

**570. Non-catalytic Reduction of Thiophens. Part I. Thiophen.**

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

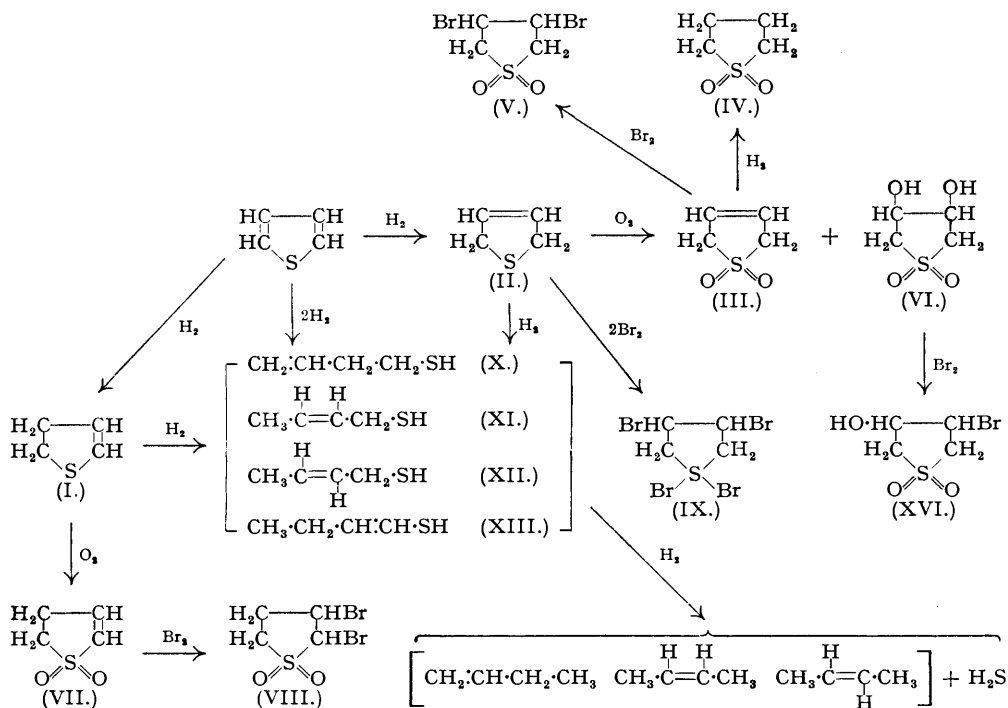
The non-catalytic reduction of thiophen in liquid ammonia by sodium in the presence of methanol yields the isomeric dihydrothiophens as primary products. Concomitant reactions give *n*-butenethiols as secondary and *n*-butenes and hydrogen sulphide as end-products. The structure of the hitherto unknown dihydrothiophens has been established by oxidation to known sulphones; a number of derivatives have been prepared. The presence of three of the four possible *n*-butenethiols in the reaction products was demonstrated by infra-red spectroscopic analysis, genuine specimens of these thiols being synthesised for comparison.

UNTIL recently, attempts to hydrogenate thiophen by the usual hydrogenation procedures using metallic catalysts such as nickel, platinum, and palladium invariably failed, presumably owing to the powerful poisoning effect of this type of sulphur compound. More success, however, attended the use of hydrogenation-dehydrogenation catalysts of the metallic sulphide type. Moldavski and Propopchuk (*J. Appl. Chem. Russia*, 1932, 5, 619), using a molybdenum sulphide catalyst, found that thiophen was converted into thiophan and butanethiol at 350°, and Moldavski and Kumari (*J. Gen. Chem. Russia*, 1934, 4, 298) isolated butane and hydrogen sulphide, as well as the products mentioned above, as was confirmed by Cawley and Hall (*J. Soc. Chem. Ind.*, 1943, 62, 116). More recently, Mozingo *et al.* (*J. Amer. Chem. Soc.*, 1945, 67, 2092) successfully hydrogenated thiophen to thiophan over a palladium catalyst, with a very high catalyst-to-thiophen ratio to overcome the poisoning effect. No intermediate products were reported. Fricke and Spilker (*Ber.*, 1925, 58, 24, 1589) showed that reduction of thionaphthen in boiling ethanol with sodium gave as main product *o*-ethylthiophenol together with an appreciable amount of dihydrothionaphthen. They suggested that the yield of the latter might be greater at a lower temperature but did not confirm this. Since reduction of certain aromatic hydrocarbons in liquid ammonia by means of sodium and methanol has been shown by Wooster and Godfrey (*J. Amer. Chem. Soc.*, 1937, 59, 596) to yield the corresponding cyclohexadienes in excellent yields, it was considered that the reduction of thiophen

in liquid ammonia offered a possible route to the hitherto unknown dihydrothiophens. The method was accordingly investigated.

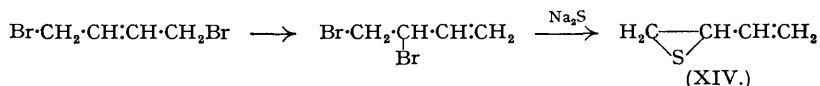
The reduction of thiophen in liquid ammonia solution at  $-40^\circ$  with sodium in the presence of methanol proceeded readily and smoothly. Preliminary experiments showed that the reaction products consisted of unchanged thiophen, a neutral, higher-boiling fraction, some unsaturated thiol, and butenes and hydrogen sulphide (*Nature*, 1950, 165, 899). In these experiments sodium equivalent to two molecules of hydrogen per molecule of thiophen was used, resulting in a relatively high yield of thiols, butenes, and hydrogen sulphide. By halving the proportion of sodium used, an enhanced yield of the higher-boiling neutral fraction was obtained which, when the accumulated product from several runs was fractionated, yielded two distinct compounds identified through their derivatives as 2:3- (I) and 2:5-dihydrothiophen (II). During this fractionation some polymerisation occurred and a relatively large high-boiling residue remained. For this the 2:3-dihydrothiophen was eventually shown to be responsible, readily undergoing polymerisation on prolonged heating at atmospheric pressure. Subsequent distillations were carried out at reduced pressure in an atmosphere of nitrogen, polymerisation then being largely avoided.

No evidence was obtained for the addition of a second hydrogen molecule to the remaining ethylenic linkage to yield thiophan. Instead, hydrogenolysis of the ring took place, yielding a mixture of butenethiols which were further reduced to hydrogen sulphide and a mixture of *n*-butenes. Variation in the proportion of sodium used only altered the relative proportions of the various products, optimum yields (*ca.* 40%) of the dihydrothiophens being obtained by using sodium equivalent to one molecule of hydrogen per molecule of thiophen. In the absence of methanol, the reduction proceeded entirely to the thiol stage and beyond, and no intermediate dihydrothiophens were isolated. Variation in the quantity of sodium used led only to a corresponding variation in the ratio of unchanged thiophen to thiol in the product. The reduction of thiophen, with sodium in methanol solution alone, proceeded along the same general route as when ammonia was present but the rate of reaction was much slower.



Although the sulphones corresponding to both dihydrothiophens are known ("Sulfolenes") only one reference to the preparation of a dihydrothiophen was found. Slobodin (*J. Gen. Chem. Russia*, 1938, 8, 714) claimed to have obtained 2:5-dihydrothiophen, amongst other products (including rubber-like polymers, tars, and butadiene), by the action of an

aqueous-alcoholic solution of sodium sulphide on 1:4-dibromobut-2-ene. The supposed dihydrothiophen was obtained from the tar, by distillation, as an oil, b. p. 103—105°,  $n_D^{20}$  1.4814,  $d_4^{21}$  0.978. The mercuric chloride complex and methiodide are reported as melting at 92—94° and 122—123°, respectively. Since both dihydrothiophens described in the present work boil appreciably higher and possess much higher refractive indices, there can be little doubt that Slobodin's compound was not a dihydrothiophen. When the physical properties of the material are compared with those of other sulphur compounds boiling in the same range, and Winstein and Young's work (*J. Amer. Chem. Soc.*, 1936, **58**, 104) on the isomerisation of alkenyl bromides is borne in mind, it appears likely that his compound was vinylthiairane (XIV) or some such similar compound formed as follows :



The identification of the two isomeric dihydrothiophens followed from their conversion into known sulphones. The sulphone (III) of 2:5-dihydrothiophen has been prepared by Staudinger (B.P. 361,341/1930) and by many other workers, including Zuydewijn (*Rec. Trav. chim.*, 1937, **56**, 1047; 1938, **57**, 445) by 1:4-addition of sulphur dioxide to butadiene. Zuydewijn characterised his product by reduction of thiophan sulphone (IV) and by conversion into the dibromide (V) (cf. Staudinger and Ritzenthaler, *Ber.*, 1935, **68**, 455) by the addition of bromine in carbon tetrachloride solution. Some difficulty was at first experienced in crystallising the sulphone from 2:5-dihydrothiophen but this was eventually traced to the presence of the diol (VI) which resulted from the use of an excess of peroxide. Both sulphone and diol, after purification, had melting points corresponding to Zuydewijn's preparation, as did the dibromide derived from the sulphone. The sulphone (VII) of 2:3-dihydrothiophen was obtained by Zuydewijn (*loc. cit.*) from the 2:5-derivative by isomerisation in aqueous alkali under the influence of ultra-violet light. The thiophen-derived product agreed in melting point with that recorded by Zuydewijn and gave a dibromide (VIII) of slightly higher melting point than his.

Both methiodides and mercuric chloride complexes were prepared from each of the two dihydrothiophens; in general, 2:5-dihydrothiophen yielded stable derivatives of simple structure whereas the few stable derivatives which could be prepared from 2:3-dihydrothiophen had complex structures, owing possibly to some polymerisation occurring during reaction. Bromine added readily to both isomers, and 2:5-dihydrothiophen gave a stable tetrabromide of definite melting point, with two ionisable bromine atoms, undoubtedly 1:1:3:4-tetrabromothiophan (IX). 2:3-Dihydrothiophen in similar circumstances added only two bromine atoms per molecule, yielding a highly unstable, yellow solid which immediately decomposed to a black tar with copious evolution of hydrogen bromide.

Both isomers are colourless liquids of unpleasant odour, but whereas 2:5-dihydrothiophen is quite stable, 2:3-dihydrothiophen slowly polymerises and deposits a hard yellow solid of complex structure on storage. The physical properties of 2:3- and 2:5-dihydrothiophen are given, together with those of thiophen and thiophan for comparison, in Table I. The melting points given in this table, and those used in the experimental work to calculate the purities of certain compounds, were determined by the procedure described by Mair, Glasgow, and Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591). The chemical properties of the two dihydrothiophens, which are very reactive chemically, with pronounced olefinic behaviour, will form the subject of a later paper.

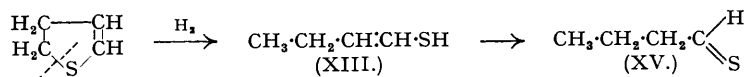
TABLE I.

Compound.	B. p.	M. p.	M. p. for zero impurity. <sup>b</sup>	$n_D^{20}$ .	$d_4^{20}$ .	Estimated purity, mol. %.
Thiophen .....	84.0°	— 38.7° <sup>a</sup>	— 38.2°	1.5286	1.0642	99.5
2:3-Dihydrothiophen ...	112.0	— 110.2	— 108.7	1.5311	1.0361	97.5
2:5-Dihydrothiophen ...	122.3	— 50.3	— 49.3	1.5306	1.0591	98.5
Thiophan .....	121.2	— 96.2° <sup>a</sup>	— 96.1	1.5047	0.9998	99.7

<sup>a</sup> Determined in these laboratories. <sup>b</sup> Extrapolated value (for significance, see Taylor and Rossini, *J. Res. Nat. Bur. Stand.*, 1944, **32**, 197). <sup>c</sup> Calculated on an assumed value of the cryoscopic constant.

The complete identification of the unsaturated thiol formed by further reduction of the dihydrothiophens proved difficult. Apart from the extremely objectionable odour of these thiols, they easily polymerise to high-boiling, dense, yellow oils (cf. von Braun and Plate, *Ber.*,

1934, 67, 281). The most satisfactory approach was by comparison of the infra-red absorption spectrograms of the various samples of unsaturated thiols obtained, with those of synthetic butenethiols.\* Since these compounds polymerise rapidly when heated, all distillations were carried out at low temperature under reduced pressure, and all samples were examined when freshly prepared and distilled. The general properties of the thiophen-derived thiols were in good agreement with those described by von Braun and Plate (*loc. cit.*). Synthetic samples of but-3-enethiol (X) and both *cis*- and *trans*-but-2-enethiol (XI and XII) were prepared by the action of thiourea on the corresponding bromide. The appropriate butenyl 2 : 4-dinitrophenyl sulphides were prepared from the thiols and appear to offer the most reliable chemical means of characterisation. The fourth possible isomer, but-1-enethiol (XIII), has not been



synthesised, but Campaigne's review (*Chem. Reviews*, 1946, 39, 1) suggests that it would immediately isomerise to thiobutaldehyde (XV) which would then polymerise to a more complicated molecule. If the cleavage of the 2 : 3-dihydrothiophen occurred as shown below then such a series of reactions would probably take place.

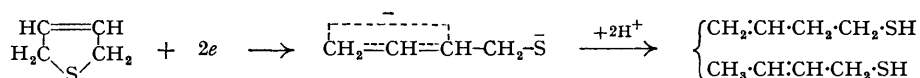
The thiol obtained *directly* from thiophen, by use of a molecular excess of sodium, failed to yield a solid derivative. Examination of the infra-red absorption spectrogram confirmed the presence of approximately 15% of but-3-enethiol (absorption peaks at 10.1 and 10.9  $\mu$ .), and 5—10% of *trans*- (peak at 10.4  $\mu$ .) and 30% of *cis*-but-2-enethiol (peak near 13.5  $\mu$ .). There were indications of the presence of a small quantity of material which had high general absorption above 13  $\mu$ . which is thought to be indirectly due to but-1-enethiol.

Both isomeric dihydrothiophens were reduced to the thiol by the action of sodium equivalent to one molecule of hydrogen per molecule of dihydrothiophen, and the products were examined chemically and spectroscopically.

The thiol from 2 : 5-dihydrothiophen yielded a solid butenyl 2 : 4-dinitrophenyl sulphide, m. p. 56—56.5° (after repeated crystallisation from alcohol), which did not depress the melting point of but-3-enyl 2 : 4-dinitrophenyl sulphide (m. p. 57°). Spectroscopic examination confirmed the presence of at least 30% of but-3-enethiol and revealed that about 55% of *cis*- but essentially no *trans*-but-2-enethiol was present.

The thiol from 2 : 3-dihydrothiophen yielded only a liquid derivative, and the spectrogram showed the presence of about 15—20% of but-3-enethiol, only a little *cis*-, and no *trans*-but-2-enethiol. The sample contained a substantial amount of the material of high general absorption above 13  $\mu$ . which is believed to be indirectly due to but-1-enethiol.

From these results, it is apparent that some degree of isomerisation occurs when the dihydrothiophens are reduced by sodium and methanol in liquid ammonia. The exact mechanism by which this takes place is not clear, but the work of A. J. Birch (*Quart. Reviews*, 1950, 4, 69), on the reduction of organic compounds by metal-ammonia solutions, offers a possible explanation. The addition of two electrons to the dihydrothiophen nucleus gives rise to a charged transition complex, *i.e.*, a mesomeric anion, which is then stabilised by proton addition (the methanol acting as proton donor). Proton addition occurs at points of greatest charge stability, the governing factor of which is molecular structure. By this means, but-3-enethiol as well as the  $\Delta^2$ -isomer could be formed from 2 : 5-dihydrothiophen :



The last stage of the non-catalytic reduction of thiophen is the formation of *n*-butenes and hydrogen sulphide. Since the presence of large quantities of ammonia made this particular stage of the reduction rather difficult to investigate, samples of thiol directly from thiophen and also from each of the dihydrothiophens were caused to react with sodium in refluxing alcohol. The low-boiling hydrocarbon products were collected in a suitable cold trap and analysed. The residual alkaline solution was rich in sodium sulphide and, on acidification to recover unchanged thiol, much hydrogen sulphide was evolved.

\* These spectrograms are being submitted for inclusion in the A.P.I. Project No. 44, U.S. Bureau of Standards Catalogue of Infra-red Spectrograms, and so are not shown here.

The thiol from 2 : 3-dihydrothiophen yielded only a negligible amount of butenes, and a large proportion of the non-thiol material recovered consisted of a high-boiling *neutral* oil of

TABLE II.

Component.	Weight % of hydrocarbon product.	
	Thiol direct from thiophen.	Thiol from 2 : 5-dihydrothiophen.
But-1-ene .....	27.4	23.2
<i>cis</i> -But-2-ene .....	51.5	76.0
<i>trans</i> -But-2-ene .....	25.1	0.8

unpleasant odour. This again might be an indirect result of the formation of but-1-enethiol. It must be pointed out that, under the conditions specified, break-down of the other two thiol samples was limited to about 25% of the theoretical. Analytical results are given in Table II.

## EXPERIMENTAL.

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

*Preparation of Dihydrothiophens.*—Thiophen (420 g., 5 mols.) and methanol (1.5 l.) were placed in a 5-l. three-necked flask fitted with a sealed stirrer, toluene thermometer, and solid carbon dioxide reflux-trap to which a vent-line was attached. The flask and its contents were cooled to  $-40^{\circ}$ , and liquid ammonia (*ca.* 1.5 l.) blown in. Sodium (253 g., 11 mols.) was then added in small pieces to the cooled, stirred solution during 8 hours, after which the product was allowed to warm to room temperature overnight to evaporate off the ammonia. The reaction mixture was then carefully diluted with ice-water (2.5 l.) during vigorous stirring while the temperature was kept below  $20^{\circ}$ , and the resultant aqueous alkaline solution was extracted with *isopentane* to remove unchanged thiophen and neutral reaction products, and finally acidified with dilute hydrochloric acid whilst being cooled. The liberated thiol separated as an oil which was extracted with *isopentane*, and the solvent was removed to leave crude butenethiol (71 g., 17%), b. p.  $14-16^{\circ}/20$  mm. ( $101-103^{\circ}/760$  mm.),  $n_D^{20}$  1.4735 (Found : C, 54.4; H, 9.5; S, 35.4. Calc. for  $C_4H_6S$ : C, 54.5; H, 9.1; S, 36.4%). The butenyl 2 : 4-dinitrophenyl sulphide from this sample was an oil which could not be induced to crystallise. The neutral product, fractionated through a 20-plate glass-packed column at reduced pressure under an atmosphere of nitrogen, yielded unchanged thiophen (128 g.) and crude dihydrothiophens (164 g., 39%). The accumulated crude product from three such runs was fractionated, yielding 2 : 3-dihydrothiophen (12.3%), b. p.  $112.0^{\circ}/760$  mm.,  $n_D^{20}$  1.5311,  $d_4^{20}$  1.0361 (Found : C, 55.7; H, 7.3; S, 36.5.  $C_4H_6S$  requires C, 55.8; H, 7.0; S, 37.2%), and 2 : 5-dihydrothiophen (26.2%), b. p.  $122.3^{\circ}/760$  mm.,  $n_D^{20}$  1.5306,  $d_4^{20}$  1.0591 (Found : C, 56.0; H, 7.3; S, 36.1%).

2 : 5-Dihydrothiophen yielded a *mercuric chloride* complex (from ethanol, m. p.  $128^{\circ}$  (Found : C, 21.7; H, 3.0; S, 13.6; Cl, 15.2.  $2C_4H_6S.HgCl_2$  requires C, 21.65; H, 2.7; S, 14.45; Cl, 16.0%). A mixed m. p. with the corresponding derivative (m. p.  $127-128^{\circ}$ ) of thiophan gave a depression of  $8^{\circ}$ . The *methiodide* crystallised from ethanol in colourless needles, m. p.  $147^{\circ}$  (sealed tube) (Found : C, 27.2; H, 4.1; S, 13.9; I, 55.3.  $C_4H_6SI$  requires C, 26.4; H, 4.0; S, 14.05; I, 55.6%). Drop-wise addition of bromine to a solution of 2 : 5-dihydrothiophen (8.6 g.) in *isopentane* (150 ml.) continuously precipitated a yellow powder until the permanent red colour of bromine indicated the end-point of the reaction. The weight of bromine added (33 g.) indicated that four atoms of bromine were absorbed per molecule, and the addition compound (34 g., 85%) recrystallised from carbon tetrachloride as orange crystals, m. p.  $101-102^{\circ}$  (decomp.). These crystals were relatively stable and gave off only traces of hydrogen bromide after exposure to air for some weeks. The addition compound is undoubtedly 1 : 1 : 3 : 4-tetrabromothiophan (IX) (Found : C, 12.2; H, 1.8; S, 7.7; Br, 78.4.  $C_4H_6SBr_4$  requires C, 11.8; H, 1.5; S, 7.9; Br, 78.8%). Titration of an aqueous-alcoholic solution against silver nitrate solution showed there to be two ionisable bromine atoms per molecule [Found : Br, 40.5.  $C_4H_6SBr_4$  (IX) requires Br, 39.4%].

2 : 3-Dihydrothiophen yielded a *mercuric chloride* complex (from ethanol) which was resolved into an ethanol-insoluble, amorphous, white powder, m. p.  $130-131^{\circ}$ , and colourless needles melting, after repeated crystallisation, at the same temperature (Found : C, 22.2; H, 4.3; S, 8.1; Cl, 9.2%). A mixed m. p. gave no depression and both compounds were shown by analysis to have the same complex empirical formula. Attempts to prepare a methiodide in the normal way, in refluxing ethanol, only yielded a dark viscous oil but, by working at low temperature, colourless needles were obtained, having m. p.  $79-80^{\circ}$  (decomp.). This methiodide rapidly decomposed with the liberation of free iodine, rendering accurate analysis impossible. Treatment of 2 : 3-dihydrothiophen with bromine yielded a yellow precipitate which immediately decomposed to a black tar with copious evolution of hydrogen bromide. The relative weight of bromine added indicated the addition of two bromine atoms per molecule.

*Identification of 2 : 5-Dihydrothiophen.*—Oxidation to 2 : 5-dihydrothiophen 1 : 1-dioxide ( *$\beta$ -butadiene sulphone*). A 50% excess over theory of hydrogen peroxide (42 ml.; 100-vol.) was added to 2 : 5-dihydrothiophen (12 g.) in acetic acid (75 ml.) and, after 24 hours at room temperature, the solution was refluxed for 3 hours to destroy excess of peroxide. On removal of the solvent on the water-bath at reduced pressure, a viscous oil remained which quickly solidified. Extraction with hot benzene left a small insoluble residue and addition of light petroleum to the benzene extract precipitated a white, crystalline solid (12.3 g., 75%) which recrystallised from ethanol as white nodules, m. p.  $65^{\circ}$  (Found :

C, 40.8; H, 5.2; S, 27.0. Calc. for  $C_4H_6O_2S$ : C, 40.7; H, 5.1; S, 27.1%. A mixed m. p. with  $\beta$ -butadiene sulphone which, according to Zuydewijn (*loc. cit.*), melts at 63–64° gave no depression of m. p.

**3:4-Dibromothiophan 1:1-dioxide.** The sulphone yielded a dibromide when treated with bromine either in refluxing carbon tetrachloride or on being kept for 12 hours in cold aqueous solution. On recrystallisation from carbon tetrachloride it formed small colourless plates, m. p. 140–141° (Found: C, 17.6; H, 2.4; S, 11.5; Br, 57.3. Calc. for  $C_4H_6O_2SBr_2$ : C, 17.3; H, 2.2; S, 11.55; Br, 57.5%). Zuydewijn (*loc. cit.*) obtained a dibromide from  $\beta$ -butadiene sulphone in a similar manner, m. p. 139–141°, to which he attributed the *trans*-structure. Staudinger and Ritzenthaler (*loc. cit.*) give m. p. 141°.

**3:4-Dihydroxythiophan 1:1-dioxide.** Treatment of 2:5-dihydrothiophen as described above, but with a 200% excess over theory of peroxide, gave only a small amount of sulphone (20%) together with the corresponding diol (80%). This remained as a residue on extraction with benzene; on recrystallisation from ethanol it formed a microcrystalline powder, m. p. 159–160° (Found: C, 31.4; H, 5.5; S, 20.9. Calc. for  $C_4H_6O_4S$ : C, 31.6; H, 5.3; S, 21.2%). Zuydewijn (*loc. cit.*) obtained this compound, m. p. 159–160°, from  $\beta$ -butadiene sulphone and peracetic acid by hydrolysing the resultant diol acetate with boiling water; he attributed to it the *trans*-structure.

**3-Bromo-4-hydroxythiophan 1:1-dioxide (XVI).** The insoluble oil formed by heating the crude diol under reflux with a solution of bromine in carbon tetrachloride for 2 hours solidified on storage and crystallised from ethanol as a colourless, microcrystalline powder, m. p. 190–191° (Found: C, 22.5; H, 3.3; S, 14.9; Br, 36.8. Calc. for  $C_4H_7O_3SBr$ : C, 22.5; H, 3.3; S, 14.2; Br, 37.15%). Van Lohuizen and Backer (*Rec. Trav. chim.*, 1949, **68**, 1137) obtained this compound, m. p. 189–190°, by the action of bromine on  $\beta$ -butadiene sulphone in acetic acid solution.

**Thiophan 1:1-dioxide.** 2:5-Dihydrothiophen sulphone was hydrogenated at room temperature and pressure in 25% aqueous-alcoholic solution over colloidal palladium. The product was distilled under reduced pressure to give a quantitative yield of thiophan 1:1-dioxide, b. p. 115°/3 mm., m. p. 20.5–21.5°. The product derived from  $\beta$ -butadiene sulphone, by this method, melted at 20–21° (Zuydewijn, *loc. cit.*). The m. p. of a sample of dioxide, prepared by a different route, was 24.78°, and the estimated purity 96 mol. %. The calculated m. p. for zero impurity was 28.86°, thus indicating a very low cryoscopic constant.

**Identification of 2:3-Dihydrothiophen.—Oxidation to 2:3-dihydrothiophen 1:1-dioxide ( $\alpha$ -butadiene sulphone).** A solution of the isomer (2.2 g.) in acetic acid (20 ml.) was oxidised with hydrogen peroxide (7.5 ml.; 100-vol.) as previously described. On removal of the solvent, the crude product slowly solidified and was extracted with benzene. Dilution with light petroleum precipitated a solid which recrystallised from ethanol as colourless, crystalline granules, m. p. 49.0–49.5° (Found: C, 40.4; H, 5.3; S, 27.2. Calc. for  $C_4H_6O_2S$ : C, 40.7; H, 5.1; S, 27.1%).  $\alpha$ -Butadiene sulphone, according to Zuydewijn (*loc. cit.*), melts at 48.5–49.5°.

**2:3-Dibromothiophan 1:1-dioxide.** On treatment of an aqueous solution of the sulphone with bromine, colourless needles of the dibromide were deposited during 2 days in the refrigerator and they were crystallised from carbon tetrachloride; they had m. p. 117–118° (Found: C, 17.4; H, 2.3; S, 11.4; Br, 57.3. Calc. for  $C_4H_6O_2SBr_2$ : C, 17.4; H, 2.2; S, 11.5; Br, 57.5%). The dibromide from  $\beta$ -butadiene sulphone had m. p. 112–115° (Zuydewijn, *loc. cit.*).

**Reduction of Dihydrothiophens to Butenethiols.—2:5-Dihydrothiophen (129 g., 1.5 mols.)** was reduced, in the usual way, with sodium (69 g., 3 mols.) and methanol (500 ml.) in liquid ammonia (750 ml.). During the reaction, red globules of "amalgam" appeared on the surface and slowly reacted. The products consisted of recovered dihydrothiophen (6.5 g., 5%) and butenethiol (105 g., 80%) which was immediately distilled at 15–16°/20 mm. (b. p. 101–103°/760 mm.),  $n_D^{20}$  1.4770, leaving only a small residue (5 g.). The thiol formed a *butenyl 2:4-dinitrophenyl sulphide* as an oily precipitate which slowly solidified. After repeated crystallisation from methanol, it formed pale yellow crystals, m. p. 56–56.5° (Found: C, 47.1; H, 4.1; N, 10.9; S, 12.4.  $C_{10}H_{10}O_4N_2S$  requires C, 47.2; H, 4.0; N, 11.0; S, 12.6%). A mixed m. p. with *but-3-enyl 2:4-dinitrophenyl sulphide* (m. p. 57°) gave no depression.

**2:3-Dihydrothiophen (129 g., 1.5 mols.)** was likewise reduced and yielded recovered dihydrothiophen (14 g., 10%) and butenethiol (90 g., 68%) which was immediately distilled but gave only 40% of b. p. 20–24°/30 mm. (102–106°/760 mm.),  $n_D^{20}$  1.4690, and only 60% below 50°/30 mm. (125°/760 mm.), with a high-boiling viscous residue,  $n_D^{20}$  1.5190. The *butenyl 2:4-dinitrophenyl sulphide* of the 40% distillate was a semi-solid oil which could not be further purified.

**Synthesis of Butenethiols.—But-3-enethiol** and both *cis*- and *trans*-but-2-enethiol were synthesised by the same general route. The appropriate alcohol was prepared and purified before conversion into the bromide by the method of Winstein and Young (*loc. cit.*). The bromide was then converted into the thiol through the thiuronium bromide complex (*Org. Synth.*, **21**, 36). Since much confusion exists in the literature on the physical constants of certain of the intermediates, some preparative details are given.

**But-3-enol.—Attempts** to prepare this alcohol by a modification of Juvala's method (*Ber.*, 1930, **63**, 1989), using allyl chloride and trioxymethylene, gave low yields (*ca.* 10%); better results were obtained by partial dehydration of butane-1:3-diol. Toluene-*p*-sulphonic acid (75 g.) and butane-1:3-diol (300 g.) were placed in a 1-l. flask fitted with a dropping-funnel and a long glass-packed column leading in turn to a downward condenser, an ice-cooled receiver, and finally a carbon dioxide-cooled trap. The flask was heated in an oil-bath at 200–210°, and more glycol (1000 g.) was slowly added during 7 hours with an overhead temperature of 85–90°, after which the oil-bath temperature was slowly raised to 230° for an hour. The product in the ice-cooled trap was freed from butadiene (which was collected in the second trap, stabilised, and stored) and saturated with anhydrous potassium

carbonate, and the aqueous layer run off. The oil layer was distilled, and crude but-3-enol (248 g., 23%) was obtained, b. p. 95—130°. The combined product from two runs was fractionated in a 20-plate glass-packed column to give the pure alcohol, b. p. 113.5°/760 mm.,  $n_D^{20}$  1.4200. The but-3-enyl 3 : 5-dinitrobenzoate was obtained from light petroleum as needles, m. p. 50.5°, and the phenylurethane derivative from the same solvent as needles, m. p. 27—28°.

**4-Bromobutene.**—The alcohol (96 g.) was mixed with pyridine (36 ml.) in a 250-ml. flask fitted with a dropping-funnel, toluene thermometer, and calcium chloride tube. Phosphorous tribromide (52 ml.) was added dropwise during 1—1.5 hours, the flask being cooled at  $-15^\circ$  and shaken regularly. The product was distilled directly from the flask at low pressure, washed with ice-water and chilled sodium hydrogen carbonate solution, and dried. The 4-bromobutene (97 g., 35%) was a dense, colourless oil, b. p. 14°/10 mm.,  $n_D^{20}$  1.4575.

**But-3-enethiol.**—The bromide (97 g., 0.75 mol.) and thiourea (57 g., 0.75 mol.) were refluxed for 3 hours in ethanol (250 ml.). The solvent was removed under reduced pressure, and the thiuronium bromide complex shaken with a solution of potassium hydroxide (84 g., 1.5 mol.) in water (400 ml.). On acidification with dilute hydrochloric acid, and cooling to below 20°, the thiol separated as a green oil (20 g., 30%), which was washed with water and dried. Only 60% of the product boiled at 8—12°/18 mm. (100—104°/760 mm.),  $n_D^{20}$  1.4690, the remainder boiling over a wide range. The but-3-enyl 2 : 4-dinitrophenyl sulphide crystallised from ethanol as yellow plates, m. p. 57°.

**trans-Crotyl Alcohol (But-2-enol).**—This alcohol was prepared from *trans*-crotonaldehyde (the normal commercial material), b. p. 100.5°,  $n_D^{20}$  1.4367, and aluminium isopropoxide by the method of Young, Hartung, and Crossley (*J. Amer. Chem. Soc.*, 1936, **58**, 100). The crude alcohol (61%), b. p. 115—125°, was fractionated through a 20-plate column, to yield *trans*-crotyl alcohol, b. p. 121.2°/760 mm.,  $n_D^{20}$  1.4289. Its 3 : 5-dinitrobenzoate was obtained from light petroleum as pale yellow needles, m. p. 72°, and the phenylurethane derivative as fine needles, m. p. 79—80°.

**trans-Crotyl Bromide (1-Bromobut-2-ene).**—The alcohol (126 g.), treated by the general method previously described, yielded *trans*-crotyl bromide (190 g., 81%) which was distilled at low pressure (3 mm.) to avoid isomerisation. No attempt was made to obtain an accurate b. p. of the bromide ( $n_D^{20}$  1.4820).

**trans-But-2-enethiol.**—Treatment of the bromide (190 g.) in the usual way yielded the *trans*-thiol (40 g., 33%), which was distilled at 15—16°/20 mm. (101—103°/760 mm.),  $n_D^{20}$  1.4765, with negligible residue. The *trans*-crotyl 2 : 4-dinitrophenyl sulphide crystallised from methanol as fine mustard-yellow crystals, m. p. 98.5—99°.

**cis-Crotyl Alcohol.**—This was prepared from commercial 1 : 3-dichlorobut-2-ene by Hatch and Nesbitt's method (*J. Amer. Chem. Soc.*, 1950, **72**, 727). A detailed description of the synthesis is given since certain differences were found in the physical constants of the intermediates.

**3-Chlorobut-2-en-1-ol.**—Commercial 1 : 3-dichlorobut-2-ene (4.6 kg.) was fractionated through a 40-plate glass-packed column under reduced pressure, and the lower-boiling 1 : 3-dichlorobut-2-ene (3.78 kg.), b. p. 68—69°/100 mm.,  $n_D^{20}$  1.4722, was converted into  $\alpha$ -3-chlorobut-2-en-1-ol by refluxing it with an equimolar amount of 10% aqueous sodium carbonate for 3 hours. The crude product (2.95 kg.) was fractionated as above and yielded the chlorobutenol (1.92 kg., 61%), b. p. 90—91°/50 mm.,  $n_D^{20}$  1.4671. The f. p. of  $-42.87^\circ$  and the calculated f. p. for zero impurity of  $-42.54^\circ$  indicated a purity of about 99 mol. %.

**But-2-yn-1-ol.**—3-Chlorobut-2-en-1-ol (1.92 kg.) was dehydrochlorinated by refluxing it for 2 hours with 20% aqueous sodium hydroxide (750 g.). Fractionation of the crude product (1.18 kg.) under reduced pressure in a 20-plate glass-packed column yielded a main fraction of but-2-yn-1-ol (482 g., 38.3%), b. p. 89.0°/100 mm.,  $n_D^{20}$  1.4542. The f. p. of  $-0.88^\circ$  and the calculated f. p. for zero impurity of  $-0.59^\circ$  indicated a purity of 99.0 mol. %.

**cis-Crotyl Alcohol.**—But-2-yn-1-ol (480 g.) was hydrogenated at atmospheric pressure to *cis*-crotyl alcohol, a palladium catalyst being used (Schmidt, *Ber.*, 1919, **52**, 409). Fractionation of the crude product (449 g., 93%) in a 20-plate glass-packed column at atmospheric pressure yielded *cis*-crotyl alcohol (255 g.), b. p. 123.6°/760 mm.,  $n_D^{20}$  1.4342. The alcohol melted at  $-90.15^\circ$  and the calculated m. p. for zero impurity of  $-89.44^\circ$  indicated a purity of 98 mol. %. The *cis*-crotyl 3 : 5-dinitrobenzoate was obtained from light petroleum as yellow needles, m. p. 55.0—55.5°, and the phenylurethane derivative as fine needles, m. p. 42.5—43.0°.

**cis-Crotyl Bromide.**—The alcohol (144 g.) was treated in the usual way, to yield *cis*-crotyl bromide (170 g., 63%) which was distilled at low pressure (2 mm.); it had  $n_D^{20}$  1.4830.

**cis-But-2-enethiol.**—The bromide (170 g.) was converted into the thiol (42 g., 39%), which distilled at 12°/14 mm. ( $n_D^{20}$  1.4800), with little residue. Its m. p. of  $-112.4^\circ$  and calculated m. p. for zero impurity of  $-108.4^\circ$  indicated a purity of the order of 90 mol. %. Spectroscopic examination indicated the presence of a maximum of 9% of the *trans*-isomer, indicating that relatively little isomerisation had occurred in conversion of the alcohol into the thiol. The *cis*-crotyl 2 : 4-dinitrophenyl sulphide crystallised from ethanol as a mustard-coloured powder, m. p. 63—65°.

**Reduction of Butenethiols to Butenes and Hydrogen Sulphide.**—Thiophen-derived butenethiol (88 g., 1 mol.) was dissolved in methanol (1 l.) in a 2-l. three-necked flask fitted with a sealed stirrer and a reflux condenser leading to a carbon dioxide-cooled trap. Sodium (75 g.) was added in small pieces, and the methanol was allowed to reflux freely. The low-boiling hydrocarbon product (ca. 25%) in the trap was shown by analysis to be entirely *n*-butenes. The residual alkaline solution was rich in sodium sulphide and, on acidification to recover unchanged thiol, yielded a substantial volume of hydrogen sulphide. The thiols obtained directly from thiophen and from 2 : 5-dihydrothiophen were successfully reduced, and the analysis of the gaseous products is given in Table II. The thiol from

2 : 3-dihydrothiophen yielded only a trace of low-boiling hydrocarbon, and, besides recovered thiol, a neutral oil (30 g., 34%) of evil odour, the bulk of which boiled above 200°/760 mm.

Our thanks are due to the Chairman of the Anglo-Iranian Oil Co. Ltd. for permission to publish these results. We also thank Mr. L. K. Maltby and Dr. H. Powell for the preparation and interpretation of spectrograms, and Mr. W. Crawford for the determination of purities.

ANGLO-IRANIAN OIL CO. LTD., RESEARCH STATION,  
SUNBURY-ON-THAMES, MIDDLESEX.

[Received, May 9th, 1951.]

---