

The Conversion of Thiophen into 4 : 7 : 8 : 9-Tetrahydro-4 : 7-sulphinyllthionaphthen 1 : 1-Dioxide.

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[Reprint Order No. 4570.]

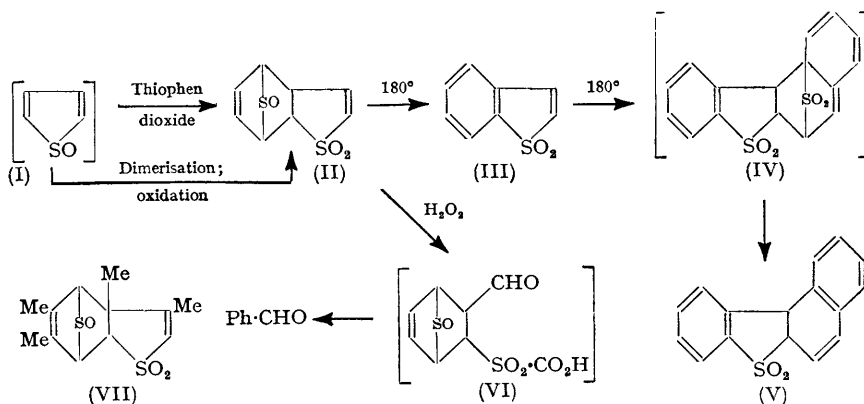
4 : 7 : 8 : 9-Tetrahydro-4 : 7-sulphinyllthionaphthen 1 : 1-dioxide (II) is produced by the oxidation of thiophen with hydrogen peroxide in acetic acid. Its structure is shown by oxidative degradation to benzaldehyde, by its conversion at about 180° into thionaphthen-1 : 1-dioxide, and by infra-red spectral analysis.

INTERACTION of thiophen and hydrogen peroxide in glacial acetic acid (Davies, Gamble, James, and Savige, *Chem. and Ind.*, 1952, 804) produces a crystalline compound, $C_8H_8O_3S_2$, which decomposes, according to the rate of heating, at 182° to 202°. At its melting point or when refluxed in a solvent (b. p. 175—180°), this is converted into products from which thionaphthen 1 : 1-dioxide (III) is easily separated. The sulphur dioxide also detected is probably from (III) which (Davies, Gamble, and Savige, *J.*, 1952, 4678) is readily converted by heat into sulphur dioxide and derivatives of 9-thiafluorene such as (V). Small yields of benzaldehyde have been isolated by steam-distillation of the oxidation products formed from the compound, $C_8H_8O_3S_2$, by hydrogen peroxide or potassium permanganate. These reactions and the infra-red spectrum (see p. 18) prove structure (II) for the compound, $C_8H_8O_3S_2$. Since benzaldehyde is not produced by oxidation of (III) under the same conditions, it seems evident that the fission of the $C_{(2)}-C_{(3)}$ link in (II) occurs before loss of the sulphinyl bridge, and the hypothetical aldehydic acid (VI) should be quickly decarboxylated and aromatised in the oxidising environment.

The loss of sulphur dioxide from benzaldehyde sulphinic acid to yield some benzaldehyde would be likely, since it is known that another electrophilic *ortho*-group (NO_2) causes some aromatic sulphinic acids to decompose readily in this way (Dann and Davies, *J.*, 1929, 1051).

There is doubt as to the exact mechanism of the formation of (II) from thiophen. It is plausible that a molecule of thiophen adds to a molecule of its monoxide (I) or dioxide to give an intermediate of type (II), in which however the bridge would be unoxidised sulphur, and the other sulphur atom would be in the sulphoxide or sulphone form. Either compound could then be oxidised to (II). Though this mechanism is at first sight supported by the three known instances of thiophen derivatives combining with a dienophile (maleic anhydride), in each of these cases every carbon atom of the thiophen nucleus is attached to an aromatic group (Barnett, *J.*, 1935, 1326; Clapp, *J. Amer. Chem. Soc.*, 1939, **61**, 2733; Allen and Gates, *ibid.*, 1943, **65**, 1283). Now, in such arylated thiophens the aromatic character of the thiophen nucleus is diminished, since such compounds, *e.g.*, dibenzothiophen and tetraphenylthiophen, give stable crystalline sulphones, unlike thiophen itself. Hence the development of an active 1 : 4 conjugated system in arylated thiophens is not cogent evidence for thiophen's behaving similarly, to form an adduct containing an unoxidised sulphur bridge. Another possible mechanism is that the unknown (I) forms a dimer [as (II) but with SO for SO_2] which is then stabilised by oxidation to (II). Though it is unusual for a compound thus to function simultaneously as diene and dienophile, there is a formal analogy in the behaviour of (III) which is converted by heat, presumably through the adduct (IV), into 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (V) (Bordwell, McKellin, and Babcock, *J. Amer. Chem. Soc.*, 1951, **73**, 5566; Davies, Gamble, James, and Savige, *loc. cit.*; Davies, Gamble, and Savige, *J.*, 1952, 4678). Moreover, Alder ("Newer Methods of Preparative Organic Chemistry," Interscience Publ. Corp., New York, 1948, p. 459) formulates the dimers of the unknown monomeric tetrachlorocyclopentadienone and cyclopentadienone oxime as Diels-Alder adducts. Perhaps the most probable mechanism is the one shown, *viz.*, that (I) combines with thiophen dioxide to form (II). It is known that a sulphinyl group can activate a 2 : 3-double bond, though not as strongly as a sulphone group which can be very powerful, especially in cyclic compounds such as 2 : 3-dihydrothiophen 1 : 1-dioxide (Alder, Rickert, and Windemuth, *Ber.*, 1938, **71**, 2451). The addition of the diene (I) to the relatively dienophilic thiophen dioxide to form (II) would then follow conventional lines.

The reactions of (II) have implications of inorganic chemical interest. The theoretical fission product in the conversion of (II) into (III) is the unknown hydrogen sulphoxide,



H_2SO , which may yet be isolated. Surprisingly, sulphur dioxide was the only inorganic sulphur compound detected when (II) was heated in the absence of air. The interaction of (II) with sodium hydroxide does not simply remove the sulphinyl bridge but produces unstable compounds which may be derived from the transient formation of an unisolated sulphenic acid. This may not exist in the free state since sulphenic acids are very unstable,

in fact apparently the only one known is anthraquinone-1-sulphenic acid, which is stabilised by hydrogen bonding (Kharasch, Potempa, and Wahrmeister, *Chem. Reviews*, 1946, **39**, 269).

Finally, Backer and Melles (*Kon. Ned. Akad. Wet.*, 1951, **54**, B, 340) refer to a white solid, $C_8H_8O_3S_2$, m. p. 177° , produced by the interaction of perbenzoic acid and thiophen (W. Stevens, Thesis, Gröningen, 1940), and this substance is doubtless identical with (II), of which the melting point varies greatly with the rate of heating. Melles (Thesis, Gröningen, 1951) describes several "sesqui-oxides" obtained by the oxidation of thiophen derivatives, and on page 26 provisionally formulates one of them, the S_2O_3 compound obtained from 3 : 4-dimethylthiophen (as VII), the main evidence for this being the analysis and the loss of sulphur dioxide at the melting point. It is probable that Melles (whose Thesis was only available to us after this paper was submitted for publication) was on the verge of suggesting from analogy the structure (II) for the "sesquioxide" of thiophen.

EXPERIMENTAL

4 : 7 : 8 : 9-Tetrahydro-4 : 7-sulphinylthionaphthen 1 : 1-Dioxide (II).—A mixture of hydrogen peroxide (6% ; 500 ml.) and thiophen (20 g.) in glacial acetic acid (200 ml.) was refluxed, and four further quantities of hydrogen peroxide (6% ; 100 ml.) were added at intervals of 15 min. Refluxing was continued for a second hour, the colour changing from yellow to orange-red and finally to yellow again, and the cooled solution, which contained sulphate ion, was extracted with ether (4×250 ml.) and then with chloroform (4×250 ml.), and the organic extracts were dried ($MgSO_4$). The ether yielded an oil which gradually deposited fumaric acid (0.3 g.), identified by its m. p. and the m. p. and mixed m. p. ($148-149^\circ$) of the di-*p*-nitrobenzyl ester. The chloroform extract gave 1.5 g. of the compound (II), m. p. $178-181.5^\circ$ (decomp.). This is also produced, in about 0.1 g. yield, from 22 g. of thiophen in glacial acetic acid (200 ml.) and hydrogen peroxide (30% ; 60 ml.) at 45° (20 hr.), but this mixture gave the best yields (1.5—4.1 g.) when kept at room temperature for 3—18 days. The maximum yield was after 7 days, and under these conditions no fumaric acid was isolated.

4 : 7 : 8 : 9-Tetrahydro-4 : 7-sulphinylthionaphthen 1 : 1-dioxide separates from alcohol in needles, m. p. $182.5-183.5^\circ$ (decomp.). The m. p., actually a decomposition temperature, varies extremely with the rate of heating; thus when the specimen is put into a bath at 197° the m. p. can be raised to 202° [Found : C, 44.4; H, 3.5; S, 29.6% ; *M* (Rast), 235, 255. $C_8H_8O_3S_2$ requires C, 44.5; H, 3.7; S, 29.6% ; *M*, 216]. It is soluble in acetone, alcohol, chloroform, carbon tetrachloride, or hot water, and insoluble in ether or benzene. It is neutral to litmus, and negative tests with isatin-sulphuric acid, *p*-nitrophenylhydrazine, and methylmagnesium iodide show the absence of certain thiophen derivatives, a carbonyl group, and active hydrogen, respectively. Though stable to hot ammonia solution it is rapidly attacked by hot dilute sodium hydroxide solution, which becomes pale green, yellow, and finally orange, and this solution gives an immediate red-purple colour with sodium nitroprusside. Acidification of the alkaline solution gives hydrogen sulphide (detected by conversion into methylene-blue) and a white solid, rapidly becoming first grey and then yellow, which separates from benzene-light petroleum as an amorphous solid, m. p. 50° to 85° . A low-melting amorphous substance and hydrogen sulphide are also formed when (II) is reduced by hydriodic acid, or by tin and zinc with hydrochloric acid. Hot aqueous ferric chloride solution and (II) produce a stable dark-green colour. Some of the above degradation and colour changes are compatible with the initial formation of an unstable sulphenic acid.

Action of Heat on (II).—Decomposition takes place apparently with the evolution of sulphur dioxide, for when (II) was gently refluxed in *o*-dichlorobenzene in an atmosphere of nitrogen a gas was given off which reacted with chromate, permanganate, and water, in ways typical of sulphur dioxide. It is not however certain whether some of the sulphur dioxide was derived from (II) or from thionaphthen dioxide; this was formed when technical *o*-dichlorobenzene (20 ml. ; b. p. $175-180^\circ$) containing 0.5 g. of (II) was refluxed for 2 hr., some sulphur dioxide being evolved. The filtered solution was poured on to a column of alumina and developed with benzene. The least adsorbed material, m. p. $136-139^\circ$, gave a strong bluish-white fluorescence in ultra-violet light, and after purification by further chromatography and crystallisation from benzene-light petroleum gave very pale yellow needles, m. p. $139.5-140^\circ$, undepressed on admixture with thionaphthen 1 : 1-dioxide (Found : C, 57.9; H, 3.8; O, 18.8. Calc. for

$C_8H_6O_2S$: C, 57.8; H, 3.6; O, 19.3%). This is also formed when (II) is kept in the molten state at about 184° for a few minutes.

Formation of Benzaldehyde from (II).—To a boiling solution of (II) (0.5 g.) in water (15 ml.), hydrogen peroxide (30%; 5 ml.) was added, and the same amount again after 15 min., the solution becoming greenish-yellow. After refluxing for a further 15 min. the solution was distilled at atmospheric pressure, the peroxide in the distillate was destroyed by permanganate, and on redistillation the distillate from this solution smelt of benzaldehyde, gave a positive Schiff test, and with *p*-nitrophenylhydrazine hydrochloride yielded sulphur-free brick-red plates (from alcohol), m. p. 182 — 183° (Found: C, 64.4; H, 4.5; N, 17.0. Calc. for $C_{13}H_{11}O_2N_2$: C, 64.7; H, 4.6; N, 17.4%). The identity of this slightly impure benzaldehyde *p*-nitrophenylhydrazone was shown by its conversion into the yellow form at 140° (Ciusa, Vecchiotti, *Chem. Zentr.*, 1911, II, 865), and also by crystallisation from benzene as yellow needles, m. p. and mixed m. p. 191° . Benzaldehyde is also obtained from (II) by oxidation with aqueous potassium permanganate but not with bromine water. In all three oxidation processes, (II) is decomposed with the formation of sulphate ion.

Infra-red Spectrum of (II).—The report received is as follows: "There are no carbonyl or hydroxyl bands. There are three strong bands at 1068, 1142, and 1292 cm^{-1} and these suggest both the sulphoxide (1068) and sulphone (1142 and 1292). The value 1292 cm^{-1} is lower than usual but both the values fall in the allowed range given by Colthup and their intensity would confirm that they are not combination bands. The band at 1600 cm^{-1} may perhaps indicate an aromatic nucleus."

The authors thank Dr. J. B. Willis and Mr. R. L. Werner for the above spectral report, the Vacuum Oil Co. Pty. Ltd., Melbourne, for a gift of thiophen, and Mr. H. Spruijt for the Dutch translation.

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[Received, August 7th, 1953.]
