

10-(1,3-Dithiolan-2-ylidene)-10*H*-indeno[1,2-*f*]pentathiepin, a Product from 2-(Inden-1-ylidene)-1,3-dithiolan and Disulphur Dichloride

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The reaction of disulphur dichloride with 2-(inden-1-ylidene)-1,3-dithiolan (I) gives the indeno[1,2-*f*]pentathiepin (IV).

DISULPHUR DICHLORIDE is a remarkably versatile reagent.^{1,2} We now report its reaction with an 8,8-ethylenedithiobenzofulvene [2-(inden-1-ylidene)-1,3-di-

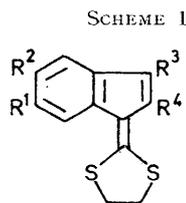
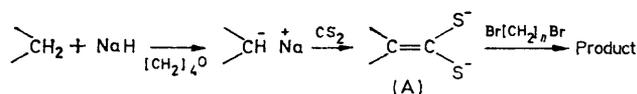
¹ L. A. Wiles and Z. S. Ariyan, *Chem. and Ind.*, 1962, 2102.

² Z. S. Ariyan and R. L. Martin, *Chem. Comm.*, 1969, 847; *J.C.S. Perkin I*, 1972, 1687.

thiolan (I)], which proceeded in an unexpected manner. Compound (I) and some derivatives (see Table) were prepared according to a procedure reported by Gompper³

³ R. Gompper and E. Kutter, *Chem. Ber.*, 1965, **98**, 2825.

for the cyclopentadiene analogue of (I). This reaction (Scheme 1) gave the intermediate indene-1-dithio-carboxylic acid disodium salt (A), which, typically, gave compound (I), ν_{\max} 1550s cm^{-1} , on treatment with 1,2-dibromoethane. Goppner reports an i.r. band at 1528 cm^{-1} for the cyclopentadiene analogue of (I), similarly at lower frequency than usual for fulvenes⁴ (ca. 1600 cm^{-1}), owing to the presence of the fused benzene ring. The naphthodithiole (II) was similarly obtained from a reaction with 1,2-dichloronaphtho-quinone, whereas the oxidation product (III) resulted from a reaction with 1,2-dibromotetrachloroethane.



	R ¹	R ²	R ³	R ⁴	M.p. (°C)
(I)	H	H	H	H	71 - 72
	H	H	Ph	H	119 - 201
	H	H	Me		190 - 191
	H	Me	Me	CO ₂ Me	134 - 135
	H	H	Me	CO-NPr ₂	118 - 119
	H	H	CO ₂ Me	H	109 - 111
	MeO	MeO	Me	CO ₂ Et	157 - 158
	H	H	Ph	Ph	215 - 216

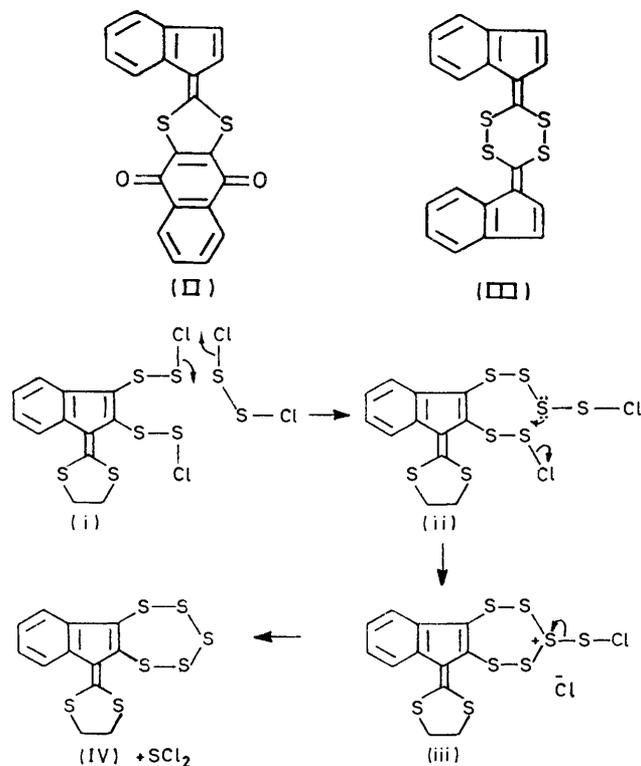
Analytical and i.r. data for these compounds are available as Supplementary Publication No. SUP 20898 (2 pp.) [for details of Supplementary Publications see *J.C.S. Perkin I*, 1972, Index Issue (Notice to Authors No. 7)].

Treatment of compound (I) with disulphur dichloride yielded bright red crystals with high sulphur content ($\text{C}_{12}\text{H}_8\text{S}_7$), isolated pure after chromatography on alumina. Reactions of disulphur dichloride are known to yield a variety of sulphides, RS_nR ($n = 1-4$) or mixtures thereof; but no linear penta- or higher sulphides have been reported under ordinary conditions (except in reactions with thiols). The cyclic pentasulphide structure (IV) was assigned on the basis of the result of desulphurisation by Raney nickel, which yielded benzofulvene, and from spectroscopic evidence. The n.m.r. spectrum of a solution in carbon disulphide

⁴ J. C. Wood, R. M. Elofson, and D. M. Saunders, *Analyt. Chem.*, 1958, **30**, 1339.

⁵ T. Nakabayashi, J. Tsurugi, and T. Yabuta, *J. Org. Chem.*, 1964, **29**, 1236; cf. C. C. Price and S. Oae, 'Sulfur Bonding', Ronald Press, New York, 1962, p. 38.

lacked the endocyclic olefin resonance (δ 6.70) of (I) and showed signals at δ 7.8-8.0 (1H, m, ArH), 7.1-7.5 (3H, m, ArH), and 3.55 (4H, s, CH_2). The 1550 cm^{-1} i.r.



band of (I) was replaced by an intense band at 1500 cm^{-1} , strongly suggestive of a conjugated cyclic C=C vibration. This is supported by the large bathochromic shift⁵ observed in the visible spectrum [λ_{\max} (CHCl_3) 445 nm ($\log \epsilon$ 4.39) for (IV); 362 nm ($\log \epsilon$ 4.30) for (I)]. The absorption could be ascribed to a $\pi \rightarrow \pi^*$ transition and the bathochromic shift, by analogy with that reported for parathiacyclophane,² may well be further indication that delocalisation of electrons occurs in the newly formed S_5 ring, which might therefore exhibit alternation of bond length.^{6,7} The ability of sulphur to participate in conjugated systems is well known and the sulphur atom has often been compared formally to a carbon-carbon double bond. The system present in compound (IV) can therefore be considered as a regular, staggered six-membered ring of cyclohexasulphur, S_6 . The photoinstability of (IV), particularly in solution, is not surprising, although the compound is stable in the solid state in the dark.

The probable course of reaction (Scheme 2) involves initial successive double electrophilic substitution of the endocyclic double bond in (I), resulting in a 2,3-bis(chlorodithio)-intermediate (i). In the halogenation of benzofulvenes the exocyclic double bond is known to be

⁶ (a) J. S. Ricci, jun., and I. Bernal, *Chem. Comm.*, 1969, 1453; *J. Chem. Soc. (B)*, 1971, 1928; (b) P. D. Sullivan, *Internat. J. Sulfur Chem. (A)*, 1972, **2**, 149.

⁷ F. Fehér, M. Langer, and R. Volkert, *Z. Naturforsch.*, 1972, **27b**, 1006.

resistant to electrophilic substitution.⁸ Tetrasulphide formation from chlorodithio-intermediates has been described.² Molecular models show that a 2,3-bis-chlorodithio-intermediate could not be expected to form a 2,3-cyclic tetrasulphide because of ring strain. To account for the production of (IV), we suggest a chain extension to give the chlorosulphane (ii), which could cyclise through a chlorothioepisulphonium intermediate (iii) to afford a seven-membered ring system devoid of strain (IV). This mechanism bears a formal resemblance to the established mechanism for addition of sulphenyl halides to olefins, and affords a further example of heterolysis of S-S bonds by an electrophilic reagent.⁹

In the mass spectrum of (IV) the primary decomposition is the expulsion of sulphur. Consequently, the expected molecular ion peak at m/e 376 was absent (*cf.* cycloheptasulphur and cyclodecasulphur,¹⁰ in the spectra of which molecular ion peaks do not appear clearly). A differential scanning calorimetric study indicated that upon melting an exothermic process occurs, and elemental sulphur was extracted from the charred decomposition product.

EXPERIMENTAL

U.v. spectra were measured for solutions in chloroform with a Perkin-Elmer 202 recording spectrophotometer and i.r. spectra with a Perkin-Elmer 421 instrument. N.m.r. spectra were recorded with a Varian HA-100 instrument (tetramethylsilane as internal standard and CS₂ as solvent) at room temperature. Indene derivatives were prepared according to reported methods.¹¹

General Method for the Preparation of 2-(Inden-1-ylidene)-1,3-dithiolans.—2-(Inden-1-ylidene)-1,3-dithiolan (I). Indene (distilled; 42 g, 0.36 mol) in tetrahydrofuran (distilled; 700 ml), was treated with sodium hydride (16 g, 0.36 mol) under a stream of nitrogen. The mixture was then refluxed for 2 h and cooled in solid carbon dioxide-acetone, and carbon disulphide (15.2 g, 0.2 mol) was added during 20 min. 1,2-Dibromoethane (38 g, 0.2 mol) in tetrahydrofuran (50 ml) was then added gradually, after removal of the ice-bath, with vigorous stirring. The product mixture was left overnight then filtered and evaporated. The resulting gum was chromatographed over alumina with 25:75 benzene-hexane as eluant. The bright yellow product crystallised (with chilling) from cyclohexane-benzene (yield 72%), m.p. 71–72° (Found: C, 66.2; H, 4.75; S, 29.15. C₁₂H₁₀S₂ requires C, 66.05; H, 4.6; S, 29.35%), λ_{\max} 362 nm (log ϵ 4.30), δ (CDCl₃) 7.08–7.93 (m, ArH), 6.70 (s, CH:CH), and 3.45 (A₂B₂m, CH₂).

Reaction of Indene-1-dithiocarboxylic Acid Disodium Salt with 1,2-Dichloronaphthoquinone.—To indene (11.6 g, 0.1 mol) in tetrahydrofuran (150 ml), sodium hydride (2.5 g) was added under nitrogen and the mixture was refluxed for 2 h. 1,2-Dichloronaphthoquinone (12.6 g, 0.1 mol) in tetrahydrofuran (250 ml) was gradually added with stirring and the solution was stirred for a further 1 h. Filtration and evaporation yielded an oil; chromatography over alumina with benzene as eluant removed unchanged dichloronaphthoquinone. Chloroform then eluted a red-

brown band which yielded a green solution. Evaporation gave 2-(inden-1-ylidene)-2H-naphtho[2,3-d][1,3]dithiole-4,9-quinone (II) as dark green crystals, m.p. 317–319° (Found: C, 68.95; H, 3.05; S, 18.3. C₂₀H₁₀O₂S₂ requires C, 69.35; H, 2.9; S, 18.5%).

3,6-Di-(inden-1-ylidene)-1,2,4,5-tetrathian (III).—To indene (11.6 g, 0.1 mol) in tetrahydrofuran (150 ml), sodium hydride (2.5 g) was added under nitrogen; the mixture was refluxed for 2 h, then cooled in solid carbon dioxide-acetone, and carbon disulphide (5 ml) in tetrahydrofuran (15 ml) was added during 30 min. 1,2-Dibromotetrachloroethane (20 g, 0.5 mol) in tetrahydrofuran (15 ml) was then added dropwise with constant stirring and the mixture was refluxed for 15 min. Filtration and evaporation yielded an oil which was chromatographed over alumina [cyclohexane-benzene (50:50) as eluant]. The product was a bright yellow solid, m.p. 145° (from cyclohexane or light petroleum) [Found: C, 63.15; H, 3.2; S, 33.75%; M, 372 (C₆H₆), 375 (CCl₄). C₂₀H₁₂S₄ requires C, 63.05; H, 3.2; S, 33.7%; M, 380], λ_{\max} 362 nm (log ϵ 4.52).

10-(1,3-Dithiolan-2-ylidene)-10H-indeno[1,2-f]pentathiepin (IV).—Initial experiments with chloroform as solvent gave 5% yields and a large amount of gummy intractable material. It was found best to carry out the reaction in a basic medium (with added triethylamine).

2-(Inden-1-ylidene)-1,3-dithiolan (11 g, 0.05 mol) was dissolved in toluene (200 ml) containing triethylamine (40 g). The solution was cooled in an ice-bath and kept at 0 °C. Gradual addition of disulphur dichloride (20 g, 0.15 mol) in toluene (100 ml) during 0.5 h resulted in a deep red colour, and the amine hydrochloride precipitated. The solution was allowed to warm to room temperature. Some charring and darkening invariably followed and the mixture was gradually warmed to reflux temperature and maintained there for 10–15 min. The brown mass was filtered off and toluene and excess of triethylamine were removed. Chromatography over alumina (benzene as eluant) removed a yellow band (sulphur) followed by a deep orange band. Evaporation and recrystallisation of the residue from toluene gave bright red crystals of the pentathiepin (IV), m.p. 169–170° (2.6 g, 14%). Two further recrystallisations from toluene gave pure material (t.l.c. on aluminium oxide IB-F; Baker-flex; chloroform), m.p. 186–187° [Found: C, 38.25; H, 2.15; S, 59.6%; M (CH₂Br₂), 358. C₁₂H₈S₇ requires C, 38.15; H, 2.15; S, 59.6%; M, 376]. An orange polymeric product also removed from the column was insoluble in most solvents (m.p. >300°; high sulphur content).

Desulphurisation of the Pentathiepin (IV).—To compound (IV) (0.5 g) in distilled tetrahydrofuran (20 ml) a slurry (15 ml) of Raney nickel was added, and the red mixture was refluxed with stirring until colourless (5 h). The slurry was filtered, the residue washed with tetrahydrofuran, and the solution evaporated *in vacuo*. T.l.c. of the resulting oil (strong naphthalene-like odour) indicated the presence of a major component with a little (unidentified) impurity. The oil crystallised when kept in an ice-bath. Washing with light petroleum gave benzofulvene as pale yellow crystals, m.p. 36–37° (lit.¹² 37°), which were unstable and readily polymerised to a gummy mass; ν_{\max} 3015, 1480, and 903 cm⁻¹.⁴

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⁸ E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.

⁹ C. G. Moore and M. Porter, *J. Chem. Soc.*, 1958, 2890.

¹⁰ U. I. Záhorszky, *Angew. Chem. Internat. Edn.*, 1968, **7**, 633.

¹¹ (a) J. Koo, *Org. Synth.*, Coll. Vol. V, 1973, p. 550; (b) H. A. Bruson and H. L. Plant, *J. Org. Chem.*, 1967, **32**, 3356.

¹² C. Courtot, *Ann. Chim. (France)*, 1915, **4**, 202.