

REACTIONS OF SULFUR WITH ORGANIC COMPOUNDS.

XXI*. THE ACTION OF SULFUR ON 2-THIENYLCHLOROMETHANE

AND DI-2-THENYL SULFIDE

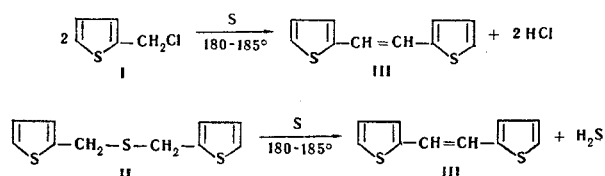
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On heating 2-thienylchloromethane or di-2-thienylsulfide with elementary sulfur in o-dichlorobenzene at 180-185°, there was obtained 1, 2-di-2-thienylethylene in yields of 10 and 19%, respectively. In contrast to stilbene, the latter on reaction with sulfur did not give tetra-2-thienylthiophene, or other low-molecular weight products. The mass, PMR, and IR spectra of 1, 2-di-2-thienylethylene were examined.

One of us has shown previously [2, 3] that phenylchloromethane, phenylbromomethane, and some *eso*-derivatives of the latter, on heating with sulfur, are converted into stilbene or its derivatives. Pyrolysis of dibenzyl sulfide, dibenzyl disulfide, and their *eso*-derivatives with sulfur also gave stilbene [4] (the reaction also proceeds in the absence of sulfur, but much less smoothly). The unsubstituted stilbene formed in these reactions is capable of reacting with an excess of sulfur, being converted into tetraphenylthiophene, and also (in the presence of HBr) into 2-phenylthianaphthene [5].

We have shown that 2-thienylchloromethane (I) and di-2-thienyl sulfide (II) behave similarly to their aromatic analogs, since on heating with sulfur in o-dichlorobenzene at 180-185° they give 1, 2-di-2-thienylethylene (III) in yields of 10 and 19%, respectively.



As distinct from stilbene, however, III is not further converted into tetra-2-thienylthiophene, and only undergoes resinification with liberation of hydrogen sulfide.

The formation of III had been observed previously on distillation of 1, 1-di-2-thienylchloroethane (no yield state) [6], on heating trithio-2-thiophenealdehyde with copper (yield low, but not given exactly) [7], and by boiling 2-acetothiopheneone and 2-mercaptoacetic acid with PbO in acetic anhydride (yield 27%) [8]. The mps of III given in these references (125° [6], 132.5° [7], and 130.5° [8]) are significantly lower than our value (137-139°).

The difference in the reactivity of III and stilbene towards sulfur is reflected in their mass spectra. A strong peak $(M - H)^+$ (90% of molecular) and $(M - 2H)^+$ (60% of molecular) is observed for stilbene. The latter is apparently due to the formation of phenanthrene. In the spectrum of III, the $(M - H)^+$ peak amounts

* For Part XX, see [1].

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TABLE 1. Main Peak Heights in the Mass Spectrum of 1, 2-Di-2-thienylethylene

m/e	Height, % of molecular peak	Suggested composition of main component
193	25	(M+H) ⁺
192	100	(M) ⁺
191	60	(M-H) ⁺
190	25	(M-2H) ⁺
147	45	(M-CH) ⁺
69	30	(C ₂ HS) ⁺
58	23	(C ₂ H ₂ S) ⁺
45	35	(CHS) ⁺

to 60% of molecular, and the (M - 2H)⁺ peak to only 25%. The drop in intensity of the (M - H)⁺ peak on passing from stilbene to III indicates the greater stability of the C-H bond in the vinylene group of III.

In the mass spectrum of III, the molecular ion peak at m/e 192 is the most intense, in support of the assumed structure. The PMR spectrum of III in CCl₄ contains only one signal, at $\tau = 3.80$ ppm, which permits no conclusions as to the structural properties of the molecule. The IR spectrum of III shows a doublet at 820 and 848 cm⁻¹ (breathing vibration of the monoalkylthiophene ring), and a band at 1225 cm⁻¹ (stretching vibration of the five-membered sulfur heterocycle) [9, 10].

EXPERIMENTAL

Preparation of 1, 2-Di-2-thienylethylene (III) from 2-Thienylchloromethane (I). To a boiling solution of 8.3 g (0.26 g-atom) of sulfur in 70 ml of o-dichlorobenzene was added dropwise 23.0 g (0.162 mole) of I, whereupon the mixture was boiled for a further 28 h. The solvent was distilled off, and the oily residue was extracted with 90% alcohol. After removal of the alcohol, the residue was purified from free sulfur by washing with a hot concentrated solution of Na₂S, then it was recrystallized from alcohol to give 9.8% of the theoretical amount of III (1.5 g) as yellow crystals, mp 137-139°. Found: C 62.80; H 4.70; S 32.8%. C₁₀H₈S₂. Calculated: C 62.45; H 4.21; S 33.34%.

Di-2-thienyl Sulfide (II). A solution of 30.3 g of I in 30 ml of toluene was added dropwise with heating at 70-80° and vigorous stirring to a solution of 30 g of Na₂S · 9H₂O and 0.5 g of emulsifier OP-7 in 45 ml of water. Stirring was continued at this temperature for a further 3 h. The organic layer was separated, washed with a saturated solution of NaCl, dried, and the toluene removed in vacuo. The residue was distilled in vacuo to give 11.2 g (43.3%) of II, bp 160-162° (5 mm), as a colorless oil. Found: C 53.51; H 4.89; S 41.89%. C₁₀H₁₀S₂. Calculated: C 53.06; H 4.45; S 42.49%.

Compound II was obtained previously from 2-thienyl mercaptan, bp 129-131° (1.5 mm) [11].

Synthesis of Di-2-thienylethylene (III) from Di-2-thienyl Sulfide. To a solution of 5.6 g (0.025 mole) of II in 20 ml of o-dichlorobenzene was added 2.4 g (0.025 g-atom) of sulfur, and the mixture was heated at the boil for 12 h. After removal of the solvent, the residue was extracted with n-hexane. The residue after removal of the hexane was treated with a hot, concentrated solution of Na₂S, and recrystallized from alcohol to give 0.9 g (18.9%) of III, mp 137-139°. The identity of III with a sample of material obtained by a known method was demonstrated by mixed mp and thin layer chromatography.

Mass spectra were obtained on an MX-1303 mass spectrometer with an ionizing energy of 70 ev. The mass spectrum was obtained on an NMR-5535 TsLA spectrometer with a working frequency of 40MHz. Compound III was examined as an 0.5 M solution in CCl₄, using cyclohexane as internal standard. The IR spectrum was obtained on an IKS-14 spectrometer, in Vaseline oil and hexachlorobutadiene. It exhibited the following frequencies (cm⁻¹): 688 (5), 820 (3), 848 (4), 944 (4), 1042 (2), 1077 (2), 1191 (3), 1224 (2), 1290 (3), 1411 (2), 1442 (3), 2842 (3), 2915 (3), 3020 (3), 3064 (3), 3075 (3), 3092 (3).

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