60. *The Isomeric Dithiacyclopentenethiones.*

By FREDERICK CHALLENGER, ERNEST A. MASON, and (in part) ERNEST C. HOLDSWORTH and ROBERT EMMOTT.

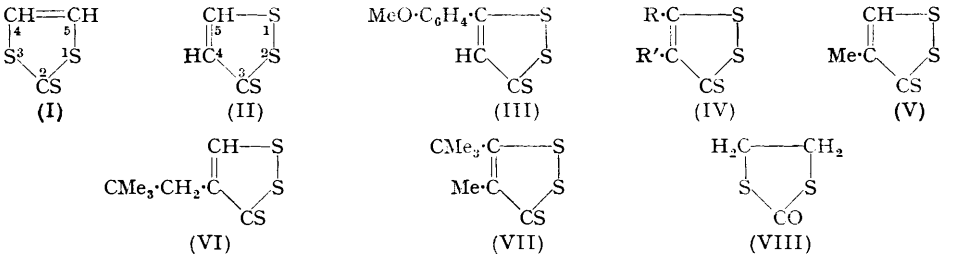
The reaction between acetylene and boiling sulphur gives, in addition to carbon disulphide, hydrogen sulphide, thiophen, dithienyls, thionaphthen, and the isomeric thiophthens, two isomeric compounds, identified as 1 : 3-dithia-*cyclo*pent-4-ene-2-thione (I) and 1 : 2-dithia*cyclo*pent-4-ene-3-thione (II). The properties and reactions of these two compounds and their ultra-violet and infra-red spectra have been examined.

THE reaction between acetylene and sulphur at about 450° yields large quantities of hydrogen sulphide, carbon disulphide, and thiophen together with a red oil, obtained by distillation in superheated steam. Fractionation of this oil gave (1) the isomeric thiophthens, b. p. 90—120°/15 mm. (Challenger and Harrison, *J. Inst. Pet. Tech.*, 1935, **21**, 135; Challenger, Clapham, and Emmott, *J. Inst. Pet.*, 1948, **34**, 922; Challenger and Emmott, *ibid.*, 1951, **37**, 395), (2) the isomeric dithienyls, b. p. 120—140°/15 mm. (Bruce, Challenger, Gibson, and Allenby, *ibid.*, 1948, **34**, 226), and (3) a dark red oil, b. p. 140—165°/15 mm. The yield of this oil was greater at lower reaction temperatures, and the yield of the isomeric thiophthens decreased accordingly, suggesting that some interconversion occurs.

Fraction (3) deposited a bright orange solid with an unpleasant odour. Fractional crystallisation gave some deep-orange prisms and yellow needles, both of molecular formula $C_3H_2S_3$. The needles were at first incorrectly believed to be homogeneous and for brevity will be termed M.O.S. (mixed orange solids). They did not contain a thiol group, react with mercuric oxide or cyanide or with lead acetate, or form a picrate or give a colour with sulphuric acid or the indophenin reaction. Aniline gave hydrogen sulphide, indicating the presence of a thio-ketonic group. Addition products were formed with 1 mol. of methyl iodide, silver nitrate, cupric chloride, silver and copper azides, mercuric chloride, and cyanogen bromide. With chlorine, bromine, and iodine, dihalides were formed by addition; water regenerated M.O.S. Treatment of the mercurichloride with potassium iodide also regenerated M.O.S. but the product, although still having the composition $C_3H_2S_3$, was much paler and slightly lower-melting. A similar difference was noticed on regenerating M.O.S. from the silver azide compound. The behaviour towards cyanogen bromide suggested that M.O.S. might contain two ingredients of different reactivity. Further crystallisation of M.O.S. was ineffective but a complete separation in benzene was obtained by chromatography on active alumina, yielding a yellow and an orange solid. Analysis and determination of molecular weight in each case agreed with the formula $C_3H_2S_3$. Structures (I) and (II) are proposed for these yellow and orange solids respectively. Pure (I) was also obtained by boiling M.O.S. with aqueous sodium hydroxide, (II) being destroyed.

Reactions of 1 : 2-*Dithia*cyclo*pent*-4-*ene*-3-*thione* (II), m. p. 82°.—A compound of this structure incorrectly termed " propylene trithione," had been prepared from propylene and sulphur (Lüttringhaus, König, and Böttcher, *Annalen*, 1948, **560**, 201). The structure was

determined from its mode of formation and the reactions of the analogous " *p*-anisyltrithione," (III), prepared from ethyl *p*-methoxycinnamate, sulphur, and phosphorus pentasulphide at 250°. Oxidation and degradation reactions were studied. Many other substituted " trithiones " of the type (IV) were obtained from α-methylstilbene and other



substituted ethylenic hydrocarbons and sulphur, and their reactions studied (Böttcher and Lüttringhaus, *Annalen*, 1947, **557**, 89; Böttcher, *Ber.*, 1948, **81**, 376; Böttcher and Bauer, *Annalen*, 1950, **568**, 218; *Ber.*, 1951, **84**, 289; Lüttringhaus and Cleve, *Annalen*, 1951, **575**, 112).

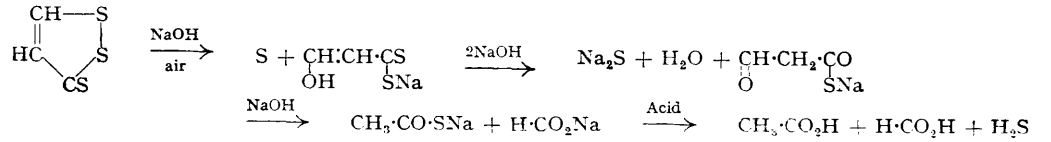
(*a*) Sulphur and *iso*butylene and (*b*) sulphur and di*iso*butylene below 200° were shown by Spindt, Stevens, and Baldwin (*J. Amer. Chem. Soc.*, 1951, **73**, 3693) to give a compound of structure (V) from (*a*), and two isomeric compounds (VI) and (VII) from (*b*). Several similar compounds have been prepared by Voronkov, Broun, and Karpenko (*J. Gen. Chem., Russia*, 1949, **19**, 1927; *Chem. Abs.*, 1950, **44**, 1955) from sulphur and olefins of the type R·CH:CRMe or R·CH_2·CR:CH_2. They gave addition products with metallic salts and methyl iodide. Schmitt and Lespagnol (*Compt. rend.*, 1950, **230**, 551) describe a number of compounds analogous to (II), prepared from sulphur and arylpropylenes.

" Propylene trithione," prepared by Lüttringhaus, König, and Böttcher's method (*loc. cit.*), had m. p. 82°, was similar in appearance to (II), and gave no depression in m. p. on mixing. The methiodide and mercurichloride of the two products were also identical. The formation of (II) in our work may be due to acetone with which the acetylene (from a cylinder) was contaminated. Under the experimental conditions this might yield propylene. The reaction has not been carried out in absence of acetone.

The ultra-violet spectrum of (II) (see p. 296) closely resembles those obtained for the " trithiones " by Lüttringhaus and Cleve (*loc. cit.*) and by Spindt, Stevens, and Baldwin (*loc. cit.*). Its infra-red spectrum (p. 297) also agrees with the structure assigned. Bromine in carbon tetrachloride gives a dibromide which is unstable to water, regenerating (II) (see p. 292). This suggests that the double bond is not involved. The disulphide link appears to be unreactive. Potassium cyanide gives no thiol, and with mercuric chloride the resulting addition product readily regenerates (II), suggesting that the >C:S and not the ·S·S· group is involved. Aliphatic disulphides R·S·S·R undergo fission with mercuric chloride, giving R·S·HgCl and other products (Challenger and Rawlings, *J.*, 1937, 868).

No oxime was obtained with hydroxylamine, although 4-*p*-methoxyphenyl-1 : 2-dithia*cyclo*pent-4-ene-3-thione gives one (Böttcher and Lüttringhaus, *loc. cit.*). With sodium and alcohol, (II) gave hydrogen sulphide and traces of a thiol. However, butenethiols, sodium, and methyl alcohol in liquid ammonia give *n*-butenes (Birch and McAllan, *J.*, 1951, 2556), and possibly propylene may have been formed from (II).

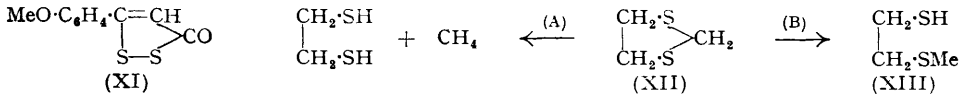
With hot aqueous sodium hydroxide, (II) gave hydrogen sulphide, free sulphur, and a formate. The following mechanism for this reaction is proposed, by analogy with a similar reaction (Böttcher and Lüttringhaus, *loc. cit.*) on 4-*p*-methoxyphenyl-1 : 2-dithia*cyclo*-pent-4-ene-3-thione :



Triphenylphosphine gave triphenylphosphine sulphide. Schönberg and Krüll (*Ber.*, 1926, **59**, 1403) obtained triethylphosphine sulphide from di-*p*-methoxyphenyl thioketone and triethylphosphine. Grote's reagent (*J. Biol. Chem.*, 1931, **93**, 25) gave a positive test for the dithio-acid group, ·S·CS·.

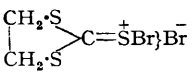
Reactions of 1 : 3-*Dithia*cyclo*pent*-4-*ene*-2-*thione* (I), *m. p.* 50°, *b. p.* 122—123°/0·8 *mm.*—The compound (I) gave a mono- and a di-mercurichloride which were decomposed by potassium iodide, regenerating (I); Bost and Cosby (*J. Amer. Chem. Soc.*, 1935, **57**, 1404) showed that thioketones form mercurichlorides. The monomethiodide regenerated (I) on decomposition with pyridine. Methyl sulphate in acetone yielded a solid which gave the monomethiodide with potassium iodide. Grote's reagent (*loc. cit.*) gave a positive test for the dithio-acid group with (I).

Comparison of Certain Reactions of Ethylene Trithiocarbonate and (I).—(*a*) *Ethylene trithiocarbonate.* The reaction of piperidine with ethylene trithiocarbonate (Husemann, *Annalen*, 1862, **123**, 67), together with that of other secondary amines (Delaby, Piganiol, and Warolin, *Compt. rend.*, 1950, **230**, 1671), was found to give compounds of the structure $R_2N{\cdot}CS{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SH$. With piperidine and ethylene trithiocarbonate at room temperature we obtained the compound described by Delaby *et al.*, m. p. 108°. This, heated with excess of piperidine at 100°, was unchanged. Piperidine and ethylene trithiocarbonate at 100°, however, gave piperidinium piperidine-1-dithiocarboxylate, $C_5H_{10}N{\cdot}CS{\cdot}SH,C_5H_{10}NH$, and an unidentified white compound, $C_{16}H_{28}N_2S_4$, m. p. 212°, which was shown not to be a piperidinium salt. Reaction with propylene trithiocarbonate (Husemann, *Annalen*, 1863, **126**, 295) gave only the above piperidinium salt. Ethylene trithiocarbonate with dilute nitric acid at room temperature gives ethylene dithiocarbonate (VIII; see p. 293) (Husemann, *ibid.*, p. 269), which was obtained by us from ethylene trithiocarbonate and mercuric acetate in acetic acid. It was hoped that dehydrogenation of the trithiocarbonate would occur to form (I), since mercuric acetate dehydrogenates emetine (Battersby and Openshaw, *J.*, 1949, S 67) and δ-lupanine (Manion and Leonard, *Canad. J. Chem.*, 1951, **5**, 360). However, Böttcher (*loc. cit.*) obtained the ketone (XI) from *p*-methoxyphenyl trithione and mercuric acetate. In our reaction, a white insoluble solid was also obtained, which with potassium hydroxide became orange and finally black. Hydrogen sulphide gave mercuric sulphide. Comparison with a specimen of $HgS,Hg(OAc)_2$ (Bernardi and Rossi, *Gazzetta*, 1922, **52**, i, 139) showed that the two compounds were probably identical. The black compound formed with alkali was probably HgS,HgO, since the white compound $2HgSe,HgCl_2$ also gives black 2HgSe,HgO on similar treatment (Uelsmann, *Annalen*, 1860, **116**, 126).

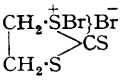


Reduction of ethylene trithiocarbonate and of diethyl trithiocarbonate with sodium and alcohol gave ethane-1 : 2-dithiol and ethanethiol, respectively (cf. Salamon, *J. pr. Chem.*, 1873, **6**, 446). In both cases hydrogen sulphide but no methanethiol was evolved on acidification. It seemed possible that, in the case of ethylene trithiocarbonate, 1 : 3-dithiolan (XII) might be an intermediate product yielding ethane-1 : 2-dithiol and methane on further reduction according to (A). However, this is not the case, since we find that reduction of 1 : 3-dithiolan (Gibson, *J.*, 1930, 13) gave 2-methylthioethanethiol (XIII) in good yield according to (B). This was characterised by comparison with a synthetic specimen prepared from sodium methyl sulphide and ethylene sulphide (Meade and Woodward, *J.*, 1948, 1894). The isomeric thiol $CH_3{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}SH$ (Böhme, Fischer, and Frank, *Annalen*, 1949, **563**, 67) was not detected. In all cases the thiols were identified as derivatives with mercuric cyanide or *p*-chloronitrobenzene or chloro-2 : 4-dinitrobenzene (Bost, Turner, and Norton, *J. Amer. Chem. Soc.*, 1932, **54**, 1985). We found that with sulphur at 200—230° 1 : 3-dithiolan gave ethylene trithiocarbonate and hydrogen sulphide. Wallach (*Annalen*, 1890, **259**, 302) obtained a thioketone from *pp'*-bisdimethylaminodiphenylmethane and sulphur. Ethylene trithiocarbonate formed a dibromide which evolved hydrogen bromide

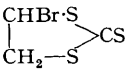
in moist air, and with cold water regenerated the trithiocarbonate. It probably has the structure (XIV) or less probably (XV).



(XIV)



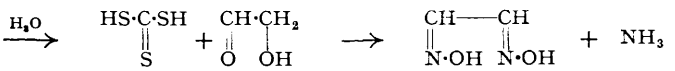
(XV)



(XVI)

A compound such as 1 : 4-dithian gives a tetrabromide and this on hydrolysis gives the corresponding disulphoxide (Husemann, *Annalen*, 1863, **126**, 287). The thermal decomposition of the dibromide (XIV or XV) was then studied. It was hoped that elimination of two molecules of hydrogen bromide and formation of (I) might occur or else that hydrogen bromide and a monobromo-derivative (XVI) might be formed. Further elimination of halogen acid with pyridine might then yield (I). However, the decomposition was complex; ethylene dibromide, sulphur bromide, hydrogen bromide, and traces of sulphur and carbon disulphide were formed.

(*b*) *Reactions of* (I). Piperidine at 100° gave piperidinium piperidine-1-dithiocarboxylate (see p. 296), affording clear evidence for the grouping –S–C:S or –S–C(:)–S– (A).* When boiled with neutral hydroxylamine, (I) gave hydrogen sulphide, sulphur, glyoxime, and thiosulphate, probably by the reactions :



The last stage is analogous to the formation of glyoxal phenylosazone from phenylhydrazine and glycollaldehyde (Fisher and Landsteiner, *Ber.*, 1892, **25**, 2553). The formation of glyoxime establishes the presence of two adjacent carbon atoms (B). The non-formation of (I) from propylene and sulphur is evidence against the presence of three adjacent carbon atoms therein.

Evidence of the presence of a monothione group in (I) was obtained by the action of mercuric acetate (C) which gave the compound (XVII), together with an insoluble white solid (see p. 300). This ketone was unreactive to bromine and mercuric chloride, indicating that the addition compounds of (I) with these reagents involve the thioketonic and not the sulphide group. The normal ketone reactions with hydroxylamine, semicarbazide, or 2 : 4-dinitrophenylhydrazine failed. Attempts to establish the structure of (I) by catalytic hydrogenation of the ketone (XVII) to (VIII) were unsuccessful.

Aqueous-alcoholic sodium hydroxide with (I) gave a good yield of sodium trithiocarbonate, thus proving the presence of the trithiocarbonate group ·S·CS·S· (D). Alcoholic potassium hydroxide, however, gave traces of a thiol.

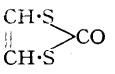
Strong evidence for the structure assigned to (I) was obtained by reduction with sodium and alcohol (E). Ethane-1 : 2-dithiol (Meyer, *Ber.*, 1886, **19**, 3263), identified as ethane bis-(2 : 4-dinitrophenyl sulphide) (see p. 299), and methanethiol, isolated as its mercury derivative, were obtained.

The formation of methanethiol recalls the reduction of phenyl *iso*thiocyanate with aluminium amalgam (Gutbier, *Ber.*, 1901, **34**, 2034). However, the reaction is complex, since much hydrogen sulphide is obtained together with traces of sulphides and other products. Probably the intermediate product is ethylenedithiol which could then lose hydrogen sulphide giving polymeric products. Hydrolysis by sodium ethoxide (see above) may also occur, accounting for the low yield of methanethiol. The production of ethane-1 : 2-dithiol in the reduction indicates the presence of the linkage ·S·C·C·S· in the molecule, and that of methanethiol the linkage ·C·S· (E). Reduction of (I) with lithium aluminium hydride in dry ether was a much smoother reaction than that with sodium and alcohol, the product again being ethane-1 : 2-dithiol.

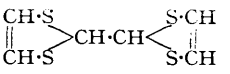
Potassium hydrogen sulphide in absolute alcohol caused fission of (I), giving potassium trithiocarbonate in good yield and a thiol, which yielded a 2 : 4-dinitrophenyl sulphide

* Letters so used refer to structures or reactions regarded as establishing the constitution of (I) (see p. 296).

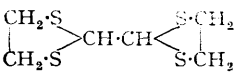
in the usual way (F). Analysis of this derivative indicated that it was possibly $(NO_2)_2C_6H_3{\cdot}S{\cdot}CH{:}CH{\cdot}S{\cdot}C_6H_3(NO_2)_2$. Its melting point was different from that of the corresponding ethane derivative. It did not, however, combine with bromine in chloroform and its structure is uncertain. In view of the importance of reaction (F) for the structure of (I), further work is in progress.



(XVII)



(XVIII)



(XIX)

Reduction of (I) with zinc and acetic acid gave hydrogen sulphide and a substance $(C_3H_3S_2)_2$ which may be (XVIII). An attempt to obtain this by dehydrogenation of glyoxal bisethylenemercaptal (XIX) (Fasbender, *Ber.*, 1888, **21**, 1476) with sulphur was unsuccessful.

The compound (I) gave a dibromide which evolved hydrogen bromide in moist air and was hydrolysed by cold water, regenerating (I). Thermal decomposition gave hydrogen bromide and an insoluble black solid, which could not be purified. No sulphur bromide was detected. This result was disappointing as it was hoped that dibromoethylene would be isolated, thus confirming the presence of a ·CH:CH· linkage in (I) (compare p. 295). The reactions A–F may, however, be regarded as establishing the structure assigned to (I). Further evidence for this is afforded by the spectroscopic data below. Triphenylphosphine had no action on (I) or on ethylene trithiocarbonate (see p. 295).

The catalytic reduction of (I) by various forms of platinum, palladium, or nickel was unsuccessful. With Raney nickel only nickel sulphide could be detected. Eight atoms of hydrogen were absorbed per molecule. Snyder and Cannon (*J. Amer. Chem. Soc.*, 1944, **66**, 155) showed that *S*-ethers of ethane-1 : 2-dithiol underwent two cleavages, one of which involved C–C fission : $2RH + 2CH_4 + 2H_2S \xleftarrow{Ni} R{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SR \xrightarrow{Ni} 2RH + CH_3{\cdot}CH_3 + 2H_2S$ (R = H or Ph). In these cases the products were hydrocarbons, and presumably (I) would give ethane and methane which could be easily lost. All attempts to synthesise (I) failed (see p. 303).

Ultra-violet spectroscopic analysis.

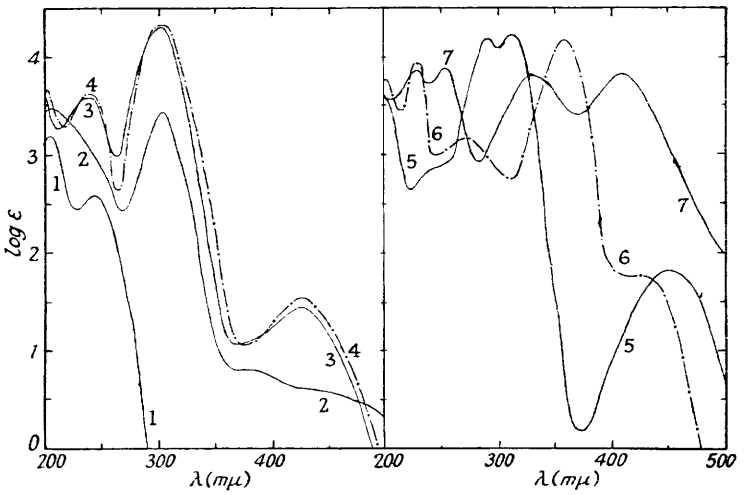
(Carried out with a " Unicam Quartz Spectrophotometer, S.P. 500," with *cyclo*hexane as solvent.)

Compound	$\lambda_{max.}$, mμ	ε	Compound	$\lambda_{max.}$, mμ	ε
1 : 3-Dithiolan	207	1,358	Ethylene trithiocarbonate	293	12,640
	247	367		311·5	14,780
				458	72·4
Methyl dithiopropionate ...	205	2,850			
	304·5	2,500	(I)	228·5	8,700
				276	1,440
Dimethyl trithiocarbonate	237·5	3,780		362	14,700
	302	16,900			
	430	28·0	(II)	230	7,450
				254	8,250
Diethyl trithiocarbonate ...	238	4,010		336	6,420
	305·5	19,400		415	6,700
	432	35·3			

The ultra-violet spectra of (I), ethylene trithiocarbonate, dimethyl trithiocarbonate (Cahours, *Ann. Chim.*, 1847, **19**, 162), diethyl trithiocarbonate (Husemann, *Annalen*, 1862, **123**, 67), methyl dithiopropionate (Houben and Schultze, *Ber.*, 1910, **43**, 2483), and 1 : 3-dithiolan (Gibson, *J.*, 1930, 13) indicated that (I) contained the trithiocarbonate group, which was probably conjugated since the principal maximum was shifted towards the long-wave region (Braude, *Ann. Reports*, 1945, **42**, 105). The trithiocarbonate group was shown to be a powerful chromophore by Purvis, Jones, and Tasker (*J.*, 1910, **97**, 2287). Our results show that the trithiocarbonate group gives a characteristic maximum, much higher than that for the dithiocarbonate group, and this is borne out by the results obtained by Purvis *et al.* (*loc. cit.*).

The structures (I) and (II) were further confirmed by measurements of the infra-red spectra in carbon tetrachloride solution. Professor Mecke writes "Eine vollständige Deutung der Spektren konnte von mir aus Zeitmangel noch nicht durchgeführt werden, jedoch gelang es in allen Fällen, die CS-Schwingung zu lokalisieren. Bei den ungesättigten Verbindungen [(I) und (II)] vermisse ich die Frequenz der Doppelbindung bei 1600, die

Absorption spectra in cyclo*hexane.*



1, 1 : 3-*Dithiolan.* 2, *Methyl dithiopropionate.* 3, *Dimethyl trithiocarbonate.* 4, *Diethyl trithiocarbonate.* 5, *Ethylene trithiocarbonate.* 6, (I). 7, (II).

jedenfalls stark erniedrigt wurde. Somit besitzt der Ring stark aromatischen Charakter. Dass Verbindung (I) die höhere Symmetrie besitzt wie Verbindung (II) geht eindeutig daraus hervor, dass das Spektrum wesentlich einfacher gebaut ist, fast zu einfach."

An *X*-ray examination of (I), (II), and ethylene trithiocarbonate is being carried out by Professor E. G. Cox and Mr. V. Balashov in the University of Leeds. The substance (I) is monoclinic and its crystal structure is quite different from that of (II), which is tetragonal, and of the trithiocarbonate which is also monoclinic. *

Experimental

Preparation of the Mixed Orange Solids (M.O.S.).—The products of the reaction between acetylene, obtained from a cylinder and therefore containing acetone, and boiling sulphur at about 450°, after removal of carbon disulphide and thiophen at 100°, were distilled in superheated steam and fractionated. The mixed thiophthens contained in the fraction of b. p. 90—120°/15 mm. were removed. The fraction, b. p. 140—165°/15 mm., was repeatedly cooled in ice, giving a solid, which crystallised from alcohol in orange plates, m. p. 45—47° (Found : C, 26·9, 27·15; H, 1·65, 1·35; S, 70·4, 71·2%; *M*, cryoscopic in benzene, 142, 137·5, 139. Calc. for $C_3H_2S_3$: C, 26·9; H, 1·5; S, 71·6%; *M*, 134. Calc. for $C_3H_4S_3$: C, 26·5; H, 2·95; S, 70·6%; M, 136).

Typical yields. 27 and 20 Kg. of sulphur gave 25·5 and 39·0 g. of M.O.S., respectively. Introduction of extra acetone vapour into the acetylene gave increased yields of M.O.S., but increased yields were also obtained at about 400° and possibly the effect of the acetone was only to lower the reaction temperature : the yield of the isomeric thiophthens was lowered in each case.

Fractional crystallisation of M.O.S. The orange solid (m. p. 44—46°; 6·7 g.), which was mainly derived from the sulphur–acetylene–acetone process, was recrystallised nine times from light petroleum (b. p. 40—60°), but a constant m. p. could not be obtained although the long, hair-like, orange needles appeared homogeneous. Typical intermediate fractions had m. p.s 45—46° (giving a yellow mercurichloride, m. p. 195—197°), 44·5—45·5°, 43·5—45°, and 43·5—

* Further *X*-ray examination has confirmed the structure (I) for the orange solid, m. p. 50°.

46°. On the tenth crystallisation small orange crystals were deposited on the sides of the flask before the long orange needles. The needles were removed with the mother-liquor. The small orange crystals melted at 60—70°, at 78—81° after one crystallisation, and finally at 80—81·5° (constant). They appeared as glittering orange prisms, and under the microscope as rectangular crystals (wt. 0·01 g.). Further small quantities were obtained from the mother-liquors. Finally, some paler yellow needles, m. p. 44–47° (giving a light yellow mercurichloride, m. p. 221—223°), were obtained, which after two crystallisations from light petroleum (b. p. 40—60°) had a constant m. p., 47·5—48°. Prolonged recrystallisation of the intermediate fractions finally yielded the pure orange prisms, m. p. 80—81·5° (p. 298), and the yellow needles, m. p. 47·5—48°, which were still non-homogeneous.

The orange prisms. These had a slightly stronger smell than the yellow needles and melted to a red liquid. The solutions in the usual solvents were deep orange [Found: C, 26·9; H, 1·6; S, 71·9%; *M* (in camphor), 133. $C_3H_2S_3$ requires C, 26·9; H, 1·5; S, 71·6%; *M*, 134]. With alcoholic mercuric chloride a canary-yellow mercurichloride, m. p. 218—219°, was obtained which with potassium iodide regenerated the orange prisms, unchanged in properties or m. p. (80—81·5°).

The yellow needles (Found: C, 26·9; H, 1·6; S, 72·4%; *M*, 137). With alcoholic mercuric chloride a very pale yellow mercurichloride was precipitated, m. p. 223—224°, mixed m. p. with above mercurichloride, 217—218°. With aqueous potassium iodide the non-homogeneous yellow needles were regenerated, unchanged in properties and m. p.

In other experiments M.O.S. gave a mercurichloride, m. p. 193·5—195·5° (Found: S, 23·7; Cl, 17·05. Calc. for $C_3H_2S_3Cl_2Hg$: S, 23·7; Cl, 17·5%). Its behaviour on crystallisation from acetone suggested the presence of a mixture. The specimen was clearly a monomercurichloride and the weight obtained from known amounts of the ingredients was in agreement with this view.

Isolation of Pure O.S. (I) (1 : 3-*Dithia*cyclo*pent*-4-*ene*-2-*thione*).—*Action of sodium hydroxide.* M.O.S., m. p. 44—47°, and aqueous sodium hydroxide (33%) were warmed under reflux at 100° for 5 hours. A brown oil remained, which was unaffected by more sodium hydroxide and solidified to pale yellow needles of constant m. p. 50° from alcohol and from light petroleum (b. p. 40—60°), identical with (I) (see below). The alkaline filtrate gave hydrogen sulphide and sulphur on acidification. These were removed, and the solution exactly neutralised; it then gave a black precipitate with ammoniacal silver nitrate, a red colour with ferric chloride, and decolorised bromine water, indicating the presence of a formate. Treatment of the residue, after evaporation, with cold sulphuric acid gave carbon monoxide (reduction of palladous chloride to palladium).

The pale yellow needles, m. p. 50° (0·5 g.), were again warmed under reflux for 3 hours with sodium hydroxide (3 g.) in methyl alcohol (5 ml.) and water (2 ml.). Reaction slowly occurred and a deep-red solution was formed. Acidification gave sulphur dioxide and sulphur. Formate, aldehydes, ketones, and malonate were absent.

Separation of the orange solids. M.O.S. (0·5 g.) in dry benzene (10 ml.) was passed down a column of finely powdered activated alumina (450 × 25 mm.), suspended in dry benzene, and the lowest, yellow, band was easily eluted with benzene. Removal of the benzene (reduced pressure) gave (I) (0·3 g.), which crystallised from alcohol in pale yellow needles, m. p. 50° (constant). The middle band was eluted with acetone, and yielded 1 : 2-*dithia*cyclo*pent*-4-*ene*-3-*thione* (II) (0·1 g.), which crystallised in orange prisms, constant m. p. 82°, from alcohol (see above). [Found, for (I): C, 26·8; H, 1·75; S, 71·7%; *M*, cryoscopic in benzene, 125. Found, for (II): C, 27·1, H, 2·2; S, 71·05%; *M*, 130. $C_3H_2S_3$ requires C, 26·9; H, 1·5; S, 71·6%; *M*, 134]. (I) darkened on exposure to light, giving a brown solid, insoluble in alcohol and acetone. It is moderately soluble in alcohol, acetone, and carbon tetrachloride; easily in benzene, chloroform, and ether; slightly in light petroleum, and very slightly in water. (II) was stable to light and of similar solubility to (I). Addition of Grote's reagent (*loc. cit.*) to (I) or (II) gave a purple colour, indicating the presence of the " thioacid group " ·S·CS·.

Reactions of (I).—(1) *Methiodide.* (I) (0·2 g.) and methyl iodide (0·5 ml.) in nitromethane (1 ml.) were left at room temperature for several hours. The yellow *methiodide*, m. p. 131—132° (decomp.), crystallised from methyl alcohol, and regenerated (I), unchanged in m. p., on treatment with pyridine (Found: I, 46·2. $C_4H_5S_3I$ requires I, 46·0%).

(2) *Mercurichlorides.* (I) (0·025 g.), mercuric chloride (0·05 g.), and alcohol (2 ml.) were shaken together. The pale yellow precipitate (0·05 g.), m. p. 191° (decomp.), was insoluble in alcohol and was presumably a monomercurichloride. Similar treatment of (I) in alcohol with excess of mercuric chloride gave a pale yellow solid (0·1 g.), m. p. 222—223° (decomp.), presumably a dimercurichloride. Both the products yielded unchanged (I), m. p. 50°, on treatment

with hydrochloric acid. The mercurichloride obtained from the M.O.S. was shown to be a monoaddition compound (see p. 298).

(3) Methyl sulphate (0·5 g.), (I) (0·2 g.), and benzene (3 ml.) were left at room temperature for two days. A pale red oil separated, but did not solidify in ice. Treatment with potassium iodide solution gave an orange solid, m. p. 127° (decomp.), not depressing the m. p. of the methiodide, m. p. 131—132° (decomp.), of (I). Repetition of the experiment with acetone (3 ml.) as solvent gave colourless crystals, m. p. 132°. These also formed the methiodide, m. p. 128° (decomp.), with potassium iodide.

(4) Silver nitrate in alcohol with (I) gave a pale yellow precipitate, m. p. 124° (decomp.), and (II) gave a deep yellow precipitate, m. p. 135° (decomp.). Both contained nitrate, shown by diphenylamine–sulphuric acid test. A monoaddition compound was indicated on analysis of the product, m. p. 100—120° (decomp.), from M.O.S. and silver nitrate (Found : Ag, 34·9. Calc. for $C_3H_2S_3,AgNO_3$: Ag, 35·5%).

(5) Cupric chloride gave a brick-red precipitate with (I) in alcohol, and a deep red precipitate with (II). Analysis of the precipitate obtained from M.O.S. indicated a monoaddition compound (Found : Cu, 24·5. Calc. for $C_3H_2S_3,CuCl_2$: Cu, 24·2%).

(6) *Neutral hydroxylamine.* (I) (0·7 g.), methyl alcohol (20 ml.), hydroxylamine hydrochloride (4·1 g.), anhydrous sodium carbonate (3·1 g.), and water (30 ml.) were heated under reflux until colourless (3 hr.). Hydrogen sulphide was freely evolved, and sulphur (0·25 g.) deposited. The solution smelled of ammonia. The methyl alcohol was removed, and the aqueous solution extracted with ether. The presence of thiosulphate in the aqueous layer was proved. The ether yielded a greenish-white solid (0·2 g.) which, crystallised five times from chloroform–methyl alcohol, gave colourless plates, m. p. 176°, containing nitrogen but no sulphur. Glyoxime has m. p. 179—180° (Found : C, 26·6; H, 4·35. Calc. for $C_2H_4O_2N_2$: C, 27·2; H, 4·55%). The product gave an orange precipitate on warming with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. Neutralisation of an aqueous solution of the glyoxime with ammonia, and treatment with silver nitrate gave a white precipitate of the silver salt.

Glyoxime was also obtained from the unseparated M.O.S. under similar conditions. Thiosulphate, hydrogen sulphide, and sulphur were recognised as before. The glyoxime had m. p. and mixed m. p. 179—180° with an authentic specimen, m. p. 179—180° [Found : C, 27·7; H, 4·85%; *M* (in camphor), 98·5, 98. Calc. for $C_2H_4O_2N_2$: C, 27·2; H, 4·55%; *M*, 88]. Its properties agreed with those recorded by Ulpiani (*Gazzetta*, 1912, **42**, i, 255).

(7) *Reduction with sodium and alcohol.* (*a*) (I) (1 g.) in alcohol (25 ml.) was reduced with sodium in an atmosphere of nitrogen. Water was added, the mixture acidified, and volatile matter aspirated in nitrogen through water, 5% cadmium sulphate in N-sulphuric acid (A), mercuric cyanide (B), and mercuric chloride (C) solutions successively. A greenish-yellow precipitate was formed in (B), a yellow precipitate in (A), and a trace of a white precipitate in (C). Crystallisation of the precipitate (from B) from ethyl acetate gave white crystals, m. p. and mixed m. p. 175° with authentic bismethylthiomercury, m. p. 175° (Found : S, 21·4. Calc. for $C_2H_6S_2Hg$: S, 21·7%). A portion of (B) was insoluble in ethyl acetate, did not melt below 300°, and gave the odour of ethane-1 : 2-dithiol with dilute hydrochloric acid (see below). It presumably also contained a compound of the type $Hg(SMe)_2,HgS$ which is yellow.

(*b*) (I) (4 g.) in alcohol (100 ml.) was reduced with sodium in a nitrogen atmosphere, with cooling in ice. The red solution on acidification gave hydrogen sulphide and a thiol, which was purified by extraction with ether, solution in alkali, and subsequent acidification and distillation. It had b. p. 140—150°, and gave a white precipitate with mercuric cyanide, which was unmelted below 300°, and could not be purified; it gave a yellow amorphous derivative with chloro-2 : 4-dinitrobenzene (see p. 294), m. p. 200—230°, which crystallised to constant m. p. 244° from glacial acetic acid (Found : C, 39·7; H, 2·6; S, 15·11. Calc. for $C_{14}H_{10}O_8N_4S_2$: C, 39·5; H, 2·35; S, 15·05%). The derivative did not depress the m. p. of an authentic specimen of the 1 : 2-bis-(2 : 4-dinitrophenylthio)ethane, m. p. 245° (see above) (Bost, Turner, and Conn, *J. Amer. Chem. Soc.*, 1933, **55**, 4956, give m. p. 248°). Ethanedithiol was prepared by Meyer's method.

(8) *Reduction.* (i) With lithium aluminium hydride. (I) (0·2 g.), lithium aluminium hydride (0·5 g.), and dry ether (30 ml.) were warmed under reflux until colourless (30 min.). Cautious decomposition with ice-water, acidification, and extraction with ether gave a thiol. Conversion into the 2 : 4-dinitrophenyl sulphide with sodium hydroxide and chloro-2 : 4-dinitrobenzene (Bost, Turner, and Norton, *ibid.*, 1932, **54**, 1985) gave a yellow solid, m. p. 240° after four crystallisations from glacial acetic acid. Further purification was not carried out, but the derivative again gave no depression in m. p. when mixed with that of ethane-1 : 2-dithiol (Found : C, 39·9; H, 3·1%).

(ii) With zinc and acetic acid. (I) (0·3 g.) in glacial acetic acid was heated under reflux with zinc dust until the solution was colourless (30 min.). Hydrogen sulphide was evolved. Steam-distillation yielded initially a trace of a volatile sulphur compound (Z) which gave no precipitate with mercuric cyanide solution and was therefore not a thiol. A white precipitate was obtained with mercuric chloride solution, indicating a sulphide or a disulphide, and this darkened at 115° on heating but did not melt. Further steam-distillation gave a greyish-white solid, m. p. 150—151° after two crystallisations from light petroleum (b. p. 40—60°). This gave no reaction with mercuric chloride, lead acetate, or aniline.

The greyish-white *substance* was also obtained by a similar reduction of M.O.S. (p. 296), and had m. p. 149—150° after similar crystallisation [Found: C, 35·1, 35·2; H, 3·1, 3·2; S, 62·0, 61·8%; *M* (in camphor), 243. $(C_3H_3S_2)_2$ requires C, 35·0; H, 2·9; S, 62·1%; *M*, 206]. The solid gave no methiodide and no reaction with neutral hydroxylamine. It was oxidised by neutral potassium permanganate but no sulphate was formed.

Further reduction of the solid with zinc and glacial acetic acid gave hydrogen sulphide, some unchanged material, and a small amount of the volatile sulphur compound (Z).

(iii) Reduction with hydrogen and Raney nickel. (I) (0·5283 g.), Raney nickel (2 g.), and alcohol (25 ml.) were shaken in hydrogen for 3 days, a further 2 g. of nickel (total 10 g.) being added each time the absorption of hydrogen ceased. 390 Ml. of hydrogen were absorbed (8H per molecule; the amount theoretically required for production of nickel sulphide, ethane, and methane). The recovered catalyst, on treatment with hydrochloric acid gave hydrogen sulphide but no thiol or organic sulphide. The alcohol filtered from the nickel sulphide was colourless, contained no thiol or sulphide (mercuric chloride test), and yielded nothing on evaporation under reduced pressure.

(9) *Attempted catalytic hydrogenations.* (I) (0·2 g.) in alcohol (20 ml.) was shaken in hydrogen for 8 hours with: (*a*) nickel powder from nickel nitrate, (*b*) palladium chloride on gum arabic, (*c*) palladium chloride on charcoal, (*d*) Adams's platinum oxide under 4 atm. In all cases (I) was recovered in good yield, unchanged in m. p.

(10) Benzoyl peroxide (0·8 g.), (I) (0·4 g.), and light petroleum (b. p. 60—80°) (30 ml.) were heated under reflux for 2 hours. (I) was recovered unchanged on removal of the solvent and crystallisation from alcohol.

(11) *Bromination.* A solution of bromine (3 g.) in carbon tetrachloride (100 ml.) was titrated against (I) (0·1592 g.), starch–iodide paper being used. The amount of bromine required was 0·197 g. [(I) requires 0·214 g. bromine to form the dibromide]. The orange dibromide (yield 90%), m. p. 147° (decomp.), with cold water, regenerated (I) in almost theoretical yield. When heated, it decomposed to hydrogen bromide and a black insoluble solid, which could not be purified.

(12) *Attempted Diels–Alder reaction.* (I) (0·2 g.), anthracene (0·1 g.), and dry benzene (3 ml.) were heated under reflux for 3 hours and left overnight. Both ingredients were recovered unchanged on crystallisation from alcohol.

(13) *Fission of the ring of* (I) *by piperidine.* (I) (0·5 g.) and piperidine (excess) were heated at 100° for 2 hours. Addition of acetone (5 ml.) gave a dark brown solid, which was crystallised from acetone to constant m. p. 164·5°, giving white crystals which were soluble in water, sublimed on heating, and with aqueous sodium hydroxide gave the odour of piperidine [Found: C, 54·3; H, 8·9; S, 25·6. *M* (in camphor), 250. Calc. for $C_{11}H_{22}N_2S_2$: C, 53·8; H, 8·9; S, 26·0%; *M*, 246]. They did not depress the m. p. of an authentic specimen of piperidinium piperidino-1-dithiocarboxylate, m. p. 165° (Ladenburg and Roth, *Ber.*, 1884, **17**, 514). The acetone mother-liquors yielded no further product.

(14) *Mercuric acetate.* (I) (1 g.) in chloroform (20 ml.) was treated with a solution of mercuric acetate (10 g.) in glacial acetic acid (100 ml.), and left for 12 hours. The colourless solution was filtered from the white, insoluble solid (see p. 295) through a sintered-glass funnel, and the solid washed with fresh chloroform (5 ml.). The filtrate was diluted with water, the chloroform separated, and the aqueous solution extracted with chloroform (6 × 10 ml.). Distillation of the chloroform under reduced pressure yielded a pale yellow solid with a butter-like odour, m. p. 34—35° (0·4 g.), easily soluble in ether, acetone, alcohol, and chloroform, but crystallising from light petroleum (b. p. 40—60°) in white feathery crystals of constant m. p. 35° [Found: C, 30·9; H, 2·0; S, 53·8, 53·7%; *M* (in camphor), 112. $C_3H_2OS_2$ requires C, 30·5; H, 1·7; S, 54·2%; *M*, 118]. The compound appears to be 1 : 3-*dithia*cyclo*pent*-4-*ene*-2-*one* from consideration of the similar reaction with ethylene trithiocarbonate. It gave no precipitates with aqueous mercuric chloride, bromine in carbon tetrachloride, 2 : 4-dinitrophenylhydrazine, *p*-nitrophenylhydrazine, semicarbazide, or hydroxylamine in sodium acetate solution; but gave

hydrogen sulphide and a deposit of sulphur on treatment with hydroxylamine hydrochloride neutralised with aqueous sodium carbonate. It depressed the m. p. of ethylene dithiocarbonate, m. p. 35° (see p. 302).

(15) *Attempted hydrogenations of* 1 : 3-*dithia*cyclo*pent-4-ene-2-one.* (i) The carbonyl compound, $C_3H_2OS_2$, m. p. 35° (0·1 g.), was shaken with Adams's catalyst (0·1 g.) and methyl alcohol (2 ml.) in hydrogen (3 atm.) for 2 hours. Filtration and removal of the solvent gave unchanged material, m. p. 34° (0·05 g.). (ii) Palladium chloride (0·5 g.) on charcoal (4·5 g.) in methyl alcohol (50 ml.) was reduced with hydrogen at 3 atm., the carbonyl compound $C_3H_2OS_2$ (0·25 g.) added, and the shaking continued for 8 hours. Removal of the catalyst and the solvent gave unchanged material, m. p. and mixed m. p. 35°.

(16) *Action of potassium hydrogen sulphide* (see Husemann, *Annalen*, 1862, **123**, 89, for the action on ethylene trithiocarbonate). Potassium hydroxide (0·45 g.) in absolute alcohol (25 ml.) was treated with excess of hydrogen sulphide. (I) (0·5 g.) in alcohol (5 ml.) was added, and the mixture heated under reflux for 2 hours. The orange-coloured precipitate was removed, washed with alcohol, and identified as potassium trithiocarbonate by the following reactions: (i) It was very soluble in water, giving a red solution. (ii) Excess of dilute sulphuric acid on warming gave hydrogen sulphide, sulphur, and carbon disulphide; the last was identified by extraction with ether and precipitation with phenylhydrazine; the resulting compound had m. p. 100° (decomp.), and the compound prepared from phenylhydrazine and carbon disulphide in ether (Fischer, *Annalen*, 1878, **190**, 114) had m. p. 104—105° (decomp.). (iii) Ethylene dibromide (1 g.) and aqueous alcohol (1 : 1) (2 ml.) were added to the remaining precipitate and warmed. A clear yellow solution was formed. Dilution with water, extraction with ether, and crystallisation from light petroleum (b. p. 40—60°) gave yellow crystals, m. p. and mixed m. p. 35°, with authentic ethylene trithiocarbonate.

The alcoholic solution from the reaction gave a thiol, on dilution with water and acidification, which was extracted with ether, and the extract washed with 5% cadmium sulphate in N-sulphuric acid to remove hydrogen sulphide. A portion was shaken with mercuric cyanide solution, the ether removed, and the white mercury salt, m. p. 135—136° (decomp.), filtered off. It was only slightly soluble in alcohol, ethyl acetate, and acetone, and could not be crystallised.

To the remainder of the thiol in ether, alcohol (10 ml.), aqueous sodium hydroxide (1 ml., 10%), and chloro-2 : 4-dinitrobenzene (0·5 g.) in alcohol (10 ml.) were added. Heating under reflux for 20 minutes gave a yellow solid, which was slightly soluble in alcohol and glacial acetic acid. Washed with water and alcohol, it had m. p. 185° (Found : C, 40·0; H, 2·3; N, 12·6; S, 14·95. $C_{14}H_8O_8N_4S_2$ requires C, 39·7; H, 1·9; N, 13·2; S, 15·1%). The m. p.s of 1 : 2-di-(2 : 4-dinitrophenylthio)ethane, m. p. 245°, and 1 : 3-di-(2 : 4-dinitrophenylthio)propane, m. p. 192°, were depressed to 160—170° and 175—177° respectively, on mixing with the above derivative.

Reactions of (II), *m. p.* 82°.—(1) A specimen of (II) did not depress the m. p. of " propylene trithione," m. p. 82° (see p. 304), prepared from propylene and sulphur.

(2) *Mercurichloride.* (II) (0·05 g.) in alcohol (1 ml.) was treated with mercuric chloride solution. The pale yellow precipitate had m. p. 218—219° (decomp.), after washing with water and alcohol, and did not depress the m. p. of the mercurichloride of "propylene trithione" (see p. 297).

(3) *Methiodide.* (II) (0·05 g.) with methyl iodide (0·1 g.) in nitromethane (2 ml.) gave an orange addition product, m. p. 175° (decomp.), not depressing the m. p. of the *methiodide* of " propylene trithione " (see p. 304) (Found : C, 17·55; H, 1·85; I, 46·0. $C_4H_5S_3I$ requires C, 17·4; H, 1·80; I, 46·0%).

(4) and (5) Hydroxylamine hydrochloride with aqueous sodium acetate (4) or sodium carbonate (5) gave no oxime. With (5), on warming, thiosulphate but no free sulphur was obtained.

(6) Reduction with sodium and alcohol of (II) (2 g.) gave a red solution, becoming black on further reduction. The thiol, isolated as usual, was treated with chloro-2 : 4-dinitrobenzene, but no derivative was obtained.

(7) *Action of triphenylphosphine.* (II) (0·1 g.) in ethyl acetate (5 ml.) was heated under reflux for 2 hours with triphenylphosphine. Filtration from a brown, insoluble solid (A) yielded a solid which formed white crystals from alcohol, m. p. 158° (Found : C, 73·8; H, 5·15. Calc. for $C_{18}H_{15}SP$: C, 73·5; H, 5·3%). They contained sulphur and did not depress the m. p. of authentic triphenylphosphine sulphide, m. p. 158°, but depressed that of triphenylphosphine oxide (m. p. 154°) to 123°. The brown addition *compound* (A) also contained sulphur and decomposed on heating to a black residue, and evolved the odour of (II) (Found : C, 64·2; H, 4·6. $C_3H_2S_3$,$C_{18}H_{15}P$ requires C, 63·7; H, 4·3%).

Reactions of Ethylene Trithiocarbonate, m. p. 36°.—This was prepared in 60% yield according to Husemann (*loc. cit.*).

Reduction with sodium and alcohol. Ethylene trithiocarbonate was reduced with sodium and alcohol. The colourless solution was diluted with water and acidified, and volatile products were aspirated with nitrogen successively through 5% cadmium sulphate in N-sulphuric acid, sodium acetate, and mercuric cyanide solutions. The cadmium sulphide formed corresponded to 28% of the sulphur content of the trithiocarbonate. Traces of a mercury mercaptide were obtained which was insoluble in ethyl acetate and infusible but gave the odour of ethane-1 : 2-dithiol with dilute hydrochloric acid. No methanethiol was detected. Extraction of the aspirated solution with ether yielded ethanedithiol. Treatment with chloro-2 : 4-dinitrobenzene as before (p. 299) gave a yellow derivative, m. p. 245°, after four crystallisations from glacial acetic acid; mixed m. p. 245° with authentic 1 : 2-di-(2 : 4-dinitrophenylthio)ethane (Found: C, 39·2; H, 2·3; N, 13·2; S, 15·15. Calc. for $C_{14}H_{10}O_8N_4S_2$: C, 39·5; H, 2·35; N, 13·1; S, 15·05%).

Attempted dehydrogenation of ethylene trithiocarbonate. (*a*) Ethylene trithiocarbonate was not dehydrogenated by palladium powder in benzene or in absence of a solvent or palladium on charcoal in mesitylene or freshly reduced nickel powder in benzene. (*b*) Dehydrogenation was not effected by sulphur or selenium at 200°. (*c*) Tetrachlorobenzoquinone or benzoquinone in boiling xylene, or selenium dioxide in aqueous dioxan or aqueous acetic acid at 100°, or lead tetraacetate in glacial acetic acid at room temperature, failed to dehydrogenate the trithiocarbonate. (*d*) Ethylene trithiocarbonate (10 g.) and carbon dioxide were passed through a Pyrex tube 24" long, loosely packed with catalytic nickel prepared from nickel nitrate (40 g.) on porous pot (200 g.) at 320°. Extraction of the distillate and of the catalyst with acetone gave only unchanged ester (6 g.), m. p. 35°.

Action of mercuric acetate. The acetate (5 g.) in glacial acetic acid (100 ml.) was added to ethylene trithiocarbonate (2 g.) in chloroform (20 ml.). The yellow colour was discharged in 2—3 minutes and a white solid (A) was deposited. After 2 hours the mixture was filtered, and the filtrate diluted with water and extracted several times with chloroform. The aqueous layer contained no sulphate. The chloroform yielded a colourless oil which solidified in ice to a white solid, m. p. 33—34° (1·1 g.), and was crystallised from light petroleum (b. p. 40—60°) to constant m. p. 35° [Found: C, 30·3; H, 3·7; S, 53·4%; *M* (in camphor), 117. Calc. for $C_3H_4OS_2$: C, 30·0; H, 3·3; S, 53·3%; *M*, 120]. The crystals obtained in a yield of 62% did not depress the m. p. of ethylene dithiocarbonate, m. p. 35°, prepared from dilute nitric acid and ethylene trithiocarbonate (Husemann, *Annalen*, 1863, **126**, 269). No derivative was obtained with 2 : 4-dinitrophenylhydrazine, *p*-nitrophenylhydrazine, or mercuric chloride. Bromine in carbon tetrachloride was unaffected, but bromine water was decolorised. An oxime, m. p. 126—128°, was obtained with hydroxylamine hydrochloride neutralised with sodium carbonate. This did not depress the m. p. of the oxime (3-oximino-1 : 2-dithia*cyclo*pentane) obtained from ethylene trithiocarbonate and neutral hydroxylamine (Miolati, *Annalen*, 1891, **262**, 78).

The white solid (A) blackened when heated, and darkened slightly when boiled for a long time with dilute nitric acid. With aqueous sodium thiosulphate it became orange, then red and finally black. Potassium iodide gave similar results on warming, and potassium mercuric iodide was detected in the solution. With hydrogen sulphide (A) became black. It was not mercurous acetate. Aqueous potassium hydroxide yielded initially an orange colour, quickly becoming red, and finally a black precipitate (B) which was insoluble in hot nitric or hydrochloric acids but completely soluble in aqua regia, leaving sulphur; in boiling fuming nitric acid (B) gave a white solid which became yellow and finally black again when heated with aqueous potassium hydroxide.

The white compound $HgS,Hg(OAc)_2$ was prepared by passing hydrogen sulphide into excess of mercuric acetate solution with shaking. It gave exactly similar reactions to (A), including the transient orange and red colours with aqueous potassium hydroxide. These colours are not given by the compound $2HgS,HgCl_2$, only black 2HgS,HgO being obtained.

Action of piperidine. Piperidine (2 g.) and ethylene trithiocarbonate (0·5 g.) were heated together at 100° for 2 hours. Acetone (2 ml.) was added, yielding a white solid, m. p. 204—205°, separating from benzene in colourless crystals. After five crystallisations the m. p. was constant at 212° (Solid A). The acetone extract yielded greyish-white crystals, m. p. 164° (decomp.), and more were recovered from the benzene mother-liquors of Solid A. After crystallisation from acetone, the crystals were colourless and had the constant m. p. 164·5° (decomp.). These contained sulphur and nitrogen, were soluble in water, and gave piperidine on heating or with cold aqueous sodium hydroxide [Found: C, 54·0; H, 8·75; S, 25·7%; *M* (in camphor), 234.

Calc. for $C_{11}H_{22}N_2S_2$: C, 53·8; H, 8·9; S, 26·0%; *M*, 246]. No depression in m. p. was obtained with piperidinium piperidino-1-dithiocarboxylate (see p. 300).

Solid A contained nitrogen and sulphur and was insoluble in water. Sodium hydroxide gave no piperidine. When heated, it finally decomposed leaving no residue. Boiling lead acetate or mercuric chloride solution gave no precipitate. Aniline on boiling gave hydrogen sulphide, indicating the thioketonic group. Bromine in chloroform yielded an insoluble, orange addition *product*, unstable to water [Found: C, 50·8; H, 7·15; S, 34·8%; *M* (in camphor), 374. $C_{16}H_{28}N_2S_4$ requires C, 51·0; H, 7·45; S, 34·1%; *M*, 376].

Ethylene trithiocarbonate dibromide. (i) Titration of ethylene trithiocarbonate (0·18 g.) in carbon tetrachloride (5 ml.) with bromine (3 g.) in carbon tetrachloride (100 ml.), with use of starch–iodide paper, indicated the absorption of 2 atoms of bromine.

(ii) Bromine (12 g.) in chloroform (25 ml.) was added slowly with shaking to ethylene trithiocarbonate (10 g.) in chloroform (50 ml.). After 2 hours the orange-yellow dibromide was filtered off, washed with chloroform, and stored in absence of air (yield 20 g.). It had m. p. 120°. It was decomposed by water or moist air, regenerating the ester [compare analogous behaviour of the dibromide of (I), p. 300].

Action of pyridine. The dibromide (0·5 g.), pyridine (0·5 ml.), and dry ether (or alcohol; 5 ml.) were left for 8 hours. The dibromide slowly dissolved, giving a yellow solution. The solvent was removed, and the yellow residue washed with dilute hydrochloric acid and crystallised from alcohol, giving ethylene trithiocarbonate, m. p. and mixed m. p. 35—36°.

Thermal decomposition. The dibromide (20 g.) was heated in a slow stream of nitrogen at 110° for 2 days. Hydrogen bromide was evolved and precipitated as silver bromide (3·9 g., = 1·6 g. of HBr). A faint odour of carbon disulphide was noticed after removal of the hydrogen bromide. Distillation yielded a pale red oil, b. p. 130°, and extraction of the residue with carbon disulphide gave free sulphur. The oil was washed with water and distilled in steam, giving 6·90 g. of a colourless oil, b. p. 127°/731 mm., f. p. 9—10°, proved to be ethylene dibromide (b. p. 129°, f. p. 10°). This conclusion was confirmed by heating the oil with thiourea and treatment of the resulting di*iso*thiuronium bromide with picric acid. The picrate, m. p. 258° (decomp.), did not depress the m. p. of the derivative obtained from authentic ethylene dibromide, m. p. 259° (decomp.) (Levy and Campbell, *J.*, 1939, 1442, give m. p. 260°). The oil also gave a β-naphthyl ether on heating under reflux with β-naphthol; this was crystallised to m. p. 208° from alcohol–water, and did not depress the m. p. of authentic 1 : 2-di-β-naphthyloxyethane, m. p. 209—210°.

Attempted Synthesis of (I) (1 : 3-*Dithio*cyclo*pent*-4-*ene*-2-*thione*).—*cis*-Dichloroethylene, *cis*-dibromoethylene, and an unseparated mixture of *cis*- and *trans*-dibromoethylene were treated with potassium trithiocarbonate in various solvents at room temperature, at 60°, 70°, or 80° or without a solvent in a sealed tube at 180°, but no formation of (I) could be detected. Di-iodoethylene (Keiser, *Amer. Chem. J.*, 1899, **21**, 263) did not react with the trithiocarbonate in boiling alcohol.

Action of tetrabromoethane on sodium trithiocarbonate. Tetrabromoethane (34·6 g.) and sodium trithiocarbonate (15·4 g.) in alcohol (40 ml.) were heated under reflux for 1 hour. Hydrogen sulphide was evolved and sulphur deposited. Dilution with water and distillation in steam gave 4 g. of dibromoethylene, b. p. 108—110°, since, on treatment with bromine (8 g.) and water (40 ml.) and distillation in steam, tetrabromoethane, b. p. 202° (decomp.), was obtained.

Reduction of diethyl trithiocarbonate. The ester (4 g.) in alcohol (50 ml.) was reduced with sodium. Dilution with water and acidification gave a thiol, which was extracted with ether. The 2 : 4-dinitrophenyl sulphide, prepared in the usual manner, formed pale yellow crystals (from alcohol), m. p. 113·5°, not depressing the m. p. of an authentic specimen prepared from ethanethiol, m. p. 114° (Bost, Turner, and Norton, *loc. cit.*, give m. p. 115°).

Reduction of 1 : 3-*Dithiolan with Sodium and Alcohol.*—1 : 3-Dithiolan (1 g.) in alcohol (15 ml.) was reduced with sodium. Dilution with water and acidification gave a thiol on extraction with ether. The corresponding 2 : 4-dinitrophenyl sulphide formed pale yellow needles from alcohol, m. p. 81° (Found: C, 39·45; H, 3·55; N, 10·3; S, 23·15. $C_9H_{10}O_4N_2S_2$ requires C, 39·4; H, 3·6; N, 10·4; S, 23·25%). The mixed m. p. with an authentic specimen of 1-(2 : 4-*dinitrophenylthio*)-2-*methylthioethane* (m. p. 81·5°) was 81°.

Action of Sulphur on 1 : 3-*Dithiolan.*—Sulphur (5 g.) and 1 : 3-dithiolan (2 g.) were heated under reflux at 200—230° for 4 hours. Hydrogen sulphide was freely evolved, and a red solid formed on cooling. Extraction with hot alcohol and removal of the solvent and unchanged sulphur gave a yellow solid, which crystallised from alcohol to constant m. p. 36°, not depressing the m. p. of authentic ethylene trithiocarbonate. It gave a white precipitate, m. p. 166°, with

mercuric chloride solution, and an orange precipitate, m. p. 118°, with bromine in chloroform. Ethylene trithiocarbonate behaves in a similar manner.

Preparation of Reference Compounds.—(1) Dimethyl trithiocarbonate, prepared in 60% yield from sodium trithiocarbonate and methyl iodide in alcohol, had b. p. 92°/13 mm. (207°/752 mm.), f. p. −3° (Cahours, *Ann. Chim.*, 1847, **19**, 162, gives b. p. 204—205°).

(2) Diethyl trithiocarbonate, prepared similarly (yield 62%), had b. p. 113°/11 mm., f. p. −12° (Husemann, *Annalen*, 1862, **123**, 67, gives b. p. 240°).

(3) Propylene trithiocarbonate was prepared from propylene dibromide and sodium trithiocarbonate by Husemann's method (*ibid.*, 1863, **126**, 295) in 60% yield; b. p. 157°/10 mm. (Found : S, 63·7. Calc. for $C_4H_6S_3$: S, 64·0%).

(4) Methyl dithiopropionate, $CH_3{\cdot}CH_2{\cdot}CS{\cdot}SMe$, prepared according to Houben and Schultze (*Ber.*, 1910, **43**, 2483, who give b. p. 92—93°/70 mm.), was an orange oil, b. p. 83°/22 mm.

(5) 1 : 3-Dithiolan was obtained as a colourless oil, b. p. 67°/14 mm., from ethanedithiol and formaldehyde in 30% yield (Gibson, *J.*, 1930, 13, gives b. p. 61°/11 mm.). Mercuric chloride solution gave a white precipitate which crystallised from alcohol in colourless needles, m. p. 126° (Gibson gives m. p. 119°) (Found : Cl, 18·4. Calc. for $C_3H_6S_2Cl_2Hg$: Cl, 18·8%).

(6) 2-Methylthioethanethiol, $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}SH$, was obtained in 60% yield, b. p. 74·5°/34 mm., from ethylene sulphide and sodium methyl sulphide (Meade and Woodward, *J.*, 1948, 1894, give b. p. 82°/40 mm.).

The thiol (1 g.), alcohol (10 ml.), 10% sodium hydroxide solution (4 ml.), and chloro-2 : 4-dinitrobenzene (2 g.) in alcohol (5 ml.) were heated under reflux for 10 minutes. Cooling gave 1-(2 : 4-*dinitrophenylthio*)-2-*methylthioethane*, which crystallised in yellow needles from alcohol, m. p. 81·5° (Found : C, 39·4; H, 3·5; N, 10·25; S, 23·0. $C_9H_{10}O_4N_2S_2$ requires C, 39·4; H, 3·6; N, 10·2; S, 23·25%).

The thiol (0·5 g.), treated in a similar manner with *p*-chloronitrobenzene (1 g.), afforded the p-*nitrophenyl sulphide*, which separated as an oil which solidified in ice, and crystallised from alcohol or light petroleum (b. p. 40—60°) in yellow needles, m. p. 34·5° (Found : C, 47·25; H, 4·9; N, 5·9. $C_9H_{11}O_2NS_2$ requires C, 47·2; H, 4·8; N, 6·1%).

The thiol, on treatment with alcoholic mercuric cyanide gave a white precipitate, which separated from alcohol as colourless crystals of *bis*-2-*methylthioethylthiomercury*, m. p. 104·5° (Found : Hg, 47·6. $C_6H_{14}S_4Hg$ requires Hg, 48·3%).

(7) 2-Methyl-1 : 3-dithiolan was prepared by Fasbender's method (*Ber.*, 1888, **21**, 1475) from ethane-1 : 2-dithiol and acetaldehyde. The colourless oil, b. p. 58°/12 mm. (lit., b. p. 172—173°), darkened when kept. The white addition *compound* with mercuric chloride was sparingly soluble in alcohol or ethyl acetate, and did not melt when heated (Found: Cl, 18·15. $C_4H_8S_2Cl_2Hg$ requires Cl, 18·15%).

(8) "*Propylene trithione*" (1 : 2-*dithia*cyclo*pent*-4-*ene*-3-*thione*). The apparatus and procedure were essentially the same as described by Lüttringhaus, König, and Böttcher (*Annalen*, 1948, **560**, 211). Propylene was passed for 8 hours through a Pyrex tube containing crushed sulphur (150 g.) at 240°. The product was purified by steam-distillation and chromatographic separation in benzene on active alumina. Crystallisation of the product from alcohol gave orange prisms (0·2 g.), m. p. 82° (the authors give m. p. 82°), mixed m. p. 82° with (II). The mercuric chloride addition product was pale yellow, m. p. 218—219° (decomp.), mixed m. p. 218—219° (decomp.) with the derivative of (II) of the same m. p. The methiodide was orange, m. p. 173—174° (decomp.), mixed m. p. 174—175° (decomp.) with the methiodide of (II) (see p. 301) of the same m. p.

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