Reactions of Thioketones. Part II.[1] Thio-ozonide Formation in Some Nucleophilic Reactions of Thioketones with Amines and with Benzenethiol

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Thiobenzophenone (5) and thioadamantanone (15) have been shown to react with certain amines under ambient conditions to give low yields of the thio-ozonides 3,3,5,5-tetraphenyl-1,2,4-trithiolan (1) and dispiro[adamantane-2.3′-(1.2.4-trithiolan)-5′,2″-adamantane] (16) respectively. Reaction of (5) with benzenethiol also gave the thio-ozonide (1), whereas (15) gave 2,2′-bi-2-phenylthioadamantyl disulphide (21). Aminosulphuric acid reacted with (5) in the presence of base to give benzophenone oxime and (1). Parallel reactions with aliphatic thiones gave mainly the oximes. Mechanisms are proposed to account for the formation of the thio-ozonides. Initial nucleophilic attack on the thione affords a tetrahedral intermediate which is oxidatively dimerized to an unstable disulphide. Possible intermediates leading to the thio-ozonides are suggested.

THIONES behave in many respects like the corresponding ketones, reacting with amines in the presence of acid catalyst, for example, to give imino-derivatives. Our preliminary report [1] indicated, however, that in certain nucleophilic additions of amines to thiobenzophenone (5), imine formation was accompanied by the formation of significant quantities of the thio-ozonide (1). We have investigated several reactions of amines with thiones in an effort to determine the mechanism of this process, and to ascertain the scope of the reaction. In addition, we have examined parallel reactions with other nucleophiles such as phenol and thiophenol, the latter reagent providing some unexpected products.

Nucleophilic Addition of Amines to Thioketones.—A range of experimental conditions were investigated for which the *gem*-thiolamine (3) might be capable of interception before decomposition to imines occurred. Acidic conditions were avoided because of the ready decomposition of *gem*-thiolamines in acid. We anticipated that in almost neutral, or in mildly basic media, the *gem*-thiolamines (3) would be intermediate in stability between *gem*-dithiols (2) and the unstable *gem*-diamines (4).

Preliminary reactions of thiobenzophenone (5) with primary amines at low temperature afforded the imino-derivatives in low yield, as established by t.l.c., together with a crystalline by-product which was isolated and shown to be the known thio-ozonide (1) by comparison with an authentic sample.[2] Reaction occurred rapidly with methylamine and more slowly with aniline, both in the presence and absence of solvent, affording low yields of the thio-ozonide. Reaction with secondary amines proceeded slowly, again affording (1), whereas tertiary amines such as triethylamine gave no detectable products. Phenyl hydrazine in contrast to the primary amines gave only the expected hydrazone in high yield. Toluene-*p*-sulphonamide gave no reaction.

Several mechanistic pathways may be invoked to account for the thio-ozonide formation. Each route involves initial nucleophilic attack on the thione to afford a *gem*-thiolamine (9) which dimerizes irreversibly to an unisolable disulphide (11). Possible intermediates in the subsequent formation of (1) include (12) and (13).

In an attempt to establish the intermediacy of the *gem*-thiolamine (8), the reaction of benzophenone anil

(10; R = Ph) with H_2S was investigated. An extensive series of reactions in several different solvents indicated that the only conditions which afforded isolable quantities of (1) involved saturating an ethanolic solution of

(1)

(2) $R^1 = R^2 = SH$
(3) $R^1 = SH, R^2 = NHR$
(4) $R^1 = R^2 = NHR$

(5) R = H
(6) R = NMe$_2$
(7) R = OMe

(8)
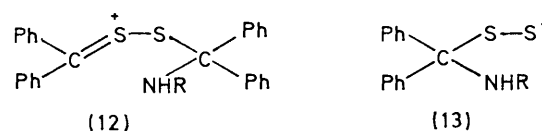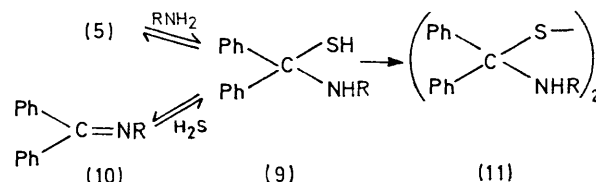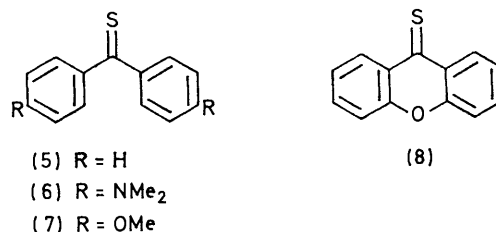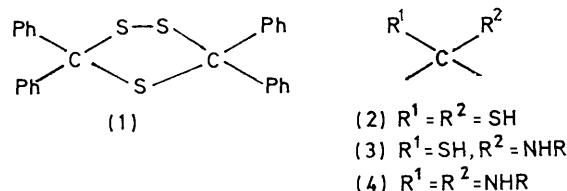
(10) with H_2S at $-70°$ and allowing the solution to attain ambient temperature. A low yield of (1) [mainly due to the low solubility of (10) in ethanol at $-70°$] was obtained, together with thiobenzophenone and aniline. It was established in a control reaction that (1) was not formed from the by-products, thiobenzophenone and aniline, under the conditions employed. Attempts to isolate, or trap the *gem*-thiolamine with acetyl chloride or trimethylchlorosilane, were unsuccessful.

(12)   (13)

[1] Part I, M. M. Campbell and D. M. Evgenios, *Chem. Comm.*, 1971, 179.

[2] H. Staudinger and H. Freudenberger, *Ber.*, 1928, **61**B, 1836; E. Campaigne and W. B. Reid, *J. Org. Chem.*, 1947, **12**, 807.

It was not possible to suppress the postulated dimerization (9) ⟶ (11) by performing the reaction in an air-free system. No differences were observed when light was excluded. Radical trapping studies were rendered difficult because of competing side-reactions with H_2S, or with thiobenzophenone, or with the amine. Hydroquinone and quinone, however, appeared not to affect the reaction. This could of course be due to much faster dimerization than radical trapping. Perhaps thiobenzophenone, which has been described by some authors [3] as a 'diradical' is implicated in the oxidation step.

The related aromatic thioketones (6)—(8) were subjected to similar reactions with a range of amines, but no thio-ozonides were obtained.

The unexpected formation of thio-ozonide from thiobenzophenone prompted an examination of the aliphatic thiones, thiocamphor (14) and thioadamantanone (15).

(14) (15)

(16) (17)
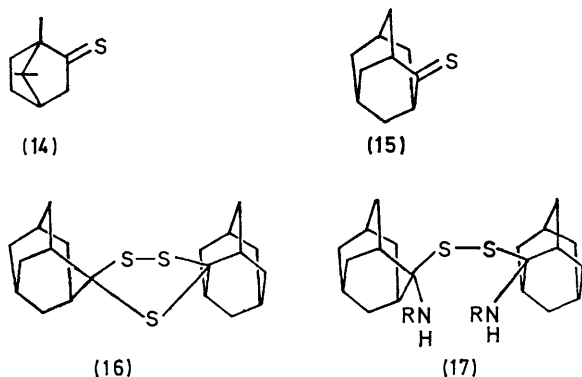
The reactions of (14) were unremarkable, affording only the imines, recovered as ketones following hydrolytic work-up. Thioadamantanone, however, afforded a more interesting reaction.

A benzene solution of thioadamantanone reacted with aniline at ambient temperature to give a stable crystalline solid, m.p. 189—191°, in 24% yield. Elemental analysis and mass spectroscopy indicated the formula $C_{20}H_{28}S_3$. The i.r. spectrum was similar in some aspects to that obtained for the thio-ozonide (1). The u.v. spectrum exhibited peaks at $\lambda_{max.}$ 222 and 253 nm. The n.m.r. spectrum was similar to that of thioadamantanone.

Accordingly, the thio-ozonide structure (16) was assigned, rather than the alternative 1,2,3-trithiolan structure.[4] This previously unknown thio-ozonide represents a new member of an uncommon group of compounds.[5] Secondary and tertiary amines did not react with (15) under similar conditions.

Mechanistic pathways proceeding through a *gem*-thiolamine and thence the disulphide (17) can be invoked. As with the corresponding thiobenzophenone reactions, the dimerization step could not be suppressed.

An unexpected reaction was encountered when (15) was refluxed in dioxan with toluene-*p*-sulphonamide,

affording thio-ozonide (16) in very low yield, together with dimerized [6] and trimerized [6] thioadamantanone. The reaction, when performed under nitrogen, gave a lower yield of (16), apparently indicating inhibition of the oxidative dimerization step in this case.

Nucleophilic Reaction of Benzenethiol with Thiones.— In an extension of the investigation of the nucleophilic reactions undergone by thioketones, several aromatic and aliphatic thiones were treated with benzenethiol.

A benzene solution of thiobenzophenone (5) when treated with excess of benzenethiol either in the presence or absence of air, was shown to afford the thio-ozonide (1), together with diphenyl disulphide and an unstable compound which rapidly decomposed on standing even at low temperature to give thiobenzophenone and more diphenyl disulphide. The instability of this compound prevented spectroscopic and analytical characterization, but the i.r. spectrum indicated the absence of the mercaptan group. It was noted that when the reaction solution was treated with aqueous alcoholic sodium hydroxide the unstable product was immediately converted into thiobenzophenone. We therefore suggest that this reaction product may be an intermediate such as (19) in a reaction sequence (5) ⟶ (18) ⟶ (19) ⟶ (20) ⟶ (1). Other polar constituents in this reaction proved too unstable to be characterized.

In a parallel study it was established that phenol did not react with thiobenzophenone. Thiophenol was treated with the related aromatic thiones (6) and (7) but afforded no thio-ozonides, again illustrating the differences in reactivity in this series.

The corresponding reactions of benzenethiol with the aliphatic thioketones (14) and (15) were investigated. Compound (14) was recovered unchanged after several

days, perhaps because of unfavourable steric interactions in the formation and subsequent reaction of a tetrahedral dithiohemiacetal. Thioadamantanone, in contrast, reacted slowly at ambient temperature, affording diphenyl disulphide and a white crystalline compound, m.p. 76—78°, which decomposed slowly on

[3] Y. Minoura and S. Tsuboi, *J. Polymer Sci., Part A*-1 *Polymer Chem.*, 1970, **8**, 125.

[4] The preparation and physical characteristics of a 1,2,3-trithiolan have been described, T. C. Shields and A. N. Kurtz, *J. Amer. Chem. Soc.*, 1969, **91**, 5415.
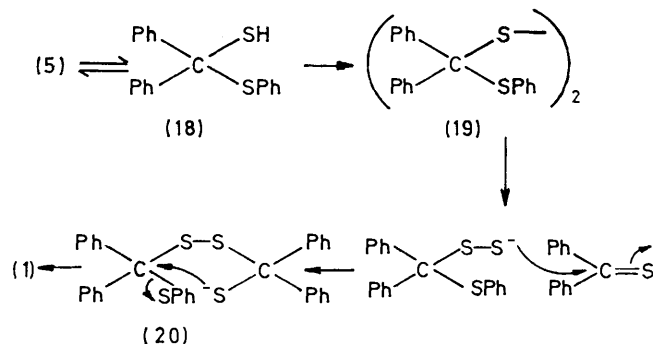
[5] W. J. Linn and E. Ciganeck, *J. Org. Chem.*, 1969, **34**, 2146; R. M. Moriarty, M. Ishibe, M. Kayser, K. C. Ramsey, and H. J. Gisler, *Tetrahedron Letters*, 1969, 4883; G. C. Forward and M. C. Whiting, *J. Chem. Soc.* (C), 1969, 1647; L. Cambi, G. Bargigia, L. Colombo, and E. P. Dubine, *Gazzetta*, 1969, **99**, 780.

[6] J. W. Greidanus, *Canad. J. Chem.*, 1970, **48**, 3530.

standing to give diphenyl disulphide and thioadamantanone. Elemental analysis indicated the formula $(C_{16}H_{19}S_2)_n$. The i.r. spectrum was similar to that of (15), containing, in addition, aromatic absorption bands. The u.v. spectrum contained peaks at $\lambda_{max.}$ 223 and 277 nm. No molecular ion could be detected in the mass spectrum because of ready thermal decomposition to (15). The n.m.r. spectrum contained a multiplet $[(5H)_n]$ in the aromatic region and a multiplet $[(14H)_n]$ corre-
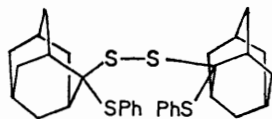

(21)

sponding to the adamantyl skeleton. These analytical and spectral data together with the ready transformation into (15) on standing, and instantaneously when treated with aqueous ethanolic NaOH, pointed to the novel disulphide (21). Isolation of this product provides some support for structure (19) which was tentatively assigned to the unstable reaction product of benzenethiol and (5).

It was of interest to attempt to convert (21) into the thio-ozonide (16). Accordingly, an alcoholic solution of (21) was saturated with H_2S, affording a very low yield of (16). This reaction does not of course prove that nucleophilic displacement by H_2S is a general step in the formation of thio-ozonides. The isolation of (21) lends credence to reaction pathways involving the dimerization of tetrahedral intermediates such as (18).

Some Reactions of Aminosulphuric Acid with Thiones.
—Base-catalysed reactions of aminosulphuric acid with aromatic and aliphatic thiones were of interest in order to determine whether the expected *gem*-thiolamine intermediate (22) would afford a thio-ozonide, or alternatively lead to the hitherto unisolated thiaziridine ring system (23).[7]
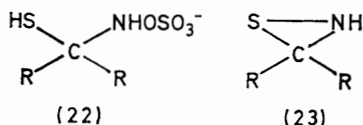
(22)   (23)
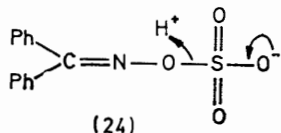
(24)

Thiobenzophenone (5) reacted exothermally with aminosulphuric acid following the addition of ethanolic sodium hydroxide. A low yield of thio-ozonide (1) was obtained, possibly by a mechanism involving oxidative dimerization of (22). In addition, elemental sulphur and benzophenone oxime (25) were obtained. An unisolable thiaziridine (23; R = Ph) may account for the sulphur and perhaps even the oxime formation. Alternatively, the oxime (25) may be formed from (24). It

was noted that under similar conditions benzophenone did not react. The reactions of the related aromatic thioketones (6) and (8) were highly complex, but no thio-ozonides were formed.

The aliphatic thioketones (14) and (15) when treated with aminosulphuric acid and base afforded the corresponding oximes in modest yield. Thiocamphor, however, gave as a by-product bis-(1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl) disulphide in low yield. The origin of this compound is rather obscure, and may involve hydrogen atom abstraction by imidogen, followed by dimerization. Related reactions of thiocamphor leading to this product are described in the following paper.

EXPERIMENTAL

M.p.s were recorded on a Gallenkamp m.p. apparatus. I.r. spectra were recorded on Perkin-Elmer 457 and 257 grating spectrophotometers. U.v. spectra were measured for 1% solutions in ethanol or cyclohexane on an SP 800 spectrophotometer. [1]H N.m.r. spectra were recorded on a Perkin-Elmer R12 instrument and mass spectra were obtained from an A.E.I. MS-30 spectrometer. Adsorption chromatography was carried out using Kieselgel (Merck; 0·05—0·2 mm; 70—325 mesh) or on alumina (Woelm; Grade I; neutral). T.l.c. was carried out using Kieselgel G and Kieselgel G Nach Stahl 254 as adsorbents. Light petroleum refers to the fraction with b.p. 40—60°.

Preparation of 3,3,5,5-Tetraphenyl-1,2,4-trithiolan (1) [2] *by the Reaction of Thiobenzophenone with Air.*—Thiobenzophenone (500 mg) was dissolved in benzene (30 ml) and air bubbled through the solution till the blue colour of the thione disappeared (3 days). The solution was filtered, the solvent removed *in vacuo* and the remaining oil was chromatographed on silica gel (eluant light petroleum), affording (1) (50 mg), m.p. 122—124° (Found: C, 72·8; H, 4·65; S, 22·4. Calc. for $C_{26}H_{20}S_3$: C, 72·9; H, 4·65; S, 22·7%).

Reaction of Thiobenzophenone with Amines.—In a typical reaction, thiobenzophenone (1 g) was dissolved in benzene (10 ml) under nitrogen, with magnetic stirring. Methylamine (0·314 g in aqueous solution) was added at room temperature. The blue colour of the thioketone was discharged rapidly and the solution smelled strongly of hydrogen sulphide. The solution was washed twice with 2N-HCl, with saturated aqueous hydrogen carbonate, and dried (MgSO₄). The solvent was removed *in vacuo* at low temperature to minimize decomposition of the oily product, affording 0·95 g of crude yellow oil. Separation of products was achieved either by column chromatography on alumina or by preparative t.l.c. For example, 100 mg of the crude product was adsorbed onto a preparative t.l.c. plate and eluted with light petroleum, affording the major reaction products, the thio-ozonide (1) (31 mg, 14%), benzophenone (17 mg, 19%), and traces of thiobenzophenone. The residual material was observed to be a complex mixture of unstable, polar, base-line products.

The reaction was repeated with a range of re-distilled amines (Table). T.l.c. analysis of the crude products, prior

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[7] The reaction of certain ketones with aminosulphonic acid gives oxaziridines, presumably *via* an intermediate *gem*-hydroxy-hydroxylamine-*O*-sulphonate, T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes and Arynes,' Nelson, London, 1969, p. 34.

to separation of the thio-ozonide (1), indicated the presence of imines which on subsequent work-up were hydrolysed.

Products of reaction of thiobenzophenone with amines

Amine	Time required to complete reaction	Products
MeNH$_2$(aq.)	30 s	Thio-ozonide (1) (14%) Benzophenone (19%) Thiobenzophenone (traces) Polar products
Et$_2$NH	2·5 h	Thio-ozonide (1) (12%) Benzophenone (12%) Thiobenzophenone (traces) Polar products
Et$_3$N		No reaction
PhNH$_2$	15 h	Thio-ozonide (1) (14%) Benzophenone anil (14%) Benzophenone (9%) Thiobenzophenone (traces) Polar products
Me$_2$NNH$_2$	30 s	Thio-ozonide (1) (13%) Benzophenone (17%) Thiobenzophenone (traces) Polar products
PhNHNH$_2$	1 min	Hydrazone (100%)
p-MeC$_6$H$_4$SO$_2$NH$_2$		No reaction

Reaction of Benzophenone Anil with Hydrogen Sulphide.—The reaction of benzophenone anil with hydrogen sulphide was investigated for a range of solvents at varying temperatures, in an attempt to form thio-ozonide (1). In many of the reactions, thiobenzophenone was the predominant product. However, when benzophenone anil (1 g) in ethanol (100 ml) was saturated with hydrogen sulphide, under nitrogen, at $-75°$, the formation of (1) as the sole non-polar product was indicated by t.l.c. The colourless solution was allowed to attain room temperature, but turned deep blue. The solvent was removed *in vacuo* and the resultant solid mass extracted twice with cold light petroleum. The extract was subjected to preparative t.l.c. affording (1) (25 mg), together with anil and thiobenzophenone each of which had been formed from an unstable precursor during the work-up. The yield of (1) was not significantly affected by the presence of quinone or hydroquinone (100 mg). Added hydrogen peroxide (5 ml; 30% aqueous) appeared to increase the yield of (1) to 70 mg.

Reaction of Adamantanethione with Aniline.—Aniline (168 mg) was added to a solution of adamantanethione (200 mg) in benzene (10 ml). The red colour of the thione was discharged after 15 h at room temperature, and the reaction smelled strongly of hydrogen sulphide. T.l.c. indicated a complex mixture, although one major product was apparent. The solvent was removed *in vacuo* affording a reddish oil which crystallized on addition of ethanol, affording pure *dispiro[adamantane-2,3'-(1,2,4-trithiolan)-5',2''-adamantane]* (16) (53 mg, 24%), m.p. 189—191° (Found: C, 65·85; H, 7·5; S, 26·7. C$_{20}$H$_{28}$S$_3$ requires C, 65·95; H, 7·7; S, 26·35%), $\nu_{max.}$ (KBr) 1450, 1345, 1325, 1195, 650, and 500 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 222 (ε 1290) and 253 nm (960), m/e 364 (5%, M^+).

Reaction of Adamantanethione with Toluene-p-sulphonamide.—Adamantanethione (200 mg) in dioxan (10 ml) was refluxed with toluene-p-sulphonamide (205 mg) for 2 h. The red colour of the thione disappeared and the reaction smelled strongly of hydrogen sulphide. The solution was

filtered, affording a solid (75 mg) which was washed with petroleum, recrystallized from chloroform and shown to be the trimer trispiro-[1,3,5-trithian-2,2':4,2'':6,2'''-tri-adamantane] [6] (65 mg, 32%). Crystallization of the filtrate afforded the thio-ozonide (16) (60 mg, 40%). Preparative t.l.c. of the mother liquors yielded adamantanethione (10 mg) and the dimer, dispiro[adamantane-2,2'-(1,3-dithietan)-4',2''-adamantane] [6] (10 mg).

In a similar reaction in a degassed solution under nitrogen the yield of (16) was reduced to 1% after refluxing for 2 h.

It was shown in a control reaction that adamantanethione was recovered unchanged after refluxing for 2 h in dioxan.

Reaction of Thiobenzophenone with Benzenethiol.—Thiobenzophenone (0·97 g) was dissolved in benzene (15 ml). Benzenethiol (1·62 g) was added and the solution stirred at room temperature until the colour of the thioketone disappeared (20 h). T.l.c. indicated a complex reaction mixture containing four main products. The solution was extracted four times with water, dried (MgSO$_4$), and the solvent was removed at low temperature *in vacuo*. Addition of ethanol to the resultant blue-green oil afforded the crystalline thio-ozonide (1) (190 mg, 27%), the structure of which was established by m.p. and spectroscopic comparison with an authentic sample. The residual material was rapidly passed through a silica gel column, eluting with benzene–light petroleum. The principal products obtained were diphenyl disulphide (270 mg, 8%), together with a very unstable oil (110 mg), thiobenzophenone (300 mg, 31%), and benzophenone (40 mg). No attempt was made to elute unchanged benzenethiol and polar by-products.

It was established that the thiobenzophenone originated from the decomposition of the unstable oil whose rapid decomposition precluded a study. The i.r. spectrum indicated only aromatic peaks and possible C–S vibrations (800—450 cm^{-1}), but showed the absence of the SH group. It was noted during an earlier attempt to remove benzenethiol by washing with 2N-NaOH that the unstable product was immediately decomposed into thiobenzophenone. A parallel experiment established that the 1,2,4-trithiolan did not decompose to thiobenzophenone at a significant rate under similar conditions.

Reaction of Adamantanethione with Benzenethiol.—Benzenethiol (661 mg) was added to a stirred solution of adamantanethione (930 mg) in light petroleum (20 ml). The reaction was washed with water, dried (MgSO$_4$), and the solvent was removed *in vacuo*, leaving an oil which crystallized from ethanol–light petroleum to give a solid (700 mg). Recrystallization from light petroleum afforded pure 2,2'-*bis*-(2-*phenythioadamantyl*) *disulphide* (21) (500 mg, 49%), m.p. 76—78° (Found: C, 69·55; H, 7·15; S, 23·4. C$_{32}$H$_{38}$S$_4$ requires C, 69·8; H, 6·9; S, 23·25%), $\nu_{max.}$ 3070, 2960, 1280, 1100, 1075, 1030, 965, 800, 785, 760, 755, 705, 700, and 695 cm^{-1}, $\lambda_{max.}$ (cyclohexane) 223 (ε 22,900) and 277 (4100) nm, τ (CCl$_4$) 2·5—2·7 (10H, m) and 7·6—8·7 (28H, m). No molecular ion was observed in the mass spectrum, but significant peaks appeared at m/e 166 (C$_{10}$H$_{14}$S$^{+•}$) and 218 (C$_{12}$H$_{10}$S$_2^{+•}$).

The mother liquors were subjected to column chromatography on silica gel, affording 2-adamantanethione (400 mg) and diphenyl disulphide (200 mg).

The crystals of (21) on standing at room temperature slowly decomposed to adamantanethione and diphenyl disulphide. Treatment of a benzene solution of the crystals with aqueous or ethanolic 2N-NaOH rapidly afforded adamantanethione and diphenyl disulphide as

shown by preparative t.l.c. and spectroscopic identification of the products.

A reaction of 2-adamantanethione with benzenethiol was performed in the absence of air, and also in the presence of hydroquinone, but the products were unaltered.

Reaction of Disulphide (21) *with Hydrogen Sulphide.*— Disulphide (21) (200 mg) was dissolved in absolute ethanol (70 ml) and hydrogen sulphide was passed through the solution for 5 h. T.l.c. indicated the slow formation of the dispiro-compound (16). The solution was left to stand overnight and the solvent removed at low temperature *in vacuo* to minimize decomposition. Preparative t.l.c. afforded pure (16) (20 mg, 15%) identical with an authentic sample (m.p., i.r.). Diphenyl disulphide (23 mg, 29%) was also isolated.

Reaction of D-*Thiocamphor with Benzenethiol.*—D-Thio-camphor (385 mg) was dissolved in benzene (10 ml) and benzenethiol (300 mg) was added. After 10 weeks at room temperature no reaction could be detected. A brief reflux produced no reaction.

Reaction of Thiobenzophenone with Aminosulphuric Acid. —Thiobenzophenone (1 g) was dissolved in ethanol (20 ml) and aminosulphuric acid (605 mg) in ethanol (25 ml) was added. No reaction occurred under these conditions. Addition of aqueous sodium hydroxide (2N; 15 ml) in ethanol (15 ml) caused immediate decolourization of the thione with evolution of heat. The solution was filtered, washed with water, and extracted with ether which on drying (MgSO₄) and concentrating *in vacuo* afforded crystalline sulphur (100 mg). Further concentration of the solution gave a semi-solid precipitate (600 mg) which after several recrystallizations from light petroleum–chloroform gave benzophenone oxime (400 mg, 40%), m.p. 143—144°, the structure of which was confirmed by elemental analysis and spectroscopic comparison with an authentic sample. Column chromatography of the combined mother liquors

on silica gel (light petroleum–benzene) gave pure 3,3,5,5-tetraphenyl-1,2,4-trithiolan (1) (130 mg, 18%).

No reaction of benzophenone with aminosulphuric acid occurred under these conditions, the ketone being recovered quantitatively.

Reaction of D-*Thiocamphor with Aminosulphuric Acid.*— To D-thiocamphor (200 mg) in ethanol (10 ml) was added a solution of aminosulphuric acid (268 mg) in ethanol (15 ml). No reaction occurred. Addition of sodium hydroxide (200 mg) in ethanol (15 ml) caused rapid decolourization. T.l.c. indicated the formation of several non-polar and polar products. The solution was filtered, concentrated *in vacuo* and the resultant solid mass extracted with ether which was washed with water and dried (MgSO₄). Concentration of the ether afforded a pungent oil (180 mg). Column chromatography on silica gel (light petroleum) gave bis-(1,7,7-trimethyl[2.2.1]bicyclohept-2-en-2-yl) disulphide (30 mg, 15%) the structure of which was confirmed by comparison with an authentic sample (m.p., i.r.). Further elution with benzene–light petroleum (1 : 1) afforded camphor oxime (60 mg, 30%), m.p. 118—119°.

Reaction of Thioadamantanone (15) *with Aminosulphuric Acid.*—To thioadamantanone (500 mg) in ethanol (20 ml) was added aminosulphuric acid (339 mg) in ethanol (10 ml). Addition of sodium hydroxide (200 mg) in ethanol (20 ml) caused immediate reaction which was accompanied by the evolution of hydrogen sulphide. The solution was filtered, concentrated *in vacuo* and the resulting solid extracted with benzene which was washed with water and dried (MgSO₄). Concentration of the benzene extract afforded a solid (400 mg) which after recrystallization from ethanol was identified from its m.p., analysis, and spectroscopic data, as adamantanone oxime [8] (320 mg, 62%).

[8] G. W. Smith, U.S.P. 3,328,251.