

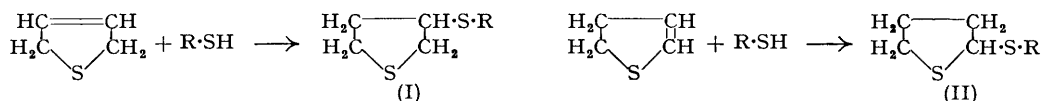
46. *Non-catalytic Reduction of Thiophens. Part III.* The Reaction of the Isomeric Dihydrothiophens with Thiols.*

By S. F. BIRCH and D. T. McALLAN.

The dihydrothiophens react with thiols at 200°, in the presence of elemental sulphur as catalyst, to yield two isomeric series of alkyl (and aryl) tetrahydrothienyl sulphides. These new compounds have been characterised as solid disulphones.

SINCE olefins react with thiols to form sulphides, the corresponding reaction of dihydrothiophens was investigated with a view to preparing a new type of disulphide containing two non-adjacent sulphur atoms in the molecule.

A great variety of catalysts has been described for the preparation of organic sulphides from olefins and thiols. We adopted Jones and Reid's method (*J. Amer. Chem. Soc.*, 1938, **60**, 2452) in which the reactants were heated in a steel reactor at about 200° for several hours with a trace of elemental sulphur as catalyst. The crude product was an orange-red viscous oil which distilled at reduced pressure to yield a variable amount of unchanged material, a main fraction of high-boiling yellow oil, and a dark polymeric residue.



2:5-Dihydrothiophen reacted with ethanethiol, propane-1-thiol, 2-methylpropane-2-thiol, thiophenol, toluene- ω -thiol, cyclohexanethiol, and thioglycolic (mercaptoacetic) acid. The resultant disulphides (I) were characterised by oxidation to the solid disulphones.

2:3-Dihydrothiophen reacted similarly with ethanethiol, propane-1-thiol, and toluene- ω -thiol to yield disulphides (II) from which solid disulphones were prepared. The reaction with toluene- ω -thiol was incomplete and the disulphone was isolated as a brown syrup. The reaction with thioglycolic acid produced much hydrogen sulphide and a low yield of crude product which decomposed on distillation.

The addition of thiols to 2:5-dihydrothiophen is unambiguous and yields only 3-derivatives, but with 2:3-dihydrothiophen substitution might occur in the 2- or the 3-position. Since each dihydrothiophen gives different products, it follows that 2:3-dihydrothiophen yields only 2-derivatives when treated with thiols in the presence of elemental sulphur. This parallels the work of Kipnis and Ornfelt (*J. Amer. Chem. Soc.*, 1951, **73**, 822) who prepared 2-substituted tetrahydropyranyl sulphides from dihydropyran and thiols in the presence of catalytic quantities of hydrogen chloride.

EXPERIMENTAL

Analyses by Drs. Weiler and Strauss, Oxford.

General Method of Preparation.—The dihydrothiophen (0.25 mol.), slightly less than the theoretical quantity of thiol (0.2 mol.), and elemental sulphur (1 g.) were heated in a steel vessel at 200° (oil-bath) for 8 hours and the resultant red, viscous oil filtered and distilled at reduced pressure. Any unchanged material distilled over first, followed by the main product as a yellow viscous oil; the residue was probably polymeric. When necessary, the sulphide was washed with hot 30% potassium hydroxide solution to remove traces of thiol.

The disulphide (0.05 mol.) was dissolved in acetic acid (60 ml.), and hydrogen peroxide (30 ml.; 100-vol.; 50% excess) added with cooling. The solution was gently heated on the water-bath and, when the initial exothermic reaction had subsided, heating was continued for 3 hours. The solvent was finally removed under reduced pressure and the residual disulphone crystallised to constant m. p.

* Part II, *J.*, 1951, 3411.

The products are listed in Tables I and 2.

TABLE 1. Alkyl (or aryl) tetrahydrothienyl sulphides.

B. p./mm.	n_D^{20}	Yield, %	Formula	Found, % :			Required, % :			
				C	H	S	C	H	S	
<i>Tetrahydro-2-thienyl series.</i>										
Et	76—81°/3	1.5500	66	$C_6H_{12}S_2$	49.2	8.1	42.5	48.6	8.2	43.2
Pr ⁿ	85—90/2	1.5410	67	$C_7H_{14}S_2$	52.0	8.8	39.2	51.8	8.7	39.5
Ph	140—145/2.5	1.6250	72	$C_{10}H_{12}S_2$	61.1	6.0	32.9	61.2	6.2	32.7
CH ₂ Ph	160—165/3	1.605	25	$C_{11}H_{14}S_2$	61.6	6.6	30.6	62.8	6.7	30.5
<i>Tetrahydro-3-thienyl series.</i>										
Et	83/3	1.5485	66	$C_6H_{12}S_2$	49.2	8.4	42.6	48.6	8.2	43.2
Pr ⁿ	95/3.5	1.5350	60	$C_7H_{14}S_2$	51.7	8.8	39.8	51.8	8.7	39.5
Bu ^t	90/2	1.5350	34	$C_8H_{16}S_2$	53.3	9.4	36.8	54.5	9.1	36.4
Ph	130—135/1	—	62.5	$C_{10}H_{12}S_2$	61.0	6.4	32.6	61.2	6.2	32.6
CH ₂ Ph	162/2.5	1.61	56	$C_{11}H_{14}S_2$	62.2	6.7	31.3	62.8	6.7	30.5
cycloHexyl ...	144—148/3	1.5580	60	$C_{10}H_{14}S_2$	58.5	8.8	32.0	59.35	9.0	32.0

TABLE 2. Alkyl (or aryl) sulphonyltetrahydrothiophen 1 : 1-dioxides.

M. p.	Crystal form	Solvent *	Formula	Found, % :			Required, % :			
				C	H	S	C	H	S	
<i>2-Sulphonylthiophen series.</i>										
Et	110° ^a	Plates	EtOH	$C_6H_{12}O_4S_2$	33.8	5.6	30.4	33.95	5.7	30.2
Pr ⁿ	78.5—79.5 ^b	—	C_6H_6 -Pet.	$C_7H_{14}O_4S_2$	36.9	6.2	28.5	37.1	6.2	28.4
Ph	164—165	Needles	EtOH	$C_{10}H_{12}O_4S_2$	46.4	4.7	24.7	46.2	4.7	24.6
CH ₂ Ph ...	Syrup	—	—	—	—	—	—	—	—	—
<i>3-Sulphonylthiophen series.</i>										
Et	115° ^a	Needles	EtOH	$C_6H_{12}O_4S_2$	34.0	5.8	30.4	33.95	5.7	30.2
Pr ⁿ	88—88.5 ^b	—	C_6H_6	$C_7H_{14}O_4S_2$	37.1	6.6	28.5	37.1	6.2	28.4
Bu ^t	172.5—173	Plates	EtOH	$C_8H_{16}O_4S_2$	39.8	6.7	26.8	40.0	6.7	26.7
Ph	161—162	Needles	EtOH	$C_{10}H_{12}O_4S_2$	46.0	4.7	24.8	46.15	4.65	24.6
CH ₂ Ph ...	183—184	Needles	COMe ₂ - EtOH	$C_{11}H_{14}O_4S_2$	48.0	5.0	23.3	48.0	5.1	23.3
cycloHexyl	106—107	—	EtOH	$C_{10}H_{18}O_4S_2$	45.0	6.7	24.1	45.1	6.8	24.1

* Pet. = light petroleum.

^a Mixed m. p. 85—88°.

^b Mixed m. p. 55—58°.

Reactions with Thioglycollic Acid.—(a) 2 : 5-Dihydrothiophen gave a disulphone as a benzene-insoluble oil which slowly solidified after several days and crystallised from acetone at low temperature as a brownish solid which decomposed slowly above 150° and liquefied at 210° (Found : C, 28.5; H, 4.8; S, 26.8. $C_6H_{10}O_6S_2$ requires C, 29.8; H, 4.2; S, 26.5%).

(b) The reaction of thioglycollic acid and 2 : 3-dihydrothiophen evolved much hydrogen sulphide and distillation of the dark viscous oil gave only a small amount of product up to 150°/3 mm., at which temperature decomposition set in leaving a black tarry residue.

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