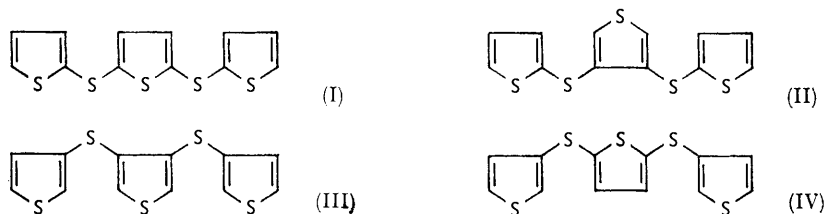


1295. Di(thienylthio)thiophens. Condensation of Thiopen Thiols with Dibromothiophens

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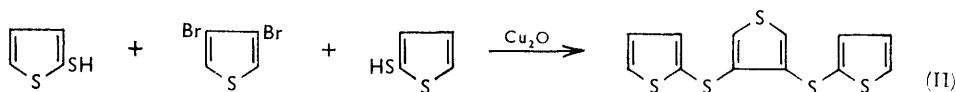
A general route to the di(thienylthio)thiophens has been developed. Four isomers (I—IV) have been prepared by condensation of thiophen 2- or 3-thiol with 2,5- or 3,4-dibromothiophen in the presence of cuprous oxide in dimethylformamide. These compounds may be oxidised using hydrogen peroxide to the corresponding sulphones.

RECENTLY we reported the synthesis of the isomeric dithienyl sulphides by condensation of a thiophen thiol with a halogenothiophen promoted by cuprous oxide in dimethylformamide.¹ We have now extended this work to the preparation of four of the isomeric di(thienylthio)thiophens (I)—(IV). Of these isomers only 2,5-di-(2-thienylthio)thiophen



(I) had been reported,² having been prepared by the reaction of 5-lithiodi-2-thienyl sulphide with di-2-thienyl disulphide. This method, however, is laborious and not readily adaptable to the synthesis of the other isomeric di(thienylthio)thiophens.

The isomers (I)—(IV) have now been synthesised in fair yield by the condensation of the appropriate thiophen-2- or -3-thiol with 2,5- or 3,4-dibromothiophen in the presence of cuprous oxide in dimethylformamide. These isomers are viscous oils which decompose on prolonged heating above 230°.



Several workers have discussed the infrared spectra of substituted thiophens,³⁻⁵ and the bands in the 1600—1000 cm^{-1} region have been assigned to the thiophen ring itself. The characteristic substitution pattern is usually shown by bands in the 1000—700 cm^{-1} region. The spectra of isomers (I)—(IV) show the expected absorption pattern of compounds containing both mono- and di-substituted thiophen rings.

Oxidations of the di(thienylthio)thiophens using a hydrogen peroxide-glacial acetic acid mixture yield the corresponding sulphones. Reaction occurs readily with isomers (II) and (III) but is more difficult with (I) and (IV).

EXPERIMENTAL

The ultraviolet spectra of the isomeric di(thienylthio)thiophens were measured in hexane, and those of the sulphones, their oxidation products, in ethanol using a Hilger and Watts spectrophotometer.

Thiophen-2- and -3-thiols were prepared by standard procedures based on the sulphuration

¹ E. Jones and I. M. Moodie, *Tetrahedron*, 1965, **21**, 2413.

² B. P. Federov and F. M. Stoyanovich, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 2251.

³ A. R. Katritzky and A. J. Boulton, *J.*, 1959, 3500.

⁴ S. Gronowitz, A. R. Katritzky, and R. E. Reavill, *J.*, 1963, 3881.

⁵ H. D. Hartough, "Thiophene and its Derivatives," Interscience, New York, 1952, ch. IV.

of 2-thienylmagnesium bromide⁶ and 3-thienyl-lithium,⁷ respectively. 3,4-Dibromothiophen was obtained by a controlled debromination of tetrabromothiophen using zinc in glacial acetic acid.⁸ Other chemicals used were obtained commercially.

Preparation of Di(thienylthio)thiophens (I)–(IV).—The general procedure employed is exemplified in the preparation of 2,5-di-(2-thienylthio)thiophen (I).

Thiophen-2-thiol (37.0 g., 0.32 mole) was added slowly to a stirred mixture of 2,5-dibromothiophen (39.65 g., 0.16 mole), freshly precipitated cuprous oxide⁹ (23.0 g., 0.16 mole), potassium hydroxide (18.0 g., 0.32 mole), and dimethylformamide (325 ml.). The mixture, under nitrogen, was heated for 24 hr. at 140°, cooled, and poured into a stirred mixture of 4*N*-hydrochloric acid in crushed ice. Stirring was maintained for *ca.* 1 hr. and the brown solid filtered off. Both solid and filtrate were thoroughly extracted with benzene. These extracts were combined, washed with water until neutral, and dried over anhydrous sodium sulphate. Vacuum distillation furnished (I) as a yellow oil (22.9 g., 46%), b. p. 214–220°/10⁻⁴ mm. (lit.,² 196–198°/0.05 mm.).

TABLE 1

Preparation of the isomeric di(thienylthio)thiophens (I)–(IV)

Thiophen thiol	Dibromo-thiophen	Product (I)	Yield (%)	B. p./10 ⁻⁴ mm.	<i>n</i> _D ²⁵	Found * (%)			$\lambda_{\max.}$ (m μ)	ϵ
						C	H	S		
2-	2,5-	(I)	46.0	214–220°	1.6988	46.0	2.8	51.1	205 †	35,870 †
									240	18,440
									274	11,800
2-	3,4-	(II)	38.5	180–184	1.7130	46.3	2.5	51.1	206	35,450
									237	20,120
									276	8070
3-	3,4-	(III)	44.0	175–180	1.7149	45.5	2.5	51.9	208	44,360
									274	9952
									206	37,180
3-	2,5-	(IV)	15	170–180	1.7180	46.1	2.5	51.4	206	37,180

* Calc. for C₁₂H₈S₅: C, 46.2; H, 2.6; S, 51.3%. † E. M. Popov, F. M. Stoyanovich, B. P. Federov, and G. M. Andrianova, *J. Gen. Chem. (U.S.S.R.)*, 1963, **33**, 2261, give $\lambda_{\max.}$ 238,282 (ϵ 18,000, 11,200).

Oxidation of Di(thienylthio)thiophens to the Corresponding Sulphones.—The sulphide was dissolved in glacial acetic acid and excess hydrogen peroxide (100 vol.) added. After refluxing for 10 hr., a white crystalline solid was obtained on addition of excess water. Consecutive recrystallisations from benzene and ethanol furnished the sulphone as white needles or plates.

TABLE 2

Oxidation of di(thienylthio)thiophens to their sulphones

Thiophen (I)	Product	M. p.	Found * (%)			$\lambda_{\max.}$ (m μ)	ϵ
			C	H	S		
(I)	2,5-Di-(2-thienylsulphonyl)thiophen	167–168° †	38.3	2.2	43.0	255	10,880
						295	13,000
						209	10,700
(II)	3,4-Di-(2-thienylsulphonyl)thiophen	214–215	38.5	2.3	43.2	242	14,050
						268	12,560
						209	25,360
(III)	3,4-Di-(3-thienylsulphonyl)thiophen	206	38.4	2.0	43.4	245	19,120
						206	9590
						231	8846
(IV)	2,5-Di-(3-thienylsulphonyl)thiophen	164	38.5	2.0	43.2	277	13,810

* Calc. for C₁₂H₈O₄S₅: C, 38.3; H, 2.1; S, 42.5%. † Lit.,² m. p. 162–164°.

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⁶ W. H. Houff and R. D. Scheutz, *J. Amer. Chem. Soc.*, 1953, **75**, 6316.

⁷ S. Gronowitz and R. Håkansson, *Arkiv Kemi*, 1960, **16**, 309.

⁸ S. Gronowitz, *Acta Chem. Scand.*, 1959, **13**, 1045.

⁹ A. King, "Inorganic Preparations," Allen and Unwin, London, revised edn., 1950, p. 40.