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THE REACTION OF TRITHIONE AND ITS SALTS WITH AMINES

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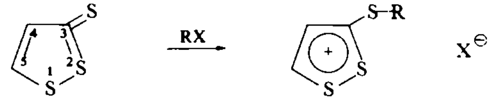
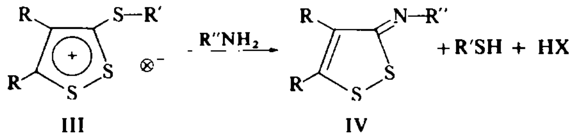
Abstract—The reaction of trithione (3H-1,2-dithiole-3-thione) with primary and secondary amines gives 3-aminothioacrylamides. The S-alkyltrithionium salts with amines give 3-aminodithioacrylic esters in a similar way. Electronegatively-substituted trithiones and 4-alkyl or aryl-substituted trithionium salts give correspondingly substituted ring-opened products.

WE HAVE studied the reactions of trithione (I)[1] and of its S-alkyltrithionium salts (II) with primary and secondary amines and find that a rearrangement takes place, with loss of sulphur, to give derivatives of 3-aminodithioacrylic acid.

The aryl-substituted trithiones and their salts were already described as reacting quite differently with amines. For example, 5-aryltrithiones react with aniline and benzylamine only under drastic conditions to give, with benzylamine, dibenzylthiourea and, with aniline, low yields of several products which have not been clearly identified.[2] Corresponding trithionium salts (III) react at the 3-position giving dithiolimides (IV).[3,4]



I II



III IV

Reactions with trithione

In contrast we find unsubstituted trithione reacts under comparatively mild conditions with various primary or secondary amines; e.g. aniline at 100° gave a yellow crystalline compound $C_{15}H_{14}N_2S$, together with hydrogen sulphide and

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[1] B. Böttcher and A. Lüttringhaus, *Liebigs Ann.* **557**, 89 (1947).

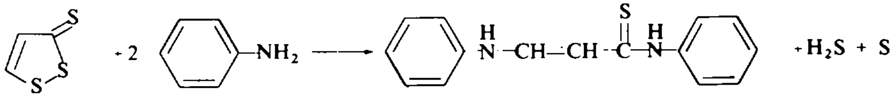
[2] B. Böttcher and F. Bauer, *Liebigs Ann.* **58**, 227 (1950).

[3] P. S. Landis, *Chem. Rev.* **65**, 237 (1965).

[4] U. Schmidt, A. Lüttringhaus and F. Hubinger, *Liebigs Ann.* **631**, 138 (1960).

sulphur. Similarly, *p*-toluidine and trithione gave the compound $C_{17}H_{18}N_2S$; and pyrrolidine and trithione gave a pale yellow compound, $C_{11}H_{18}N_2S$. All these compounds were obtained in high yield and they clearly belonged to the same class. The compounds were found to be weakly amphoteric, resistant to mild acid or alkaline hydrolysis, and gave the parent amine, hydrogen sulphide and a brown resin on vigorous hydrolysis with hydrochloric or hydrobromic acid in glacial acetic acid. These properties suggested a thioamide structure. The IR spectrum of the compound from aniline, $C_{15}H_{14}N_2S$, showed it had N—H of secondary amide type (3180 cm^{-1} in the solid, shifted to 3380 cm^{-1} in $CHCl_3$ solution) as well as an amine N—H (3280 cm^{-1} in the solid);[5] thiol absorption was absent. A band at 1602 cm^{-1} was attributed to an ethylenic double bond and strong absorptions at 1550 cm^{-1}, and 1300 cm^{-1} to thioamide and at 1190 cm^{-1} to C═S, but because of the scarcity of information on thioamide spectra these correlations were treated as tentative. Treatment of this compound with Raney nickel removed sulphur[6] and the double bond and gave 1,3-dianilinopropane in a high state of purity.

The NMR spectrum of the compound $C_{15}H_{14}N_2S$ showed 10 protons of 2 benzene rings (multiplet between $\tau = 2{\cdot}3$ ppm and $\tau = 3{\cdot}1$ ppm), 2 broad absorptions ($\tau = -3{\cdot}0$ ppm and $\tau = 1{\cdot}0$ ppm) each equivalent to 1 proton attached to nitrogen and a pair of protons on an isolated double bond ($\tau = 2{\cdot}5$–$2{\cdot}9$ ppm and $\tau = 4{\cdot}51$ ppm, $J \sim 9$ Hz, complicated by the aromatic proton absorption overlying the lower region). The mass spectrum of this compound gave a molecular ion peak at *m/e* 254, confirming the molecular weight found cryoscopically. A strong peak at *m/e* 221 ($C_{15}H_{13}N_2^+$) indicated a loss of SH via rearrangement to an isothioamide. Other prominent peaks occurred at *m/e* 162 ($C_9H_8NS^+$), indicating the loss of an anilino group, and at *m/e* 128 ($C_9H_6N^+$) by further loss of aniline from the 221 fragment and cyclization to a stable quinolinium ion.



V

This evidence is compatible with only one structure, the aminothioamide V. The structure of the product from p-toluidine, $C_{17}H_{18}N_2S$ (VI), followed from its similar IR and NMR spectra. In the NMR spectrum, two broad absorptions ($\tau = -2{\cdot}9$ and $1{\cdot}9$ ppm) are assigned each to one proton on nitrogen, a multiplet between $\tau = 2{\cdot}4$ and $3{\cdot}2$ ppm, due to 8 aromatic protons and one of the olefinic protons. The second olefinic proton absorbs as a doublet centred at $\tau = 4{\cdot}58$ ppm ($J \sim 9$ Hz); and there are 2 singlets at $\tau = 7{\cdot}65$ and $7{\cdot}7$ ppm of total area equivalent to 6 protons of the methyl groups.

The product from pyrrolidine, $C_{11}H_{18}N_2S$ (VII), by its mass, IR and NMR spectra, was shown to have the same type of structure. The NMR spectrum in this example clearly showed both olefinic protons (doublets at $\tau = 1{\cdot}65$ and $4{\cdot}86$ ppm, $J \sim 12$ Hz) and the coupling constant, together with IR absorption at 970 cm^{-1},

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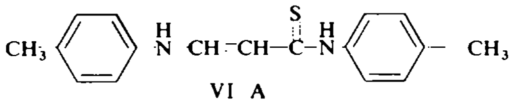
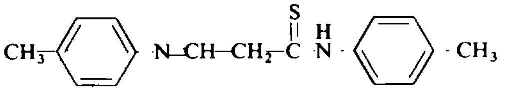
[5] D. Hadzi, *J. Chem. Soc.* **847** (1957).

[6] E. C. Kornfeld, *J. Org. Chem.* **16**, 131 (1951).

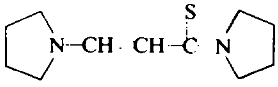
established this as a *trans*-linkage. The multiplets between $\tau = 5{\cdot}8$ and $7{\cdot}0$ ppm are due to the protons of the pyrrolidine ring on the α-carbon atoms, and the multiplet at $\tau = 8{\cdot}02$ ppm is due to the 8 protons on the β-carbon atoms. The similarity of the spectra of V, VI and VII provides confirmation that the enamine form, which is the only possibility for the pyrrolidine compound, is the correct form for the aniline and p-toluidine products, as well (VI A), rather than the anil in the form B.



VI A



B



VII

In the case of morpholine, it was possible to carry out the reaction in two stages: first, a stoichiometric reaction at room temperature leading to formation of salt VIII and sulphur; and secondly, on heating, a further reaction to the thioamide and H_2S. If trithione was dissolved in benzene and two moles of morpholine were added, the yellow crystalline dithiocarbamate salt VIII precipitated after a pronounced colour reaction. The salt was soluble in water and chloroform and was shown by analysis and spectral properties to be the morpholine salt of the unstable dithioacrylic acid IX. Solution of the dithiocarbamate salt VIII in chloroform and addition of methyl iodide or benzyl bromide led to the corresponding methyl and benzyl dithioacrylate esters X and XI, with precipitation of morpholine hydroiodide or bromide. The dithioacryldisulphide XII was most readily made from compound VIII by treatment with iodine in chloroform. However, it was detected in small amounts in many reactions of compound VIII: e.g. from recrystallizations of compound VIII from benzene or ethanol or in the benzene filtrate from the preparation of dithiocarbamate salt VIII. Finally, simply heating the morpholine salt VIII in morpholine converts it to the thioamide XIII. This compound can also be made from the methyl ester X and morpholine with loss of methyl mercaptan.

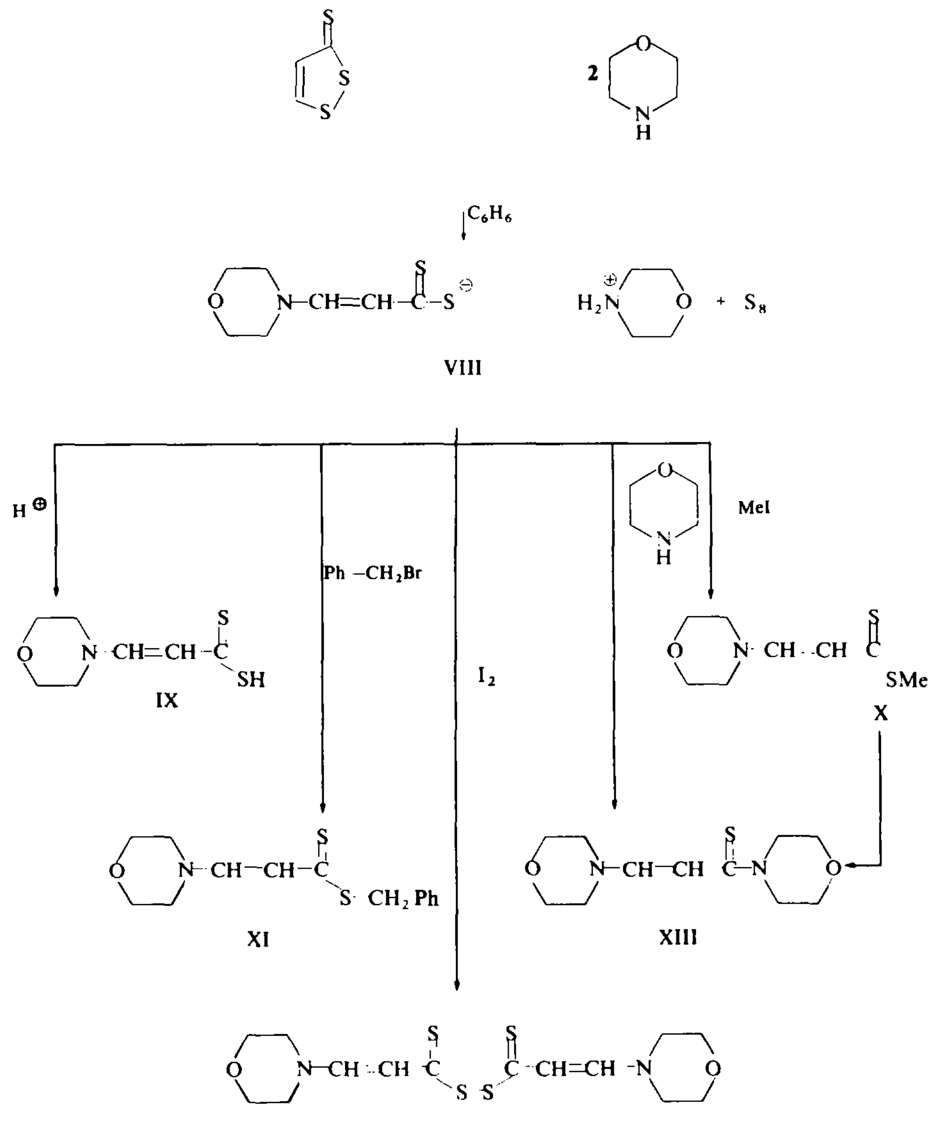
The reaction of trithione with pyrrolidine could be shown to occur in two steps also, but the intermediate salt was not isolated. In general, the reaction proceeds best with secondary aliphatic or alicyclic amines and aromatic amines with a *p*-electron donating substituent (*p*-anisidine). *o*-Substituted anilines and N-methylaniline are unreactive towards trithione.

Reactions with trithionium salts (II)

Trithionium salts are readily formed from trithione and alkyl halides,[3,7] benzyl and phenacyl halides and dialkyl sulphates. These may be formulated as having aromatic resonance as in the dithiolium ion.[8] Such salts of aryl-substituted trithiones

[7] B. Böttcher and A. Lüttringhaus, *Liebigs Ann.* **557**, 89 (1947).

[8] E. Klingsberg, *J. Am. Chem. Soc.* **83**, 2934 (1961).



have been described,[3] together with their reactions with amines and hydrazines to form anil and hydrazone derivatives of trithione. We have prepared a number of these salts of unsubstituted trithione. By far the easiest to prepare are the salts from methyl iodide, dimethyl sulphate and benzyl bromide. We found that these salts react with amines in a way similar to that of trithione, with ring opening and loss of sulphur to give 3-aminodithioacrylic esters.

When the methiodide of trithione[9] (II, R = Me, X = I) was treated with morpholine in benzene or dimethylsulphoxide, reaction occurred immediately, with precipitation of sulphur and formation of a yellow crystalline compound, $C_8H_{13}NOS_2$,

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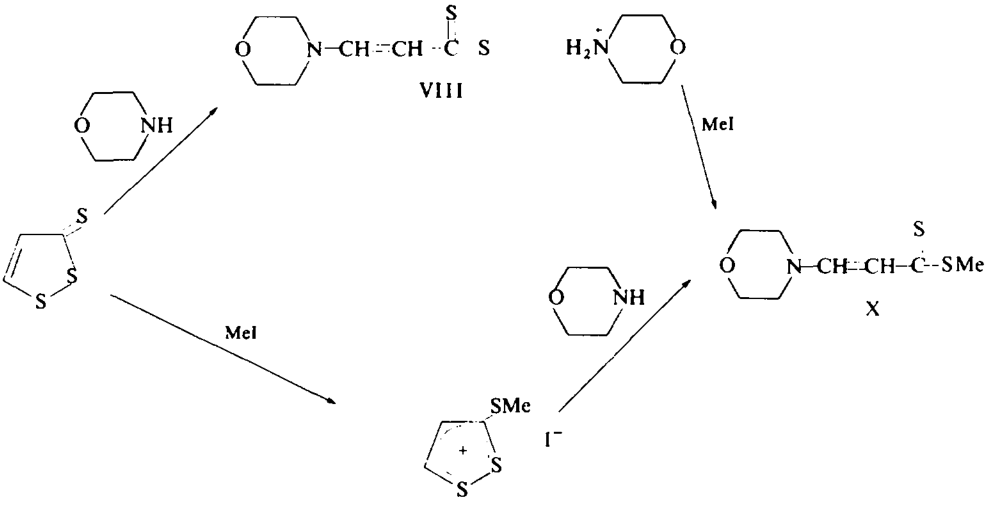
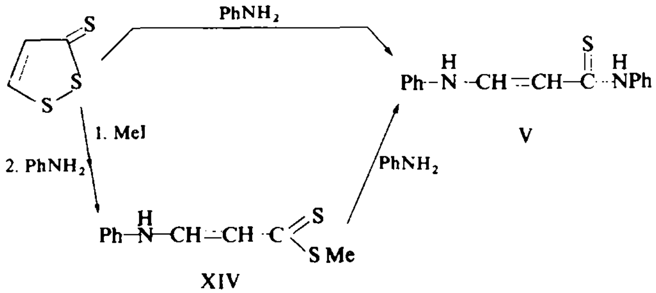
[9] F. Challenger, E. A. Mason, E. C. Holdsworth and R. Emmott, *J. Chem. Soc.* 292 (1953).

which was identical with that obtained by treating the morpholine salt VIII with methyl iodide. Similarly, heating aniline and trithione methiodide gave a thioester (XIV) which could be converted to the thioamide (V) and methanethiol, by further heating with aniline.

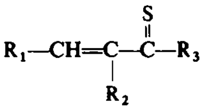




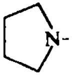
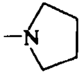
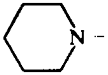
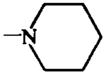
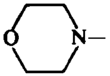
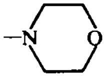
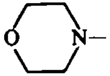
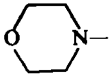
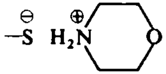
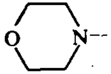
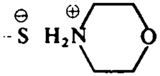
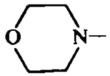
A number of dithioesters of this type have been prepared from various amines and they are summarized in Table 1. They were all characterized extensively by microanalysis, molecular weight, NMR, IR, UV and mass spectrometry. The reactions of the methiodides or methosulphates are conveniently carried out in alcohol or benzene, in which the salts are insoluble, but which give very clean products, or in dimethylsulphoxide, in which the salts are soluble and reaction is more rapid but the products are less pure. The benzyl bromide salt (II, R = benzyl, X = Br) was insoluble in dimethylsulphoxide as well as in other organic solvents; it gave none of the desired product in dimethylsulphoxide, but reacted with aniline in ethanol to give benzyl 3-anilinodithioacrylate.

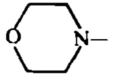
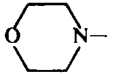
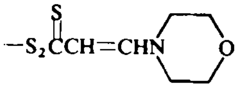
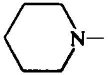
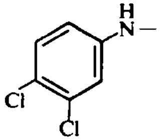
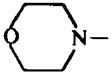
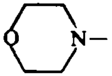
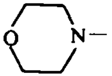
Electronegatively substituted trithiones behave similarly to trithione. Thus, 4-cyanotrithione (XV) in benzene with the stoichiometric quantity of morpholine gave the cyano-dithio salt (XVI) which can be converted to the methyl ester (XVII,

TABLE 1. SPECTRAL DATA FOR AMINOTHIOACRYLATES



$$R_1{-}CH{=}\underset{\displaystyle R_2}{\underset{|}{C}}{-}\overset{\displaystyle S}{\overset{\|}{C}}{-}R_3$$

Compound	R_1	R_2	R_3	UV Maxima								IR Absorption		NMR of olefinic hydrogens (τ)[h]		
				λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε	$\nu_{C=C}$ (cm^{-1})[d]		Low field	High field	J
V	$C_6H_5\overset{H}{N}$—	H	$—\overset{H}{N}—C_6H_5$			241[a]	16,300			348	26,000	1636	(1602, 1589)[e,f]	2·5–2·9	4·51	9
VI	p-$CH_3C_6H_4\overset{H}{N}$—	H	$—\overset{H}{N}C_6H_4—pCH_3$									1636	(1600, 1588)[g,f]	2·6–3·2	4·58	9
XXIX	p-$CH_3C_6H_4\overset{H}{N}$—	H	$—\overset{H}{N}—C_6H_5$									1650[g]		2·4–3·2	4·55	9
VII		H						294[a]	25,700	344	17,900	1609	(1531)	1·65	4·8	12·5
		H						295[b]	20,400	345	18,750	1609		1·8	4·65	12·5
XIII		H						296[b]	23,400	346	18,300	1606	(1522)	1·8	4·5	12·5
IX		H	—SH									1590[g]		2·05	3·75	12
VIII		H				250[a]	6,100	340	21,600	396	19,000	1583	(1606)	1·9	3·4	12·5
XVI		CN						303[a]	13,300	387	8100			1·0	—	—
X		H	—SMe	221[a]	12,400			321	17,800	387	32,900	1593		1·9	3·7	12

XI		H	—$SCH_2C_6H_5$	$220^{b, j}$	17,500			325	17,500	390	33,200	1589		2·0	3·9	12
XII		H				270^a	13,350	338	16,900	407	43,600	1589	(1524)	1·8	3·2	12
XIV	$C_6H_5\overset{H}{N}$—	H	—SMe	217^c	13,700	247	15,300	340	8800			1626	$(1600, 1588)^i$	2·5–2·9	3·86	9
	$C_6H_5\overset{H}{N}$—	H	—$SCH_2C_6H_5$	$216^{b, j}$	20,700	242	14,700	338	11,300			1624	$(1599, 1587)^i$	2·4–2·9	3·75	8·5
	Me_2N—	H	—SMe	$220^{b, j}$	9200			318	16,000	386	31,500	1606				
		H	—SMe	226^c	9100			323	16,600	378	32,500	1592		1·7	3·7	12·5
		H	—SMe	215^c	24,800	255	16,300	347	9700			1625	$(1597, 1568)^{f, i}$			
XVII		CN	—SMe			263^b	10,300	317	16,800	373	21,600	1595		1·3	—	—
XIX		CH_3	—SMe					323^b	12,000	393	28,900	1574		1·86	—	—
		C_6H_5	—SMe					324^b	15,800	396	27,600·	1575		1·6	—	—
XXVII												1618^g		3·15	3·93	9
XXVIII												1620^g		3·22	4·10	8
XXXI												1642	$(1617, 1588)^{e, i}$	2·6–3·4	3·72	8
XXXII														2·5–3·2	5·25	8·5

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[a] In dioxan.

[b] In ethanol.

[c] In cyclohexane.

[d] In chloroform; data in ( ) have not been assigned.

[e] In KBr pressed plate bands at: 1554, 1587, 1602, 1650 cm^{-1}.

[f] In KBr pressed plate bands at 1567, 1594, 1636, 1624 cm^{-1}.

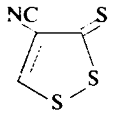
[g] Nujol.

[h] In deuterochloroform measured either with Varian A-60 or Perkin–Elmer R-10; temperature ~37° with TMS internal standard at τ = 10 ppm.

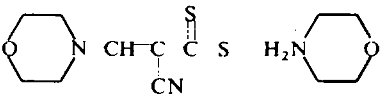
[i] Double-band assignment tentative; see text.

[j] Shoulder.

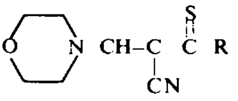
R = SMe). In contrast, 4-methyl- and 4-phenyltrithione do not give thioacrylic compounds under these conditions, even after 3 months. 4-Methyltrithione only reacted with aniline at the boiling point of the latter and gave a low yield of diphenylthiourea (compare the formation of dibenzylthiourea from benzylamine and 5-(p-methoxyphenyl trithione[2]). 4-Methyltrithione and pyrrolidine gave two products, one of which, by analysis and IR spectrum, is probably XVIII. However, the methiodide of 4-methyltrithione and of 4-phenyltrithione on treatment with morpholine gave the corresponding dithiomethacrylic esters (XIX) (R = Me, C_6H_5).



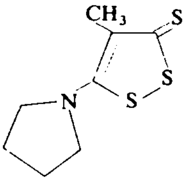
XV



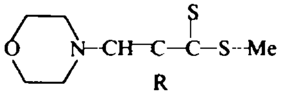
XVI



XVII R SMe

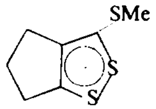


XVIII

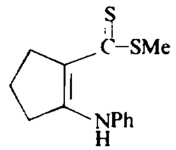


XIX R - Me

R C_6H_5

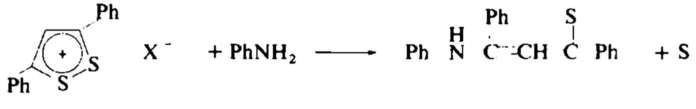


XX



XXI

Since this work was undertaken, other authors have found similar ring-opening reactions in dithiolium salts. The methiodide of trimethylene trithione (XX) with benzylamine or aniline gave dithioesters (XXI from aniline) but resins with aliphatic amines.[10] Another group has confirmed that 5-aryltrithionium salts give anils with aromatic primary amines but that trithionium salts with a 4-aryl substituent undergo the same ring-opening reaction we describe, to give dithioesters.[11] 1,2-Dithiolium salts (XXII) also have been shown recently to undergo ring-opening with amines, with loss of sulphur to aminothiones (XXIII).[12]



XXII XXIII

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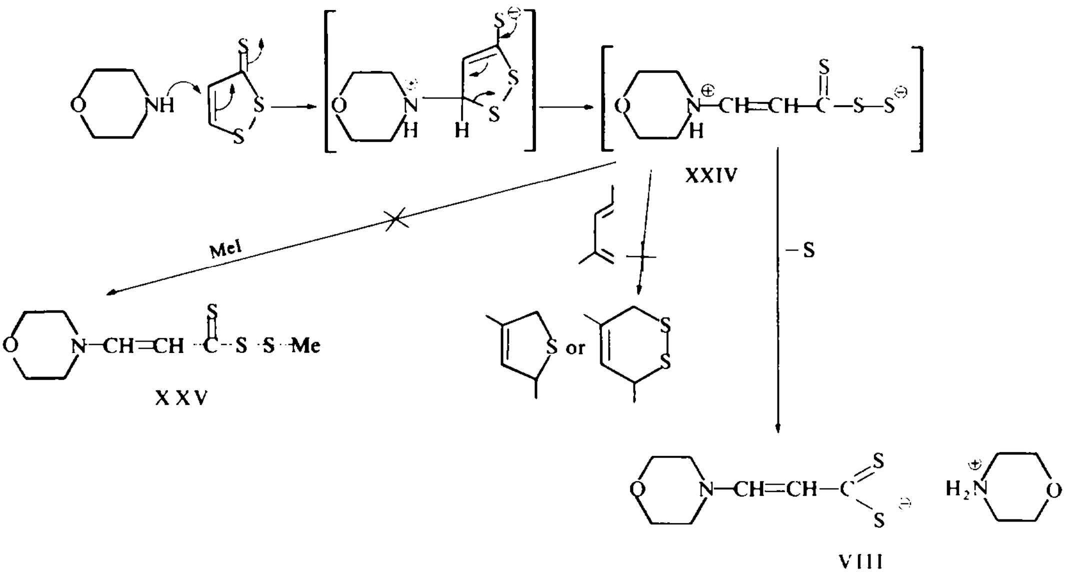
[10] R. Mayer and H. Hartmann, *Ber. Dtsch. Chem. Ges.* 97, 1886 (1964).

[11] C. Paulmier, Y. Mollier and N. Lozac'h, *Bull. Soc. Chim. Fr.* 2463 (1965).

[12] D. Leaver, D. M. McKinnon and W. A. H. Robertson, *J. Chem. Soc.* 32 (1965).

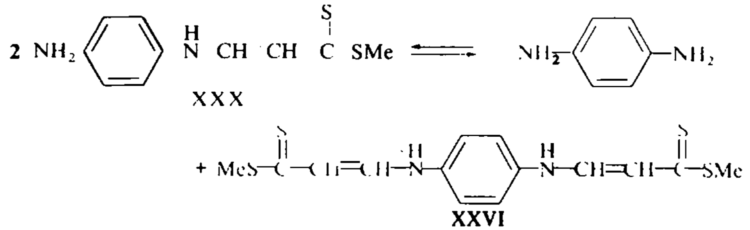
Mechanism

The isolation of the intermediate salt VIII and sulphur in the first stage of the reaction of morpholine with trithione and the elimination of 1 mole of hydrogen sulfide in the second step provide the stoichiometry of the reaction and enable us to suggest a mechanism. Clearly, an electron-deficient centre at position 5 is required. Initial anionoid attack at position 5 of trithione leads, with electron shift, to a pertrithio acid (XXIV), which loses sulphur, giving the dithio acid (IX) which forms a salt with a second molecule of amine. Attempts to prove the intermediate existence of XXIV and to find how the third sulphur atom eventually becomes S_8 have been inconclusive. Carrying out the reaction in the presence of methyl iodide gave none of the hoped-for methyl trithioester XXV. The addition of styrene, in the hope of picking up atomic sulfur as styrene thioepoxide or as a polymer, was unsuccessful, as was adding 1,3-dimethylbutadiene.



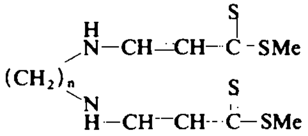
Diamines

Reactive diamines, such as p-phenylenediamine, and trithione give yellow polymeric solids. With trithionium salts, the diamines give diesters, e.g. XXVI from *p*-phenylenediamine, XXVII from ethylenediamine. These diesters are obtained even under conditions in which an amino ester should be favoured. This is due to the lability of the amino groups in these 3-aminoacrylic esters and amides which permits an equilibrium in solution. Heating 3-anilinothioacrylanilide (V) with *p*-toluidine in benzene gives 3-*p*-toluidinothioacrylanilide XXIX; and the diester XXVII with aniline gives the anilinodithioester XIV. The symmetrical diesters are precipitated from the reaction mixture because of their lower solubility. In the case of *p*-phenylenediamine, an amino ester (XXX) has been isolated in an impure state, but this disproportionates to XXVI and phenylenediamine during crystallization. With *o*-phenylenediamine steric hindrance discourages the formation of the diester and the 1 : 1 reaction product XXXI is obtained.

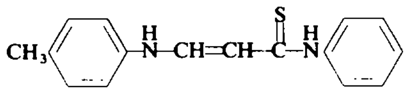


XXX

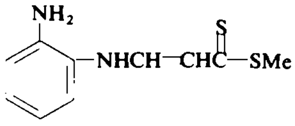
XXVI



XXVII n = 2
XXVIII n = 6



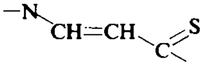
XXIX



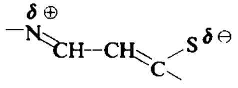
XXXI

Spectra

All the aminothioacrylic compounds described here show a prominent band or series of bands in the IR between 1660 and 1570 cm^{-1}. We have assigned this strong absorption to the polarized double bond which conjugates the electron-donating nitrogen and the electron-accepting sulphur (A — B).



A



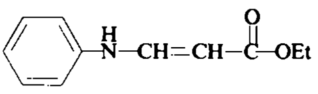
B

In the case of the aromatic amino derivatives, mixing of the double-bond stretching vibration with the ring vibrations occurs and, as a consequence, all of the observed frequencies are mixtures of these vibrations. No one band can then be assigned with certainty to the double-bond stretching. We have, however, tentatively assigned the highest frequency in these compounds as the most probable double-bond vibration since its molar absorptivity was consistently closest to that found for the aliphatic amino derivatives. Amides have a higher frequency than corresponding esters. Table 1 summarizes the principal spectra features.

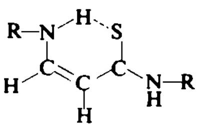
In the NMR spectra, the olefinic proton absorptions can be assigned with certainty. The high-field doublet is due to the proton α- to the thiocarbonyl group, and the low-field absorption is due to the proton on the β-carbon atom. Evidence for this is provided by the observation of coupling between N—H of the 3-amino group and the low-field proton in compounds V, XXVII, XXIII and XXXII. In compounds VII and

IX, there is a broadening of the low-field absorption due to the non-spherical distribution of charge near the nitrogen atom; and finally correlations between groups of compounds in which the 3-amino group is common to all but in which different groups are attached to thiocarbonyl give rise to wide variations of the high-field absorption, but little change in the low-field absorption, as for example in the series of morpholino compounds VIII, X, XII, XIII. Similarly, comparing methyl-3-anilinoacrylate[13] (XXXII) shows a marked shift only in the high-field proton. Of course, the conclusive evidence is from the cyano, methyl or phenyl-substituted thioacrylate compounds XVI, XVII, and XIX.

All unsubstituted compounds showed the typical AB pattern in their spectra characteristic of spin–spin splitting of non-equivalent protons. The coupling constants are consistent with a *trans* double bond in some cases ($J \sim$ 12–13 Hz). In others, particularly those cases in which the nitrogen bears a hydrogen atom, the coupling constant is smaller ($J \sim$ 8–9 Hz) than that normally associated with a *trans* linkage and would suggest a *cis* configuration, especially since a hydrogen bond to the thiocarbonyl group is possible (XXXIII). This conforms with coupling constants from *trans*-β-chlorovinylketones, β-aminovinylketones[14] and *cis* and *trans*-β-arylmercaptoacrylates.[15] This decrease in coupling constants from that normally observed for *cis* and *trans* protons could be caused by the increase of the electronegativity of the substituents on the double bond.[16]



XXXII



XXXIII

The UV spectra of the 3-aminothioacrylates are summarized in Table 1. In general the esters (e.g. X) show three major absorption bands of increasing intensity centered approximately at 220 mμ (ε 9–12,000), 330 mμ (ε 16–18,000) and 385 mμ (ε 31–33,000); whereas the amides have two major bands centred at 295 mμ (ε 20–25,000) and 345 mμ (ε 17–19,000). The aromatic amino derivatives show a hypsochromic displacement from these values.

EXPERIMENTAL

3-*Anilinothioacrylanilide* (V). Aniline (17·5 g, 190 mmole) and trithione (5 g, 37 mmole) were heated together for 1 hr on a steam bath. Hydrogen sulphide (approx 30 mmole) was evolved. On cooling, a mass of crystals formed in the solution, which was diluted with ether and filtered, giving 3-*anilinothioacrylanilide* (7·6 g 84%) as bright yellow needles from benzene, m.p. 155–157°. (Found: C, 70·72; 70·89; H, 5·54; 5·66; N, 11·22, 10·70; S, 12·78, 12·40; mol. wt. 254. Calc. for $C_{15}H_{14}N_2S$: C, 70·83; H, 5·52; N, 11·02; S, 12·55%; mol. wt. 254.)

Removal of excess aniline from the combined mother liquors of the reaction and crystallization, followed by concentration of the solution, slowly gave crystalline elementary sulphur.

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[13] F. Strauss and W. Voss, *Ber. Dtsch. Chim. Ges.* **59**, 1681 (1926).

[14] W. R. Benson and A. E. Pohland, *J. Org. Chem.* **29**, 385 (1964).

[15] W. E. Truce and B. Groten, *J. Org. Chem.* **27**, 128 (1962).

[16] T. Schaefer, *Canad. J. Chem.* **40**, 1 (1962).

The reaction was also carried out at room temperature over 3 days. A red colour, formed at first, went away as the yellow product crystallized out.

1,3-*Dianilinopropane.* The compound V (2 g) was dissolved in ethanol and treated with Raney nickel (20 g) for 1 hr on the water bath. After filtering off the nickel and extracting basic material with hydrochloric acid, 1,3-dianilinopropane (1·2 g crude) was obtained as a colourless oil. The IR and NMR spectra were identical with those of a pure synthetic specimen.[17] The material obtained from the Raney nickel treatment gave a dihydrochloride, m.p. 195–200° (lit.[18] m.p. 195°) and a diacetate, m.p. 122–130° (lit.[17] m.p. 119°); mixed melting points with authentic derivatives were undepressed.

3-*Morpholinodithioacrylic acid, morpholine salt* (VIII). Trithione (2·7 g, 20 mmole) in benzene (100 ml) under nitrogen, was cooled to 0° and a solution of morpholine (4 ml, 46 mmole) in benzene (15 ml) was added slowly with stirring. After a short time, 3-*morpholinodithioacrylic acid, morpholine salt* separated as a yellow solid (5·5 g; quantitative yield), which was filtered off and washed with benzene, m.p. 126–129°, containing benzene of crystallization. A portion was purified by dissolving it in chloroform and precipitating with ether, m.p. 138–142°. (Found: C, 52·8; H, 7·3; N, 8·6. Calc. for $C_{11}H_{20}O_2N_2S_2 \cdot \frac{1}{2}C_6H_6$: C, 53·3; H, 7·3; N, 8·9%. Found: C, 47·58; H, 7·25; N, 10·71; S, 23·85. Calc. for $C_{11}H_{20}O_2N_2S_2$: C, 47·8; H, 7·3; N, 10·3; S, 23·2%.)

The reaction can also be run at room temperature without a nitrogen blanket. The product is soluble in water and chloroform and is insoluble in carbon disulphide. High resolution mass spectrometric analysis gave an empirical formula of $C_{11}H_{18}N_2O_2S$ (XIII) with a parent ion mass of 242. NMR showed the presence of half a molecule of benzene of crystallization.

In a separate experiment, only half the stoichiometric requirement of morpholine was added, and only half the trithione reacted. To the filtrate from this reaction was added another equivalent of morpholine, and the remaining trithione was converted to product.

From the benzene filtrate, sulphur and the dithioacrylodisulphide XII were isolated.

3-*Morpholinodithioacrylic acid* (IX). The morpholine salt VIII was dissolved in aqueous sodium carbonate, the solution filtered and the clear filtrate added slowly to an excess of dil. hydrochloric acid, precipitating the free acid, which was collected on a filter, washed with a little cold water and ether and crystallized from chloroform with the minimum of heating, giving 3-*morpholinodithioacrylic acid* as orange needles, m.p. 109° (dec.). (Found: C, 44·23; H, 5·79; N, 7·41; S, 33·80. Calc. for $C_7H_{11}NOS_2$: C, 44·41; H, 5·86; N, 7·40; S, 33·88%.)

The more stable *potassium salt* of this acid was prepared by dissolving the crude acid in ethanol and neutralizing the solution with alcoholic potassium hydroxide; the potassium salt was precipitated, and crystallized from aqueous ethanol as red needles, m.p. 300° (dec.).

The *zinc salt* was obtained by double decomposition of the potassium salt with zinc sulphate in water. The zinc salt was obtained as fine orange crystals, decomposing when heated at about 230°, in an over-all yield of 87% based on trithione.

3-*Morpholinothioacrylodisulphide* (XII). The morpholine salt (VIII, 1 g) was dissolved in chloroform and a solution of iodine (0·4 g) in chloroform was added slowly. The solvent was removed under vacuum and the residue crystallized from benzene–light petroleum (b.p. 60–80°) to give the *thiuramdisulphide* (XII), m.p. 149–150° (dec.). (Found: C, 43·5; H, 5·2; N, 6·8. Calc. for $C_{14}H_{20}N_2O_2S_4$: C, 44·7; H, 5·4; N, 7·4%.)

High resolution mass spectroscopy gave the empirical formula $C_{11}H_{18}N_2O_2S$ of parent ion mass 242 (XIII).

Methyl ester of 3-*morpholinodithioacrylic acid* (X). The above dithiocarbamate salt VIII was dissolved in either chloroform or acetone and the stoichiometric amount of methyl iodide added. The morpholinium iodide which precipitated was separated, and the solvent was removed under vacuum. The product was recrystallized from methanol; m.p. 136·5–138°. (Found: C, 46·9; H, 6·9; S, 31·4. Calc. for $C_8H_{13}NOS_2$: C, 47·3; H, 6·4; S, 31·5%.)

High resolution mass spectroscopy gave an empirical formula of $C_8H_{13}NOS_2$ of parent mass 203. IR spectrum was identical to previously prepared sample.

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[17] W. L. C. Veer, *Rec. Trav. chim.* **57**, 989 (1938).

[18] R. Daniels and B. D. Martin, *J. Org. Chem.* **27**, 178 (1962).

Benzyl ester of 3-*morpholinodithioacrylic acid* (XI). Same procedure was used as described above between dithiocarbamate salt (1 g) and benzyl bromide (0·54 g) in chloroform. Recrystallized product ester from benzene–Skelly B; m.p. 94–96°. (Found: C, 61·5; H, 6·2. Calc. for $C_{14}H_{17}ONS_2$: C, 60·1; H, 6·1%.)

3-*Morpholinothioacrylomorpholide* (XIII). The morpholine salt (VIII) (2·5 g) was heated in refluxing benzene (50 ml) in a nitrogen atmosphere for 1 hr. Hydrogen sulphide was slowly eliminated and the material went into solution. The solvent was removed under vacuum and the residue crystallized from ethanol–benzene, giving fine pale buff needles, m.p. 194–196°, which may be 3-morpholinodithioacryloyl morpholinesulphenamide. From the mother liquors of this crystallization was obtained 3-*morpholinothioacrylomorpholide* (1·25 g, 48%) as a pale yellow powder, m.p. 151–152° after crystallization from ethanol and ethanol–light petroleum. (Found: C, 54·46; H, 7·40; N, 11·60. Calc. for $C_{11}H_{18}N_2O_2$: C, 54·5; H, 7·4; N, 11·6%.)

The compound XIII was also prepared by dissolving methyl 3-morpholinodithioacrylate (X) (1 g) in morpholine (8 ml) at room temperature. Slowly over 2 days the colour of the solution changed from orange to light yellow. Removal of the solvent and crystallization from benzene–light petroleum (b.p. 60–80°) gave the *amide* XIII (1·0 g, 84% yield), m.p. 147·5–148·5°.

Finally, compound XIII was prepared from the morpholine salt VIII by dissolving it in morpholine, warming gently on a steam bath and removing the excess morpholine under vacuum. The product was identical with the compound obtained above.

High resolution mass spectrometric analysis gave an empirical formula of $C_{11}H_{18}N_2O_2S_3$ of parent mass 242.

3-*p*-*Toluidinothioacrylo*-*p*-*toluidide* (VI). Trithione (2 g) and *p*-toluidine (7 g) were melted together on a steam bath. Hydrogen sulphide was evolved and after 10 min, solid began to separate. After a further 5 min, the material had set solid. It was cooled, triturated with benzene and filtered, giving 3-*p*-*toluidinothioacrylo*-*p*-*toluidide* (3·6 g, 85%) as bright yellow needles, m.p. 185–186° from toluene. (Found: C, 72·30; H, 6·41; N, 10·00; S, 11·48. Calc. for $C_{17}H_{18}N_2S$: C, 72·30; H, 6·43; N,9·92; S, 11·37%.)

3-*Pyrrolidinothioacrylopyrrolidide* (VII). A solution of trithione (2 g) in benzene (20 ml) was cooled to 10° under nitrogen and a solution of pyrrolidine (4 ml) in benzene (6 ml) added slowly to it with cooling; producing two liquid phases, the lower one deep red. The mixture was heated on a steam bath, when hydrogen sulphide was evolved. Evaporation of the solvent under vacuum left a red oil which solidified slowly. Crystallization from water gave 3-*pyrrolidinothioacrylopyrrolidide* as pale yellow needles, m.p. 112–114°. (Found: C, 62·61; H, 8·14; N, 13·87; S, 15·40. Calc. for $C_{11}H_{18}N_2S$: C, 62·81; H, 8·63; N, 13·34; S, 15·27%.)

High resolution mass spectrometry indicated a mass of 210 and a formula $C_{11}H_{18}N_2S$. NMR spectra were in accordance with the given structure.

3-*Piperidinothioacrylopiperidide*. Yellow crystals from benzene, m.p. 75–77°. (Found: S, 9·7. Calc. for $C_{13}H_{22}N_2S$: S, 9·6%.)

3-*Benzylaminothioacrylobenzylamide*. A solution of trithione (2 g) and benzylamine (7 g) in isopropanol (20 ml) was refluxed for 1 hr, then cooled and poured into water (100 ml). The oil which separated was triturated with more water and light petroleum (b.p. 60–80°). The oil slowly deposited crystals, which were recrystallized several times from benzene–light petroleum (b.p. 60–80°) and then from carbon tetrachloride to give 3-*benzylaminothioacrylobenzylamide*, m.p. 108–110°. (Found: C, 72·24; H, 6·42; N, 9·68. Calc. for $C_{17}H_{18}N_2S$: C, 72·30; H, 6·43; N, 9·92%.)

3-*p*-*Anisidinothioacrylo*-*p*-*anisidide*. The product was prepared from p-anisidine (18 g) and trithione (6 g) by the procedure used for *p*-toluidine (above). The crude product was washed with carbon disulphide to remove sulphur and then crystallized from benzene–chloroform to give 3-*p*-*anisidinothioacrylo*-*p*-*anisidide*, m.p. 169–171° as a bright yellow powder. (Found: C, 65·07; H, 5·66; N, 9·05; S, 10·28. Calc. for $C_{17}H_{18}N_2O_2S$: C, 65·02; H, 5·78; N, 8·92; S, 10·21%.)

Methyl 3-*morpholinodithioacrylate* (X). (*a*) Six g (23·1 mmole) of the dimethyl sulphate salt of trithione were added quickly, with rapid stirring, to a solution of 5·0 g (57·6 mole) of morpholine in dimethylsulphoxide (20 ml). The temperature rose rapidly to 50°, and a red colour developed. The reaction was cooled to 40° with an ice bath, and solid was precipitated. The mixture was cooled to 0°, and the solid filtered off. Further solid was obtained by diluting the filtrate first with ethanol (10 ml) and then with water. The product was recrystallized from methanol, with a decolourizing charcoal treatment, giving methyl 3-*morpholinodithioacrylate* as a bright yellow solid (4·68 g) (92%), m.p. 136·5–138°. (Found: C, 47·1; H, 6·5; N, 6·0; S, 31·0; mol. wt. (ebulliscopic in benzene) 215. Calc. for $C_8H_{13}NOS_2$: C, 47·3; H, 6·41; N, 6·90; S, 31·5%; mol. wt. 203.)

(*b*) This ester was also obtained from the morpholine salt VIII as described above.

Methyl 3-anilinodithioacrylate (XIV). (*a*) Using the same method (*a*) as for morpholine, the ester (XIV, 1·8 g; 75·5%) was obtained as orange crystals, m.p. 86·6–87·6°. (Found: C, 57·2; H, 5·4; N, 6·52. Calc. for $C_{10}H_{11}NS_2$: C, 57·5; H, 5·27; N, 6·71%; mol. wt. 209).

High resolution mass spectrum indicated $C_{10}H_{11}NS_2$; mol. wt. 209.

(*b*) The product was also obtained by mixing trithione methiodide (1 g) and aniline (5 ml) and warming very gently until a clear solution was obtained. The solution was cooled, excess aniline was dissolved in dilute hydrochloric acid, and the solid ester collected to give *methyl 3-anilinodithioacrylate* (0·7 g, 92%), m.p. 80–85°. After several crystallizations from aqueous ethanol or light petroleum (b.p. 60–80°) it had constant m.p. 87–89°.

(*c*) The product was obtained by heating the compound (XXVII, see below) (0·5 g) with aniline (3 ml) in benzene for 1 hr. There was some loss of methanethiol and tar formation. Removal of excess aniline and evaporation of the clear benzene solution gave the ester (0·4 g, 60%) identical with that obtained by the previous method, m.p. 88–90° after one crystallization from aqueous ethanol.

Methyl 3-(3′,4′-dichloroanilino)-dithioacrylate. The procedure (*a*) for morpholine was used. The product crystallized out of the reaction mixture and was recrystallized from ethanol. Contaminating sulphur was removed by washing with carbon disulphide, but this also dissolved some of the product. *Methyl 3-(3′,4′-dichloroanilino)-dithioacrylate* was obtained as yellow crystals (final yield 33%), m.p. 156–157°. (Found: C, 42·5; H, 3·4; N, 4·63. Calc. for $C_{10}H_9Cl_2NS_2$: C, 43·2; H, 3·24; N, 5·04%.)

Methyl 3-piperidinodithioacrylate. The ester was obtained as pale yellow crystals, m.p. 118–122°, from ethanol by procedure (*a*) for morpholine above. (Found: C, 53·3; H, 7·6; N, 6·81. Calc. for $C_9H_{15}NS_2$: C, 53·8; H, 7·47; N, 6·97%.)

Methyl 3-dimethylaminodithioacrylate. Trithione methosulphate (6 g, 23 mmole) was added to a solution of dimethylamine (1·03 g, 23 mmole) in dimethylsulphoxide (20 ml), causing a slight rise in temperature and a deep red colour. A flocculent precipitate was formed. Another 0·5 g amine was added. The solid was quickly collected and the filtrate diluted with water, giving more solid. The combined solids were recrystallized from benzene–light petroleum to give a dark red product, m.p. 99–102°. This was crystallized again from ethanol to give *methyl 3-dimethylaminodithioacrylate* as a yellow solid (1·0 g, 27%), m.p. 101–103°. (Found: C, 44·8; H, 7·0; N, 8·54. Calc. for $C_6H_{11}NS_2$: C, 44·7; H, 6·84; N, 8·70%.)

3-Anilinodithioacrylic acid, benzyl ester. Aniline (3·26 g, 0·035 mole) was dissolved in 25 ml of alcohol. To this was added 5·35 g (0·0175 mole) of the benzyl bromide salt of trithione. The product came out rapidly as yellow crystals, so more alcohol was added and the mixture was warmed until it was homogeneous. The solution was filtered and cooled. The product, which crystallized out, was recrystallized from alcohol to yield 3·53 g, m.p. 113–118°. This was recrystallized from benzene to yield 1·5 g (30% of theory), m.p. 120–122°. (Found: C, 66·5; H, 5·5; N, 4·67; S, 22·3. Calc. for $C_{16}H_{15}NS_2$: C, 67·4; H, 5·30; N, 4·92; S, 22·5%.)

3-Morpholino-2-cyanodithioacrylic acid, morpholine salt (XVI). 4-Cyanotrithione (1 g, 6·3 mmole) was dissolved in 150 ml of refluxing benzene; the solution was cooled to 40° and morpholine (0·55 g, 6·3 mmole) was added, producing an immediate turbidity, and a mat of yellow crystals (0·9 g) soon separated. This was filtered off and to the filtrate a further 0·55 g of morpholine was added. A second crop (1·1 g) of product was isolated, giving the *3-morpholino-2-cyanodithioacrylic acid morpholine salt*, m.p. 118–119° containing benzene of crystallization. (Found: C, 52·3; H, 6·3; N, 12·1. Calc. for $C_{12}H_{19}O_2N_3 \cdot \frac{1}{2}C_6H_6$: C, 52·9; H, 6·5; N, 12·3%.)

The IR spectrum showed the polarized double bond (~6·31 μ), a cyano group (~4·57 μ) and the amine salt (~3·7 and 4·1 μ). High resolution mass spectrometry gave an empirical formula of $C_{12}H_{17}N_3O_2S$ (XVII, R = ) of parent mass 267.

Methyl 3-morpholino-2-cyanodithioacrylate (XVII, *R* = *SMe*). The salt XVI (1 g) prepared from 4-cyanotrithione, was dissolved in chloroform (25 ml) and a solution of methyliodide (1 g) in chloroform (3 ml) added. The product was isolated as in the examples above and recrystallized from methanol to give XVII, m.p. 158–159°. (Found: C, 47·7; H, 5·3; N, 11·9. Calc. for $C_9H_{12}ON_2S_2$: C, 47·4; H, 5·3; N, 12·3%.)

High resolution mass spectrometry gave a molecular weight of 228 and $C_9H_{12}ON_2S_2$.

Methyl 3-morpholino-2-methyldithioacrylate (XIX, *R* = *Me*). 4-Methyl-3-methylthiodithiolium iodide (3·5 g, 12 mmole) was dissolved in dimethylsulphoxide (20 ml) and morpholine (3·8 g) added. The temperature rose to 35° and the solution became homogeneous. When cool, the product (1·1 g) was precipitated from solution by adding alcohol. More material (1·4 g) was precipitated by diluting the filtrate with water. *Methyl 3-morpholino-2-methyldithioacrylate* was obtained by recrystallization from alcohol, m.p. 102–104°. (Found: C, 49·6; H, 7·0; N, 6·1. Calc. for $C_9H_{15}NOS_2$: C, 49·8; H, 7·0; N, 6·5%.)

Methyl 3-morpholino-2-phenyldithioacrylate (XIX, $R = C_6H_5$). 4-Phenyl-3-methylthiodithiolium iodide (1·35 g) was mixed in dimethylsulphoxide with morpholine (0·9 g). The temperature rose to 32° and a precipitate formed. *Methyl 3-morpholino-2-phenyldithioacrylate* was isolated as described above and recrystallized from ethanol, m.p. 126–128°. (Found: C, 60·1; H, 6·3; N, 5·1. Calc. for $C_{14}H_{17}ONS_2$: C, 60·1; H, 6·1; N, 5·0%.)

High resolution mass spectrometric analysis gave an empirical formula of $C_{14}H_{17}NOS_2$, and its fragmentation pattern was consistent with the proposed structure.

N,N'-Bis(2-methylthiothiocarbonylvinyl)-p-phenylenediamine (XXVI). Trithione methiodide (3 g) was added slowly to a solution of *p*-phenylenediamine (1·5 g) in ethanol (50 ml) and the mixture stirred 1 hr at room temperature, the solid filtered off, washed with carbon disulphide and water, giving a quantitative yield of the diester (XXVI). A portion was crystallized from a large volume of benzene and then from dimethylformamide, m.p. 230–232°, bright orange plates. (Found: C, 49·75; H, 4·81; N, 8·42; S, 37·85. Calc. for $C_{14}H_{16}N_2S_4$: C, 49·38; H, 4·74; N, 8·23; S, 37·72%.)

N,N'-Bis(2-methylthiothiocarbonylvinyl)-m-phenylenediamine. The product was prepared as in the above example and recrystallized from benzene–carbon tetrachloride, m.p. 174–176° (dec.). (Found: C, 49·32; H, 4·77; N, 8·12; S, 37·82. Calc. for $C_{14}H_{16}N_2S_4$: C, 49·38; H, 4·74; N, 8·23; S, 37·72%.)

Dimethyl 4,7-diazadeca-2,8-dienedi-1,10-dithioate (XXVII). Trithione methiodide (3 g) was added slowly in portions to a stirred solution of ethylenediamine (1·45 g) in dry benzene. The mixture was stirred for 1 hr, then filtered, the solid washed with water, and crystallized from benzene to give *dimethyl 4,7-diazadeca-2,8-dienedi-1,10-dithioate* (yield quantitative), m.p 168–170° (dec.). (Found: C, 41·59; H, 5·41; N, 9·35. Calc. for $C_{10}H_{16}N_2S_4$: C, 41·07; H, 5·51; N, 9·58%.)

When the trithione methiodide was first dissolved in dimethylsulphoxide and then added slowly to a solution of ethylenediamine in dimethylsulphoxide, the same result was obtained.

Dimethyl 4,11-diazatetradeca-2,12-dienedi-1,14-dithioate (XXVIII). The reaction was carried out as in the previous reaction, using trithione methiodide (3 g) and redistilled hexamethylenediamine (1·6 g). After 1 hr, water was added and the mixture extracted three times with benzene. The benzene extracts were washed well with water, dried ($MgSO_4$) and the benzene removed under vacuum at room temperature. From 1·5 g of tarry material, by several crystallizations from light petroleum (b.p. 60–80°) containing a little ethyl acetate, were obtained yellow prisms of *dimethyl 4,11-diazatetradeca-2,12-dienedi-1,14-dithioate* (0·6 g; 32%), m.p. 76–78°. (Found: C, 48·06; H, 7·30; N, 7·90; S, 36·70. Calc. for $C_{14}H_{24}N_2S_4$: C, 48·24; H, 6·95; N, 8·05; S, 36·86%.)

3-p-Toluidinothioacrylanilide (XXIX). 3-Anilinothioacrylanilide (0·6 g) and *p*-toluidine (0·6 g) were refluxed in benzene (10 ml) for 1 hr. As the solution cooled it precipitated a mass of yellow-green plates of *3-p-toluidinothioacrylanilide*, m.p. 172–174° (0·5 g). (Found: C, 71·68; H, 5·81; N, 10·53; S, 12·02. Calc. for $C_{16}H_{16}N_2S$: C, 71·60; H, 6·01; 10·44; S, 11·95%.)

Methyl 3-(o-aminoanilino)dithioacrylate (XXXI). Trithione methiodide (3 g) was added slowly to a benzene solution of *o*-phenylenediamine and stirred and heated for 2 hr. The mixture was cooled and the solid, which was separated by filtration, was found to be the hydroiodide of XXXI. This was resuspended in benzene and washed with sodium bicarbonate solution. The benzene was dried and evaporated to dryness and the residue washed with carbon disulphide and crystallized from carbon tetrachloride to give the *amino-ester* (XXXI), m.p. 123–125°. (Found: C, 53·61; H, 5·46; N, 12·59; S, 28·35. Calc. for $C_{10}H_{12}N_2S_2$: C, 53·53; H, 5·40; N, 12·51; S, 28·57%.)

N,N'-Bis(2-methylthiothiocarbonylvinyl)piperazine. The compound was prepared as in the example for *p*-phenylenediamine, using piperazine hexahydrate. The *product* was obtained in quantitative yield, and recrystallized from dimethylformamide, m.p. 270° (dec.), as a yellow powder. (Found: C, 45·10; H, 5·77; N, 9·55. Calc. for $C_{12}H_{18}N_2S_4$: C, 45·25; H, 5·70; N, 9·08%.)

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