 53.
12. V.Konecny, S.Priehradny, S.Truchlik, and V.Sutoris, Acta Fac.Rerum.Natur.Univ.Comenianae (Chemia), 1970(14), 47.
13. R.L.Wain, W.Sobotka, and D.M.Spencer, Ann.appl. Biol., 1963. 445.
14. E.N.Cain and R.N.Warrener, Austral.J.Chem., 1970, 23, 51.
15. M.Narita and C.V.Pittman, Synthesis, 1976, 489.
16. S.Scheithauer and R.Mayer, "Thio- and Dithiocarboxylic Acids and Their Derivatives", in "Topics in Sulphur Chemistry", Vol.4 (Edited by A.Senning), G.Thieme Publishers, Stuttgart, 1979.
17. J.E.Jansen, Uspekhi Khim., 1976, 45, 2020 [Russ. Chem.Rev., 1976(11)].
18. S.R.Ramadas, P.S.Srinivasan, J.Ramachandran, and V.Sastry, Synthesis, 1983, 605.
19. M.Yokoyama and T.Imamoto, Synthesis, 1984, 797.
20. J.E.Jensen, US P.2 440 095, 1948; Chem.Abs., 1948, 42, 5473.
21. J.E.Jansen and R.A.Mathes, J.Amer.Chem.Soc., 1955, 77, 2866.
22. S.Hoff and A.P.Blok, Rec.Trav.chim., 1973, 92, 631.
23. J.L.Garraway, J.Chem.Soc., 1964, 4004.

24. J.L.Garraway, J.Chem.Soc., 1964, 4008.
25. T.R.Akopyan, R.M.Khachatryan, and S.A.Vartanyan, Arm.Khim.Zhur., 1974, **27**, 319.
26. T.R.Akopyan, R.M.Khachatryan, and S.A.Vartanyan, Arm.Khim.Zhur., 1972, **25**, 975.
27. R.Delaby, R.Damies, and R.Seyden-Penne, Compt. rend., 1954, **238C**, 121.
28. R.Delaby, R.Damies, and R.Seyden-Penne, Compt. rend., 1956, **242**, 910.
29. C.M.Buess, J.Amer.Chem.Soc., 1955, **77**, 6613.
30. R.Seyden-Penne, Ann.chim.(France), 1958, **3**, 599.
31. N.Kreutzkamp and H.Peschel, Arch.Pharm., 1971, **304**, 477.
32. K.Schweiger, Monatsh.Chem., 1980, **111**, 1175.
33. H.Nagase, Chem.Pharm.Bull., 1973, **21**, 1132.
34. E.O.Hook, L.C.Beegle, and V.P.Wystrasch, US P. 2 786 866, 1957; Chem.Abs., 1957, **51**, 12 154.
35. R.M.Rani and M.R.S.Naidu, Indian J.Chem., 1985, **B24**, 289.
36. N.Kreutzkamp, H.Y.Oei, and H.Peschel, Arch. Pharm., 1971, **304**, 649.
37. W.Scott, US P.2 414 066, 1947; Chem.Abs., 1947, **41**, 2437.
38. E.V.Rowan, US P.3 945 938, 1976; Chem.Abs., 1976, **84**, 181 914.
39. V.N.Drozd, M.L.Petrov, O.A.Popova, and A.S.Vyazgin, Zhur.Org.Khim., 1984, **20**, 1189.
40. T.Kitazume, S.Sasaki, and N.Ishikawa, J.Fluor.Chem., 1978, **12**, 193.
41. K.Hasegawa, S.Hirooka, and T.Sasaki, Bull.Chem. Soc.Japan, 1973, **46**, 696.
42. K.Hasegawa, S.Hirooko, and T.Sasaki, Bull.Chem. Soc.Japan, 1973, **46**, 2894.
43. N.Nedolya, V.I.Komel'kova, and B.A.Trofimov, Zhur. Org.Khim., 1985, **21**, 1173.
44. B.A.Trofimov, S.V.Amosova, N.I.Ivanova, O.A.Tarasova, M.L.Al'pert, G.V.Dmitrieva, and M.V.Sigalov, Zhur.Org.Khim., 1986, **22**, 2145.
45. N.Kreutzkamp and H.Peshel, Pharmazie, 1970, **25**, 322.
46. J.L.Garraway, J.Chem.Soc., 1962, 4072.
47. S.V.Tsarenko, P.P.Gnatyuk, V.A.Ignatov, and V.A.Malii, Izv.Vys.Ucheb.Zaved., Khim.i.Khim. Tekhnol., 1980, **23**, 836.
48. H.E.Simmons, R.D.Vest, S.A.Vladuchick, and O.W.Webster, J.Org.Chem., 1980, **45**, 5113.
49. M.Nikolajczyk and P.Kielbasinski, Tetrahedron, 1981, **37**, 233.
50. R.N.Warrener and E.N.Cain, Chem.Ind., 1964, 1989.
51. R.N.Warrener and E.N.Cain, Austral.J.Chem., 1971, **24**, 785.
52. C.T.Handy and J.C.Sauer, US P.2 579 384, 1951; Chem.Abs., 1952, **46**, 6149.
53. J.C.Sayer, J.Org.Chem., 1959, **24**, 1592.
54. B.A.Trofimov, N.I.Ivanova, and S.V.Amosova, Zhur. Org.Khim., 1979, **15**, 2337.
55. L.V.Sokolyanskaya, A.N.Vavilova, A.N.Volkov, and B.A.Trofimov, Zhur.Org.Khim., 1981, **17**, 2269.
56. J.L.Garraway, J.Chem.Soc., 1962, 4077.
57. L.Kishida and A.Terada, Chem.Pharm.Bull., 1968, **16**, 1351.
58. I.N.Azerbaev, L.A.Tsoi, M.Zh.Aitkhozhaeva, D.G.Kim, and L.P.Krasnomolova, Symposium, "Biologicheskoi Aktivnye Soedineniya" (Biologically Active Compounds), Izd.Nauka, Leningrad, 1968, p.116.
59. B.A.Trofimov, S.V.Amosova, N.I.Ivanova, L.I.Vereshagin, and A.D.Gavrilov, USSR P.556 137, 1975; Byul.Izobret., 1977(16), 4.
60. F.G.Baddar, T.N.Al-Hajjar, and N.R.El-Raues, J.Heterocycl.Chem., 1976, **13**, 691.
61. H.Nagase, Chem.Pharm.Bull., 1973, **21**, 279.
62. N.Ya.Kuz'mina, M.L.Petrov, and A.A.Petrov, Zhur. Org.Khim., 1984, **20**, 2551.
63. N.Ya.Kuz'mina, Abstract of Candidate's Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1985.
64. C.S.Angadiyavar, M.N.Gudy, and M.V.George, Indian J.Chem., 1972, **10**, 888.
65. M.L.Petrov, E.S.Turbanova, N.Ya.Kuz'mina, N.P.Stepanova, and A.A.Petrov, Zhur.Org.Khim. 1984, **20**, 2662.
66. J.W.Batty and B.C.L.Weedon, J.Chem.Soc., 1949, 786.
67. I.N.Azerbaev, M.Zh.Aitkhozhaeva, and L.A.Tsoi, Symposium, "Khimiya Atsetilena i Tekhnologiya Karbida Kal'tsiya" (The Chemistry of Acetylene and the Technology of Calcium Carbide), Alma-Ata, Kazakhstan, 1972, p.154; Ref.Zhur.Khim., 1973, 8Zh416.
68. W.Hanefeld, Arch.Pharm., 1984, **317**, 297.
69. W.Hanefeld, M.Schlitzer, and J.V.Gösseln, Arch. Pharm., 1985, **318**, 185.
70. B.A.Trofimov, S.V.Amosova, N.K.Gusarova, S.E.Korostova, F.G.Salimgareeva, N.N.Skatova, and M.G.Voronkov, "Doklady IV Vsesoyuznoi Konferentsii po Khimii Atsetilena" (Reports at the IVth All-Union Conference on the Chemistry of Acetylene), Alma-Ata, Kazakhstan, 1972, Vol.2, p.455.
71. A.N.Volkov, A.N.Vavilova, and B.A.Trofimov, Izv. Akad.Nauk SSSR, Ser.Khim., 1982, 2808.
72. K.Tomita, M.Nagano, and H.Oka, Chem.Pharm.Bull., 1968, **16**, 914.
73. K.Tomita and M.Nagano, Chem.Pharm.Bull., 1968, **16**, 1324.
74. K.Tomita and M.Nagano, Chem.Pharm.Bull., 1968, **16**, 1907.
75. K.Tomita and M.Nagano, Chem.Pharm.Bull., 1968, **16**, 1911.
76. W.Bergold, P.Dimroth, H.Pasedach, and E.Schefczik, 100 Jahre BASF Aus Forsch., 1965, 95; Chem.Abs., 1965, **63**, 16 322.
77. N.I.Ivanova, M.V.Sigalov, S.V.Amosova, and B.A.Trofimov, Zhur.Org.Khim., 1983, **19**, 515.
78. A.H.Cook, I.Heilbron, and A.L.Leavy, J.Chem.Soc., 1947, 1598.
79. A.H.Cook, I.Heilbron, and A.L.Leavy, J.Chem.Soc., 1947, 1610.
80. A.H.Cook, I.Heilbron, and A.L.Leavy, J.Chem.Soc., 1948, 201.
81. M.J.Jassen, in "The Chemistry of Carboxylic Acids and Esters", Intersci.Publ., London, 1969, p.705.
82. G.Levesque, G.Tabak, and F.Outurquin, Compt.rend., 1975, **280C**, 1289.
83. G.Levesque and J.-C.Gressier, Bull.Soc.chim.France, 1976, 1145.
84. G.Levesque, G.Tabak, F.Outurquin, and J.-C.Gressier, Bull.Soc.chim.France, 1976, 1156.
85. J.-C.Gressier, G.Levesque, A.Mahjoub, and A.Thuillier, Bull.Soc.chim.France, 1979, 355.
86. G.Levesque and A.Mahjoub, Tetrahedron Letters, 1980, 2247.
87. R.B.Thompson and J.A.Chenicek, US P.2 846 461, 1958; Chem.Abs., 1959, **53**, 2094.
88. S.Oae, T.Yagihara, and T.Okabe, Tetrahedron, 1972, **28**, 3203.
89. M.Neuenschwander, G.Bart, and R.Niederhauser, Chimia, 1973, **27**, 73.

90. J.Ramachandran, S.R.Ramadas, and C.N.Pillai, Org. Preparation and Procedures Int., 1981, **13**, 71.
91. J.Ramanchandran, S.R.Ramadas, and C.N.Pillai, Org.Preparation and Procedures Int., 1981, **13**, 81.
92. J.-P.Pradére, A.Guene, G.Duguay, J.-P.Guemas, and H.Quiniou, Compt.rend., 1963, **269C**, 929.
93. S.Scheithauer and R.Mayer, Z.Chem., 1969, **9**, 59.
94. M.Schonufts, J.Meijer, P.Vermeer, and L.Brandsma, Synthesis, 1978, 439.
95. S.Kato, T.Mitani, and M.Miruta, Bull.Chem.Soc. Japan, 1972, **45**, 3653.
96. R.B.Woodward and R.Hoffmann, "Conservation of Orbital Symmetry" (Translated into Russian), Izd. Mir, Moscow, 1971, p.97.
97. T.Kauffmann, Angew.Chem., 1974, **86**, 715.
98. M.L.Petrov and A.A.Petrov, Uspekhi Khim., 1987, **56**, 267.
99. N.C.Gonella, M.V.Laskhmikantham, and M.P.Cava, Synth.Comm., 1979, **9**, 19.
100. S.Tanimoto, T.Oida, K.Hatanaka, and T.Sugimoto, Tetrahedron Letters, 1981, **22**, 655.
101. K.Hatanaka, S.Tanimoto, T.Oida, and M.Okano, Tetrahedron Letters, 1981, **22**, 5195.
102. S.Tanimoto, T.Oida, T.Kokubo, and M.Okano, Bull.Chem.Soc.Japan, 1982, **55**, 339.
103. C.Lion, Compt.rend., 1982, **294C**, 431.
104. V.N.Drozd and O.A.Popova, Zhur.Org.Khim., 1980, **16**, 2616.
105. V.N.Drozd, O.A.Popova, A.S.Vyazgin, and L.B.Dmitriev, Zhur.Org.Khim., 1983, **19**, 847.
106. M.L.Petrov, V.A.Bobylev, and A.A.Petrov, Zhur. Org.Khim., 1981, **17**, 1772.
107. M.L.Petrov, V.A.Bobylev, and A.A.Petrov, Zhur. Org.Khim., 1981, **17**, 1788.
108. H.D.Hartzler, J.Amer.Chem.Soc., 1973, **93**, 4961.
109. H.D.Hartzler, US P.3 781 281, 1973.
110. C.U.Pittman and M.Narita, Chem.Comm., 1975, 960.
111. J.Kreicberga, R.Kampare, and O.Neilands, Khim. Geterotsikl.Soed., 1982, 476.
112. L.Melby, C.Russel, H.D.Hartzler, and W.A.Sheppard, J.Org.Chem., 1974, **39**, 2456.
113. M.Sato, N.Gonella, and M.P.Cava, J.Org.Chem., 1979, **44**, 930.
114. V.Yu.Khodorkovskii and O.Neilands, Izv.Akad.Nauk Latv.SSR, Ser.Khim., 1982, 131.
115. V.Yu.Khodorkovskii and O.Neilands, Izv.Akad.Nauk Latv.SSR, Ser.Khim., 1985, 645.
116. A.Krief, Tetrahedron, 1986, **42**, 1209.
117. H.Behringer and J.Falkenberg, Tetrahedron Letters, 1967, 1895.
118. W.Krasuski, D.Nikolaus, and M.Regitz, Annalen, 1982, 1451.
119. G.Purello and P.Findaca, J.Chem.Soc., Perkin Trans. I, 1976, 692.
120. N.J.Bestmann, R.Engler, H.Hartung, and K.Roth, Chem.Ber., 1979, **112**, 28.
121. E.Schaumann and F.F.Grabley, Annalen, 1979, 1702.
122. V.N.Drozd and A.S.Vyazgin, Zhur.Org.Khim., 1983, **19**, 2210.
123. V.N.Drozd and A.S.Vyazgin, Zhur.Org.Khim., 1985, **21**, 1335.
124. V.N.Drozd and A.S.Vyazgin, Zhur.Org.Khim., 1985, **21**, 454.
125. V.N.Drozd, A.S.Vyazgin, and E.N.Komarova, Zhur. Org.Khim., 1986, **22**, 2443.
126. D.S.Yufit, Yu.T.Struchkov, E.N.Komarova, A.S.Vyazgin, and V.N.Drozd, Zhur.Org.Khim., 1986, **22**, 2448.

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