

750. *Non-catalytic Reduction of Thiophens. Part II.**
2-Methylthiophen, 3-Methylthiophen, and 2 : 5-Dimethylthiophen.

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

2-Methylthiophen and 3-methylthiophen, on reduction in liquid ammonia solution by sodium in the presence of methanol, each yield two isomeric dihydromethylthiophens. Pentenethiols are formed as secondary products and the isolation of hydrogen sulphide as an end-product indicates that still further reduction occurs. The structure of the hitherto unknown dihydro-methylthiophens has been established by oxidation to known sulphones and by preparation of other derivatives. No dihydrodimethylthiophens were obtained when 2 : 5-dimethylthiophen was reduced under similar conditions, the main product consisting of a mixture of hexenethiols. Ketones have been identified as products of the sodium-methanol reduction of 2-methylthiophen and 2 : 5-dimethylthiophen, and a possible mechanism for their formation is given.

THE non-catalytic reduction of thiophen in liquid ammonia solution by sodium metal in the presence of methanol has already been discussed (Birch and McAllan, *J.*, 1951, 2556 *). Under these conditions, thiophen yielded the two isomeric dihydrothiophens as primary products. Concomitant reactions gave *n*-butenethiols as secondary, and *n*-butenes and hydrogen sulphide as end-products. The present paper describes the application of this non-catalytic method to the reduction of the two methylthiophens and 2 : 5-dimethylthiophen. Throughout this work, conditions were employed favouring the production of optimum yields of the dihydro-compounds and no experimental work was carried out on reaction variables.

The reduction of 3-methylthiophen, with sodium equivalent to 1 mol. of hydrogen, closely paralleled the reduction of thiophen (Part I). The main products were a mixture of dihydro-3-

* Part I, *J.*, 1951, 2556.

methylthiophens (44.7%) and pentenethiol (10%). The total recovery (82.5%) indicated that further reduction had occurred and, on acidification of the extracted alkaline solution much hydrogen sulphide was evolved. Comparison with the reduction of thiophen suggests that substitution in the 3-position favours increased yields of the dihydro-intermediates.

Fractionation of the crude dihydro-3-methylthiophens at atmospheric pressure in an atmosphere of nitrogen yielded 4 : 5-dihydro- and 2 : 5-dihydro-3-methylthiophen. No evidence was obtained of the presence of the third theoretically possible isomer, 2 : 3-dihydro-3-methylthiophen. The 4 : 5-dihydro-compound was much more stable than 2 : 3-dihydro-isomer since it could be distilled at atmospheric pressure in a metal-packed column without undue polymerisation. It did, however, deposit a small amount of solid polymer after several weeks' storage; the 2 : 5-isomer showed slight opalescence after a similar time.

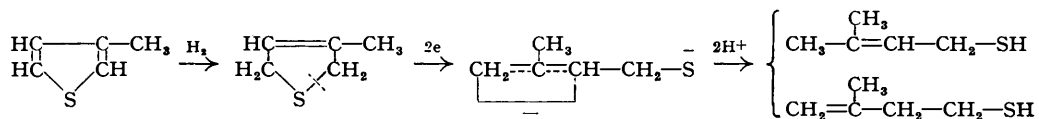
Although the sulphones corresponding to both these dihydro-3-methylthiophens are known (α - and β -isoprene sulphones), only one reference to the preparation of a dihydro-3-methylthiophen itself could be found. Karrer and Kieso (*Helv. Chim. Acta*, 1944, **27**, 1285) claimed to have obtained such a product by dehydrobromination of 3-bromo-3-methylthiophan with refluxing sodium methoxide solution. Their supposed dihydro-3-methylthiophen boiled at 108—110°, but, as the two isomers now described both boil appreciably higher, there can be little doubt that their compound was not that claimed.

The identification of the two isomeric dihydro-3-methylthiophens followed from their conversion into known sulphones. The sulphone from 2 : 5-dihydro-3-methylthiophen has been prepared by *inter al.* Eigenberger (*J. pr. Chem.*, 1930, **127**, 307; 1931, **129**, 312) and Zuydewijn (*Rec. Trav. chim.*, 1937, **56**, 1047; 1938, **57**, 445), by the 1 : 4-addition of sulphur dioxide to isoprene. Zuydewijn (*loc. cit.*) characterised this sulphone by converting it into the dibromide by addition of bromine in carbon tetrachloride solution. The sulphone derived from 2 : 5-dihydro-3-methylthiophen by the action of hydrogen peroxide in glacial acetic acid solution had a melting point corresponding to Zuydewijn's compound, as did also the dibromide derived from it.

The sulphone from 4 : 5-dihydro-3-methylthiophen was obtained by Zuydewijn from the 2 : 5-derivative by isomerisation in aqueous alkaline solution under the influence of ultra-violet light. The sulphone from 3-methylthiophen agreed in melting point with that of Zuydewijn and likewise gave a liquid dibromide. The constitution of this sulphone as the 4 : 5-dihydro-isomer and not the 2 : 3-dihydro-isomer was proved by Zuydewijn (*loc. cit.*) through oxidation to 3-ketobutane-1-sulphonic acid. Confirmatory evidence was obtained by Backer, Strating, and Zuithoff (*Rev. Trav. chim.*, 1936, **55**, 761) who synthesised this acid and compared it with an α -isoprene sulphone-derived sample. They also made a study of the crystallographic data of the barium salts of both samples of acids and found them to be identical.

Both methiodides and mercuric chloride complexes were prepared from each of the dihydro-3-methylthiophens, those prepared from 4 : 5-dihydro-3-methylthiophen being relatively unstable. Bromine added readily to both isomers in *isopentane* solution and 2 : 5-dihydro-3-methylthiophen gave a solid tetrabromide, with two ionisable bromine atoms, which decomposed to a red oil in 3 days; this is undoubtedly 1 : 1 : 3 : 4-tetrabromo-3-methylthiophan. 4 : 5-Dihydro-3-methylthiophen also added four bromine atoms but yielded only a dark red oil which immediately decomposed with evolution of hydrogen bromide. The behaviour of the dihydro-3-methylthiophens thus parallels that of the corresponding dihydrothiophens (cf. Part I).

The unsaturated pentenethiol obtained from 3-methylthiophen distilled, without polymerisation, as a colourless evil-smelling oil and appeared to be much more stable than the butenethiols. It formed a solid 2 : 4-dinitrophenylpentenyl sulphide and appeared to be substantially free from isomers. A study of the infra-red absorption spectrogram suggested that this thiol, derived from 3-methylthiophen, was formed by the reduction of 2 : 5-dihydro-3-methylthiophen and consisted mainly of 3-methylbut-2-enethiol, together with smaller amounts of 3-methylbut-3-enethiol, formed by isomerisation of the Δ^2 -thiol *via* a mesomeric anion.



The reduction of 2-methylthiophen yielded only a small amount of dihydro-2-methylthiophens (7.5%) and a high yield of pentenethiol (38%). The considerable evolution of hydrogen sulphide on acidification of the aqueous alkaline solution indicated that the reduction had proceeded

largely to completion and this would account for the relatively low total recovery (66%). Fractionation of the neutral product yielded an inseparable mixture of 2 : 5-dihydro-2-methylthiophen and most probably 4 : 5-dihydro-2-methylthiophen. On comparing the ratio of reduction products obtained from 2-methylthiophen with those from thiophen and 3-methylthiophen, it is apparent that substitution in the 2-position inhibits the production of dihydro-compounds and favours more complete reduction. Under the conditions employed, the dihydro-2-methylthiophens appear to be preferentially reduced on formation, resulting in a high yield of pentenethiol and end-products.

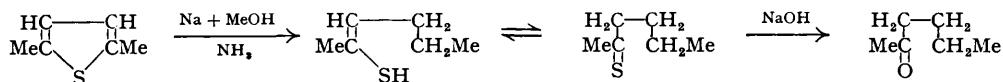
The identification of the individual components of the dihydro-2-methylthiophen fraction was accomplished by oxidation, with excess of hydrogen peroxide, to the sulphone. At 120° the purified sulphone partially decomposed to sulphur dioxide and a highly-unsaturated hydrocarbon, which boiled at about 40°. The residue solidified and, when crystallised to constant melting point, gave analytical data agreeing with a dihydromethylthiophen dioxide. Now Craig (*J. Amer. Chem. Soc.*, 1943, **65**, 1006) obtained 2 : 5-dihydro-2-methylthiophen 1 : 1-dioxide by the reaction of piperylene with sulphur dioxide. The resultant sweet, water-soluble oil, on heating at 100°, decomposed to sulphur dioxide and *trans*-piperylene (b. p. 41.7°). Therefore the dihydro-2-methylthiophen fraction must have contained a proportion of the 2 : 5-dihydro-compound, together with another isomer which could be either 4 : 5-dihydro-2-methylthiophen or 2 : 3-dihydro-2-methylthiophen. By analogy with the behaviour of 3-methylthiophen on reduction, it is concluded that the second isomer was 4 : 5-dihydro-2-methylthiophen. An examination of the infra-red absorption spectrogram of the original fraction yielded some additional evidence in support of this conclusion.

Bromine added readily to the mixed isomers in *isopentane* solution, in a quantity equivalent to four atoms of bromine per molecule. Much hydrogen bromide was evolved and the product consisted of an unstable red oil, whose carbon tetrachloride solution deposited some yellow crystals. Analysis confirmed the presence of four bromine atoms per molecule, two of them ionisable. In view of the stability of the bromine addition compounds derived from 2 : 5-dihydrothiophen and 2 : 5-dihydro-3-methylthiophen, this solid tetrabromide must be 1 : 1 : 3 : 4-tetrabromo-2-methylthiophan, derived from 2 : 5-dihydro-2-methylthiophen, and the remainder of the unstable red oil the unstable dibromide derived from 4 : 5-dihydro-2-methylthiophen.

The thiol from 2-methylthiophen was a malodorous red oil analysis of which showed it to be a pentenethiol. The 2 : 4-dinitrophenylpentenyl sulphide was an oil which could not be induced to crystallise, indicating that the sample was a mixture of isomers. The thiol polymerised rapidly and distilled over a wide range leaving a viscous residue of high refractive index. No further work was carried out on the identification of the components of this pentenethiol mixture.

In view of the abnormal behaviour of 2-methylthiophen, the reduction of 2 : 5-dimethylthiophen was investigated. It proceeded smoothly, and the product consisted of neutral oil (37.2%) and unsaturated thiol (48%). Fractionation of the neutral product revealed no trace of any dihydro-derivatives, and the distillate was shown to be an azeotrope of unreacted 2 : 5-dimethylthiophen with a small amount of hexan-2-one which was isolated as the semicarbazone. Analysis of the thiol product indicated a hexene compound and, though hydrogen sulphide was identified as an end-product, no corresponding hexenes were isolated. On further reduction of this thiol with excess of sodium, most of it was recovered unchanged and again, though some hydrogen sulphide was evolved, no hexenes were found. However, a neutral fraction (12%) was isolated as a colourless sweet-smelling oil from which a clear distillate and a high-boiling dark residue were obtained. From the former a quantity of hexan-2-one was isolated as the semicarbazone. The presence of this ketone in the reduction products of 2 : 5-dimethylthiophen can be satisfactorily explained as follows :

The crude hexenethiol probably contains some hex-2-ene-2-thiol which is capable of isomerisation to hexane-2-thione from which the ketone can be formed by the action of alkali (*cf.* Bost and Cosby, *J. Amer. Chem. Soc.*, 1935, **57**, 1404) :



These results suggest that small amounts of analogous ketones should have been formed from the other thiophens already reduced. If so, butaldehyde, valeraldehyde and pentan-2-one should be formed from thiophen, 3-methylthiophen, and 2-methylthiophen, respectively.

Whilst these compounds have not yet been detected in any of the recovered thiophens, pentan-2-one has successfully been isolated, as the semicarbazone, from the alkali-insoluble oil obtained by further non-catalytic reduction of the pentenethiol from 2-methylthiophen.

Compound	B. p.	M. p.	Calc. m. p. for zero impurity	n_D^{20}	d_4^{20}	Estimated purity, mol. %
2-Methylthiophen	112.56°	-63.34°	- 63.37°	1.5201	1.0194	99.95
3-Methylthiophen	115.44	-68.96	- 68.94	1.5202	1.0221	99.95
2 : 5-Dimethylthiophen	137.5	—	—	1.5123	0.9840	—
Dihydro-2-methylthiophens (mixed)	127—128	glass at -120	—	1.5069	1.0140	—
4 : 5-Dihydro-3-methylthiophen	139.4	- 54.7	—	1.5232	1.0055	—
2 : 5-Dihydro-3-methylthiophen	147.5	- 32.12	- 31.2	1.5196	1.0160	98.5
2-Methylthiophan	133.23	-100.79	-100.71	1.4909	0.9552	99.75
3-Methylthiophan	138.67	- 81.26	- 81.16	1.4924	0.9634	99.7
<i>trans</i> -2 : 5-Dimethylthiophan	142.0 *	- 76.70	- 76.35	1.4776	0.9177	99.3
<i>cis</i> -2 : 5-Dimethylthiophan	142.28	- 89.60	- 89.4	1.4799	0.9222	99.3

* This is an extrapolated figure owing to the thermal instability of the compound at atmospheric pressure.

The physical properties of the various dihydromethylthiophens, together with those of the corresponding thiophens and thiophans, determined during this research, are given in the table.

EXPERIMENTAL

Analyses are by Weiler and Strauss, Oxford. All m. p.s and b. p.s are corrected.

Preparation of Dihydro-3-methylthiophens.—3-Methylthiophen (392 g., 4 mols.) and methanol (1500 ml.), in liquid ammonia (ca. 1500 ml.), were treated with sodium (185 g., 8 mols.) exactly as described for the preparation of the dihydrothiophens (Part I, *loc. cit.*). Neutral products were extracted into isopentane as previously described; the evil-smelling thiol fraction distilled almost completely in the range 40—43°/35 mm. (135—138°/760 mm.) and had n_D^{20} 1.4840 (Found: C, 59.7; H, 9.5; S, 30.5. Calc. for $C_5H_{10}S$: C, 58.8; H, 9.9; S, 31.4%). A solid 2 : 4-dinitrophenylpentenyl sulphide was obtained and repeatedly crystallised from ethanol, forming a pale yellow flocculent powder, m. p. 113—115°.

A large quantity of 3-methylthiophen (1250 g.) was reduced in this manner yielding recovered 3-methylthiophen (346 g., 27.7%), crude pentenethiol (130 g.; 10%), and a mixture of dihydro-3-methylthiophens (570 g., 44.7%), b. p. 138—148°/760 mm. This mixture, on fractionation through a 50-plate metal-packed column under an atmosphere of nitrogen, gave 4 : 5-dihydro- (84 g.), b. p. 139.4°/760 mm., n_D^{20} 1.5232 (Found: C, 59.9; H, 8.2; S, 31.5. C_5H_8S requires C, 60.0; H, 8.1; S, 32.0%), and 2 : 5-dihydro-3-methylthiophen (400 g.), b. p. 147.5°/760 mm., n_D^{20} 1.5196 (Found: C, 60.0; H, 8.1; S, 31.7%).

2 : 5-Dihydro-3-methylthiophen yielded a *mercuric chloride* complex (from ethanol), m. p. 127.5—128.0° (Found: C, 16.8; H, 2.3; S, 9.4; Cl, 20.9. $C_5H_8S.HgCl_2$ requires C, 16.2; H, 2.2; S, 8.9; Cl, 20.1%). The *methiodide*, crystallised from ethanol at low temperature, formed needles, m. p. 91—92°, which were unstable on exposure to air and so gave an indifferent analysis (Found: C, 30.3; H, 4.7; S, 10.1; I, 54.7. $C_5H_8S.CH_3I$ requires C, 29.8; H, 4.6; S, 13.2; I, 52.4%).

The 4 : 5-dihydro-isomer yielded a *mercuric chloride* complex (from ethanol) as a yellowish white solid, m. p. 93—94° (decomp.), the analysis of which did not correspond to any simple empirical formula (Found: C, 14.6; H, 2.0; S, 6.2; Cl, 20.9%). The *methiodide* was obtained as an unstable liquid which solidified only at very low temperature, and no analysis was possible.

Identification of 2 : 5-Dihydro-3-methylthiophen.—*Oxidation to 2 : 5-dihydro-3-methylthiophen 1 : 1-dioxide* (β -isoprene sulphone). A 50% excess of hydrogen peroxide (30 ml.; 100-vol.) was added to 2 : 5-dihydro-3-methylthiophen (10 g.) in glacial acetic acid (60 ml.) and, after 24 hours at room temperature, the solution was refluxed for 3 hours to destroy excess of peroxide. Removal of the solvent on the water-bath at reduced pressure left a solid which crystallised from benzene-light petroleum as small needles, m. p. 63—64° (Found: C, 45.2; H, 6.2; S, 24.6. Calc. for $C_5H_8O_2S$: C, 45.4; H, 6.1; S, 24.3%). Zuydewijn (*loc. cit.*) gave the m. p. of β -isoprene sulphone as 63—64°.

3 : 4-Dibromo-3-methylthiophan 1 : 1-dioxide. The sulphone (2 g.) was refluxed in carbon tetrachloride (50 ml.) for 1 hour with the requisite amount of bromine. White plates separated; after three crystallisations from carbon tetrachloride these had m. p. 125—126° (Found: C, 20.4; H, 2.7; S, 11.2; Br, 53.8. Calc. for $C_5H_8O_2S.Br_2$: C, 20.6; H, 2.8; S, 11.0; Br, 54.7%). Zuydewijn (*loc. cit.*) recorded m. p. 125—127° for the dibromide of β -isoprene sulphone.

1 : 1 : 3 : 4-Tetrabromo-3-methylthiophan. A solution of 2 : 5-dihydro-3-methylthiophen in isopentane added 4 atoms of bromine per molecule to give a yellow *tetrabromo*-compound which crystallised from carbon tetrachloride as orange crystals, m. p. 98.5—99.0° (decomp.) (Found: total Br, 76.0; H, 4.0. $C_5H_8S.Br_4$ requires total Br, 76.1; Br', 38.1%). This solid decomposed to a red oil during 3 days.

Identification of 4 : 5-Dihydro-3-methylthiophen.—*Oxidation to 4 : 5-dihydro-3-methylthiophen 1 : 1-dioxide* (α -isoprene sulphone). A solution of the isomer (10 g.) in glacial acetic acid (60 ml.) was oxidised by hydrogen peroxide (30 ml.; 100-vol.) as previously described. After removal of the solvent, the

residue was dissolved in hot benzene from which white needles were precipitated on the addition of light petroleum. Recrystallisation from benzene-light petroleum yielded the sulphone as long white needles, m. p. 77—78° (Found: C, 45.6; H, 6.2; S, 24.4%). For α -isoprene sulphone Zuydewijn (*loc. cit.*) gave m. p. 76—77°, and Eigenberger (*loc. cit.*) gave m. p. 77.5—78.0°.

Attempts to prepare 2:3-dibromo-3-methylthiophen 1:1-dioxide and 1:1:2:3-tetrabromo-3-methylthiophen, by the methods used for the preparation of their isomers from 2:5-dihydro-3-methylthiophen, were unsuccessful.

Preparation of Dihydro-2-methylthiophens.—2-Methylthiophen (392 g.; 4 mols.) was reduced with sodium (185 g.; 8 mols.) and methanol (1500 ml.) in liquid ammonia (*ca.* 1500 ml.) at -40° . Two runs on this scale yielded neutral product (225 g.; 28.7%) and unsaturated thiol (309 g., 37.8%). There was considerable evolution of hydrogen sulphide on acidification of the aqueous solution to recover the thiol, and the low recovery of product was partly due to this further reduction. The thiol was a malodorous oil, which quickly developed a bright red colour (Found: C, 58.9; H, 9.5; S, 30.4. Calc. for $C_5H_{10}S$: C, 58.8; H, 9.9; S, 31.4%). The product of reaction with 1-chloro-2:4-dinitrobenzene was an oil which would not crystallise. Only 27% of the thiol boiled in the range 35—56°/25 mm., n_D^{20} 1.4610; the residue was a viscous red oil, n_D^{20} 1.5454.

The neutral product was fractionated in a 20-plate glass-packed column and yielded recovered 2-methylthiophen (150 g., 19%) and a mixture of dihydro-2-methylthiophens (60 g., 7.5%), the main fraction (40 g., 5%) of which had b. p. 127—128°, n_D^{20} 1.5069 (Found: C, 59.8; H, 8.1; S, 31.8%), and set to a glass at -120° ; all attempts to prepare a solid methiodide and a solid mercuric chloride complex failed.

Identification of the Dihydro-2-methylthiophens.—*Oxidation to the sulphone.* A portion of the dihydro-2-methylthiophen fraction (10 g.) was oxidised with hydrogen peroxide in acetic acid as described previously. When the solution was refluxed to destroy excess of peroxide, some sulphur dioxide was evolved and a small amount of unsaturated low-boiling hydrocarbon was isolated during the removal of the solvent. The residue was a dark oily mass which smelt faintly of sulphur dioxide. The oxidation was accordingly modified: the solution was set aside for 72 hours before removal of the solvent at low pressure at a maximum of 50°. The residual pale oil was precipitated from benzene solution by light petroleum. The oil was heated at 120° for a few minutes under reduced pressure and, from a liquid-air trap attached to the apparatus, sulphur dioxide and a highly-unsaturated hydrocarbon, b. p. *ca.* 40°, were obtained. The dark residue crystallised from ethanol as needles, m. p. 128—129° after three crystallisations (Found: C, 45.7; H, 6.1; S, 24.2. $C_5H_8O_2S$ requires C, 45.4; H, 6.1; S, 24.3%). Now Craig (*loc. cit.*) obtained 2:5-dihydro-2-methylthiophen 1:1-dioxide (piperylene sulphone) as an oil which decomposed at 100° into sulphur dioxide and *trans*-piperylene, b. p. 41.7°, and so the dihydro-2-methylthiophen mixture undoubtedly contains some 2:5-dihydro-2-methylthiophen, together with another isomer which yields a sulphone, m. p. 128—129°. This isomer may be the 2:3-dihydro- or the 4:5-dihydro-compound, but, in view of the double-bond positions in the dihydro-3-methylthiophens, it is assumed that the second isomer is 4:5-dihydro-2-methylthiophen.

Addition Compound with Bromine.—The addition of bromine to an isopentane solution of the dihydro-2-methylthiophen mixture proceeded rapidly, with evolution of hydrogen bromide, till 4 bromine atoms per molecule had been absorbed. A red oil separated, and was dissolved in hot carbon tetrachloride from which a small amount of yellow solid, m. p. 90° (decomp.), crystallised. By analogy with the tetrabromides from 2:5-dihydrothiophen and 2:5-dihydro-3-methylthiophen this is probably 1:1:3:4-tetrabromo-2-methylthiophan. Analysis indicated the presence of 4 bromine atoms per molecule, 2 of which were ionisable (Found: total Br, 75.9; Br', 38.7. $C_5H_8SBr_4$ requires total Br, 76.1; Br', 38.1%). The original crude red oil was probably a mixture with the unstable tetrabromide derived from 2-methyl-4:5-dihydrothiophen.

2:3-Dibromo-2-methylthiophan 1:1-Dioxide.—4:5-Dihydro-2-methylthiophen 1:1-dioxide (0.5 g.) was dissolved in an aqueous solution of the requisite amount of bromine, and set aside at 0° for 4 days. Long needles of 2:3-dibromo-2-methylthiophan 1:1-dioxide, m. p. 68—69°, separated (Found: C, 20.9; H, 2.4; S, 10.9; Br, 54.2. $C_5H_8O_2SBr_2$ requires C, 20.6; H, 2.8; S, 11.0; Br, 54.7%).

Reduction of 2:5-Dimethylthiophen.—2:5-Dimethylthiophen, prepared in 51% yield by Buu-Hoi and Nguyen-Hoán's method (*Rec. Trav. chim.*, 1948, 67, 309), had b. p. 137.5°, n_D^{20} 1.5123. The dimethylthiophen (336 g.; 3 mols.) was reduced with sodium (140 g., 6 mols.) and methanol (1000 ml.) in liquid ammonia (1500 ml.) at -40° , as previously described. The reaction proceeded smoothly. The combined product from two such preparations yielded neutral material (250 g., 37.2%) and crude hexene-thiol (335 g.; 48%), n_D^{20} 1.5335 (Found: C, 62.9; H, 8.9; S, 27.5. Calc. for $C_6H_{12}S$: C, 62.0; H, 10.4; S, 27.6%). Distillation at reduced pressure under nitrogen gave only 24% boiling in the range 56—60°/16 mm., (n_D^{20} 1.5030), and a further 9% at 60—100°/16 mm., (n_D^{20} 1.5200), leaving a high-boiling viscous residue (n_D^{20} 1.5570). These fractions had a typical unsaturated-thiol odour somewhat tempered by a relatively sweet background-odour; they showed a colour variation from purple to orange, and the residue was bright red.

The neutral material was fractionated at reduced pressure under nitrogen in a 20-plate glass-packed column, yielding a main fraction, b. p. 79°/130 mm., n_D^{20} 1.5050, but no material was isolated at or above the b. p. and refractive index of the original 2:5-dimethylthiophen. A freezing-point determination indicated the presence of a substantial amount of impurity and, as washing the fractions with concentrated alkaline solutions did not alter the physical constants, the distillate was refractionated in a 50-plate metal-packed column at atmospheric pressure. The maximum b. p. and refractive index then reached were 137.0° and n_D^{20} 1.5070, while some of the fore-runings had refractive indices as low as n_D^{20} 1.4620. The neutral product thus appeared to be an azeotrope of unchanged 2:5-dimethylthiophen

with an unknown product of similar b. p. The fore-runnings (12 g.), n_D^{20} 1.4620, were subsequently shaken in light petroleum solution with a saturated aqueous solution of semicarbazide hydrochloride and an equivalent of sodium acetate. Hexan-2-one semicarbazone (7 g.) separated and was repeatedly crystallised from aqueous alcohol; it had m. p. and mixed m. p. 122—123° (Found : C, 53.1; H, 9.4; N, 26.1. Calc. for $C_7H_{15}ON_3$: C, 52.8; H, 9.5; N, 26.4%).

Reduction of the Hexenethiol derived from 2 : 5-Dimethylthiophen.—Crude hexenethiol (116 g., 1 mol.) was reduced with excess of sodium (70 g., 3 mols.) and methanol (500 ml.) in liquid ammonia (750 ml.) at -40° . The products of the slow reaction were obtained as already described; unchanged thiol (77 g., 67.3%), n_D^{20} 1.4960, was recovered and the neutral fraction contained no hexenes. The residue (13 g.) was distilled under nitrogen at reduced pressure, yielding a clear distillate (5 g.), b. p. 55—62°/50 mm., n_D^{20} 1.4290, and a high-boiling residue which decomposed when heated further. The distillate clearly contained oxygenated compounds [Found : C, 71.3; H, 12.1; S, 7.5; O (by difference) 9.1%], and subsequent treatment with aqueous semicarbazide hydrochloride and sodium acetate solution gave hexan-2-one semicarbazone, which crystallised from aqueous alcohol and then had m. p. and mixed m. p. 122.5—123.5° (Found : C, 53.3; H, 9.4; N, 25.9. Calc. for $C_7H_{15}ON_3$: C, 52.8; H, 9.5; N, 26.4%).

Reduction of the Pentenethiol derived from 2-Methylthiophen.—Crude pentenethiol (102 g., 1 mol.) was reduced as described above. Unchanged thiol (72.5 g., 70%) was recovered as a red oil, n_D^{20} 1.4900. The neutral product (17.5 g.) contained no pentenes but, on treatment with semicarbazide hydrochloride solution, yielded pentan-2-one semicarbazone which crystallised from aqueous methanol and then had m. p. and mixed m. p. 110—111° (Found : C, 50.6; H, 9.0; N, 29.3. Calc. for $C_6H_{13}ON_3$: C, 50.3; H, 9.2; N, 29.4%). An attempt to distil the residual material yielded only a trace of distillate at about 100° before decomposition started.

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