

## Tellurophen and Some of its Derivatives

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The preparation of tellurophen (1) from sodium telluride and butadiyne in methanolic solution is reported. Physical and spectroscopic properties of tellurophen (1) are compared with those of furan, thiophen, and selenophen. Qualitative data show that its chemical behaviour is typical of a heteroaromatic compound with a five-membered ring. The syntheses of eight 2-substituted and of three 2,5-disubstituted derivatives are described and the structures of the products are deduced from chemical evidence and spectroscopic data. The effect of substituents on the ring-proton n.m.r. chemical shifts is examined.

WHEREAS the furan, thiophen, and selenophen systems have been extensively studied and quantitative data on their reactivity and aromaticity have been published,<sup>1</sup> no such studies of tellurophen have been reported, probably owing to difficulties of synthesis. Here we report the synthesis and characterization of tellurophen (1) and of some of its 2- and 2,5-substituted derivatives. Hitherto only some di- and tetra-substituted derivatives with all the substituents identical have been reported.<sup>2</sup>

In 1966, Mack<sup>2a</sup> described the synthesis of tellurophen (1) from sodium telluride and butadiyne,\* but his report included insufficient experimental details. We describe the preparation of (1) in detail in the Experimental section, but here point out some important points. (a) Moisture and oxygen must be rigorously excluded. (b) Butadiyne<sup>8</sup> is very readily oxidized and polymerized and therefore must be used directly after preparation by bubbling into the methanolic solution of sodium telluride. (c) Anhydrous and iron-free liquid ammonia is necessary for the preparation of sodium telluride.<sup>9</sup> (d) Commercial metallic grey tellurium must be used, for with amorphous

or partly oxidized tellurium, no reaction occurs. (e) At the end of the reaction, the methanolic solution of tellurophen must *not* be concentrated under reduced pressure, otherwise most of the product will be lost. (f) The preparation was repeated several times and the average yield was 47%.

The physical properties of tellurophen (1) are reported in Table 1 together with those of its congeners. The i.r. spectrum shows a limited number of medium and strong bands (see Table 2) and is similar to the spectra of thiophen and selenophen. The most significant differences are the presence [in the spectrum of (1)] of a band at 1316 and a doublet at 1245 and 1227 cm<sup>-1</sup>. The u.v. spectrum (in n-hexane) exhibits three bands, at 209, 241, and 279 nm (see Table 3). Although there is some controversy<sup>10</sup> over the theoretical interpretation of the u.v. spectra of five-membered heterocycles, the

<sup>5</sup> R. F. Curtis, S. N. Hasnan, and J. A. Taylor, *Chem. Comm.*, 1968, 365.

<sup>6</sup> J. Reisch and K. E. Schulte, *Angew. Chem.*, 1961, 241.

<sup>7</sup> G. Markl and R. Potthast, *Angew. Chem.*, 1967, 58; P. Coggon, J. F. Engel, and A. T. McPhail, *J. Amer. Chem. Soc.*, 1970, 92, 5779.

<sup>8</sup> J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1951, 44.

<sup>9</sup> C. A. Kraus, *J. Amer. Chem. Soc.*, 1922, 44, 1222; C. A. Kraus and C. Y. Chin, *ibid.*, p. 1999; G. Brauer, 'Handbook of Preparative Inorganic Chemistry,' vol. 1, 2nd edn., Academic Press, New York, 1963, p. 441.

<sup>10</sup> R. M. Silverstein and G. C. Bassler, 'Spectrometric Identification of Organic Compounds,' 2nd edn., Wiley, London, 1968; H. H. Jaffé and N. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, London, 1962; C. N. R. Rao, 'Ultraviolet and Visible Spectroscopy,' 2nd edn., Butterworths, London, 1967.

\* The use of butadiyne and its derivatives in the synthesis of heterocyclic five-membered rings is a general synthetic route.<sup>3-7</sup>

<sup>1</sup> G. Marino, *Adv. Heterocyclic Chem.*, in the press; N. N. Magdesieva, *ibid.*, 1971, 12, 1.

<sup>2</sup> (a) W. Mack, *Angew. Chem. Internat. Edn.*, 1966, 5, 986; (b) E. A. Braye, W. Hübel, and J. Caplier, *J. Amer. Chem. Soc.*, 1961, 83, 4406; (c) W. Mack, *Angew. Chem.*, 1965, 77, 260.

<sup>3</sup> I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1947, 1586.

<sup>4</sup> F. Bohlmann and E. Bresinsky, *Chem. Ber.*, 1967, 100, 107; K. E. Schulte, J. Reisch, and L. Horner, *Angew. Chem.*, 1960, 920.

TABLE 1

Comparison of physical properties of tellurophen and its congeners

	B.p. [ $^{\circ}\text{C}$ (mmHg)]	M.p. ( $^{\circ}\text{C}$ )	$d_4$ ( $T/^{\circ}\text{C}$ )	$n_D^{20}$	$\text{MR}_D^a$	Ref.
Furan	32 (758)		0.9366 (20)	1.4216	18.45	13
Thiophen	84.12 (760)	-38.3	1.0648 (20)	1.5289	24.32	14
Selenophen	110—110.7 (758)	-38	1.5251 (20)	1.5642	27.74	15
Tellurophen	91—92 (100)	ca. -36	2.13 (22)	1.6844	32.08	2a, this work

<sup>a</sup> Molar refraction ( $\text{cm}^3 \text{mol}^{-1}$ )

band below 220 nm has been ascribed to diene absorption. On these grounds, tellurophen (1) should be more akin to furan in aromatic character than to thiophen (see Table 3).

TABLE 2

Medium and strong bands in the i.r. spectra of tellurophen and its congeners

	$\nu/\text{cm}^{-1}$ (film)
Furan	3150, 3122, 1485, 1380, 1172, 1060, 991, 868, 740
Thiophen	3110, 1408, 1251, 1080, 1033, 832, 712
Selenophen	3105, 1428, 1242, 1080, 1015, 758, 700
Tellurophen	3090, 1431, 1316, 1245, 1227, 1078, 983, 796, 672

TABLE 3

U.v. absorption spectra of tellurophen and its congener in n-hexane

	$\lambda_{\text{max.}}/\text{nm}$ ( $\epsilon_{\text{max.}}$ )	Ref.
Furan	215.5 (5000)	16
Thiophen	231 (5900)	16
Selenophen	232 (3300), 251 (5260)	17
Tellurophen	209 (3700), 241 (2300), 279 (8600)	This work

TABLE 4

Comparison of n.m.r. data <sup>a</sup> of tellurophen and its congeners

	2-H	3-H	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	Ref.
Furan	2.71	3.76	1.75	0.85	1.40	3.30	18
Thiophen	2.82	3.01	4.90	1.04	2.84	3.50	18
Selenophen	2.12	2.78	5.40	1.46	2.34	3.74	18
Tellurophen	1.13	2.22	6.70	1.30	2.60	4.00	This work

<sup>a</sup>  $\tau$  Values (ref. internal tetramethylsilane);  $J$  in Hz.

The n.m.r. spectrum of tellurophen (1) (100 MHz;  $\text{CDCl}_3$ ) shows two multiplets (1:1) at  $\tau$  1.13 and 2.22

shows that the protons of tellurophen resonate at much lower field than those of other heterocyclic compounds. This cannot be due to the inductive deshielding effect of the heteroatom; other effects (*i.e.*, diamagnetic anisotropy and geometry of the ring) must be invoked.

The coupling constants quoted for tellurophen (Table 4) are means of the values obtained from the analysis of the single spectrum and those obtained from substituted derivatives (Table 5). The spectra of substituted tellurophenes can be readily analysed, owing to the large differences in chemical shifts of  $\alpha$ - and  $\beta$ -protons of the ring, and the ring-proton coupling constants for the available substituted tellurophenes are not greatly influenced by substituents. A similar approach has been used<sup>11</sup> for furan. The coupling constants  $J_{2,3}$  and  $J_{3,4}$  (see Table 4) increase from furan to tellurophen, in agreement both with the decrease in electronegativity of the heteroatom and with the change of angle between the bonds to the protons and the carbon-carbon bond. The spectroscopic data for tellurophen thus indicate that it possesses a heteroaromatic character similar to its congeners.

The few known derivatives of tellurophen have been synthesized<sup>2</sup> directly from suitably substituted butadiynes, but this approach has only limited application.

The derivatives described here have been prepared by submitting tellurophen (1) to classical substitution reactions. This permits both the synthesis of mono-substituted derivatives and a first qualitative study of the chemical behaviour of the tellurophen ring.

TABLE 5

N.m.r. data <sup>a</sup> of substituted tellurophenes

Substituents			3-H	4-H	5-H	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$	Additional data
2-	5-								
H	H	(1)	2.22	2.22	1.13	4.00	6.70	1.30	$J_{2,5}$ 2.60
$\text{CO}_2\text{H}$	H	(2)	1.41	2.09	0.66	4.00	6.80	1.20	$\text{CO}_2\text{H}$ (-1.78)
$\text{COMe}$	H	(8)	1.69	2.04	0.68	4.10	6.60	1.30	Me (7.45)
$\text{CH}(\text{OH})\text{Me}$	H	(9)	2.58	2.33	1.23	4.00	6.80	1.30	OH (7.57); Me (8.48); CH (5.05); $J_{\text{CH,Me}}$ 6.3;
$\text{CO}_2\text{H}$	Me	(7)	1.64	2.62		4.10			$J_{\text{Me,3}}$ 1 $\text{CO}_2\text{H}$ (-0.68); Me (7.36);
$\text{CO}_2\text{Me}$	$\text{COMe}$	(10)	1.41	1.68		4.00			$J_{\text{Me,4}}$ 1 $\text{COMe}$ (7.47); $\text{CO}_2\text{Me}$ (6.18)
$\text{CO}_2\text{H}$	$\text{COMe}$	(11)	1.31	1.66		4.10			$\text{CO}_2\text{H}$ (0.76); Me (7.45)

<sup>a</sup>  $\tau$  Values (ref. internal tetramethylsilane); solutions in  $\text{CDCl}_3$  and at room temperature;  $J$  in Hz. The spectrum of the keto-acid (11) was recorded at  $70^{\circ}$ ; at this temperature the compound was sufficiently soluble in  $\text{CDCl}_3$ .

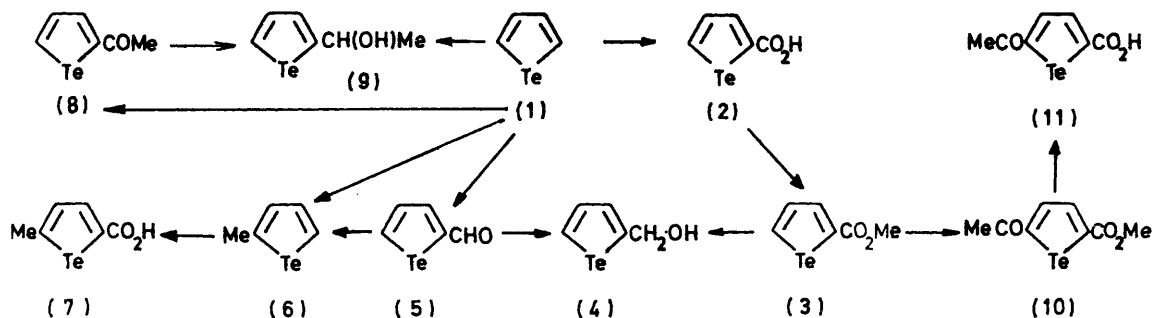
(see Table 4). We assign the low-field multiplet to the 2- and 5-protons, and the multiplet at 2.22 to the 3- and 4-protons by analogy with the spectra of furan, thiophen, and selenophen (see Table 4), and in the light of the data for substituted tellurophenes (see Table 5). Table 4

When tellurophen (1) was metallated with n-butyllithium in ether and the product then carboxylated, tellurophen-2-carboxylic acid (2) was obtained in 37%

<sup>11</sup> R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 905.

yield. The n.m.r. spectrum of the acid (2) is similar to that of 2-furoic acid<sup>11</sup> and shows three quartets at  $\tau$  0.66, 1.41, and 2.09 and a singlet at  $-1.78$ , each of which integrated for one proton. The singlet is assigned to the carboxylic proton and the three quartets to the 5-, 3-, and 4-protons respectively (see Table 5). This assignment is made on the basis of comparison with the n.m.r. spectrum of 5-methyltellurophen-2-carboxylic acid (7), and in the light of substituent effects (see before) and coupling constant data. The multiplicity of the quartets is due to the coupling of each ring proton with the other two protons.

Treatment of the acid (2) with ethereal diazomethane gave the methyl ester (3), which was converted into tellurophen-2-ylmethanol (4) by reduction with lithium



aluminium hydride. The alcohol (4) was also obtained by treating tellurophen (1) with *n*-butyl-lithium followed by *N*-methylformanilide, and then reducing the resulting aldehyde (5) with lithium aluminium hydride.

Alkylation of the tellurophen-2-yl-lithium (from tellurophen and *n*-butyl-lithium) with dimethyl sulphate gave a mixture of 2-methyltellurophen (6) (75%), unchanged tellurophen (1) (24.5%), and a minor component (0.5%; probably 3-methyltellurophen). The major component (6) was purified by fractional distillation and was also obtained by Wolff-Kishner reduction of the aldehyde (5).

The methyltellurophen (6) was metallated with *n*-butyl-lithium and the product mixture carboxylated with solid carbon dioxide to give 5-methyltellurophen-2-carboxylic acid (7). The n.m.r. spectrum shows (see Table 5) two singlets, at  $\tau$   $-0.68$  ( $\text{CO}_2\text{H}$ ) and  $7.36$  (Me), one doublet at  $1.64$  (3-H) and one multiplet at  $2.62$  (4-H,  $J_{4,3}$  4.0;  $J_{\text{Me},4}$  1 Hz). This side-chain coupling is well known<sup>11,12c</sup> in heterocyclic compounds.

Treatment of tellurophen (1) with acetic anhydride in the presence of tin(IV) chloride gave 2-acetyltellurophen (8). In the n.m.r. spectrum the ring protons reveal an AMX system identical with that of acid (2); the data in Table 5 strongly support structure (8), which also agrees with the i.r. spectrum.

<sup>12</sup> (a) Y. Pascal, J. P. Morizur, and J. Wiemann, *Bull. Soc. chim. France*, 1965, 2211; (b) J. P. Morizur and Y. Pascal, *ibid.*, 1966, 2296; (c) A. R. Katritzky, 'Physical Methods in Heterocyclic Chemistry,' vol. II, Academic Press, New York, 1963.

<sup>13</sup> 'Handbook of Chemistry and Physics,' 49th edn., 1968—1969.

The alcohol (9) was obtained both by lithium aluminium hydride reduction of the ketone (8) and by condensation of tellurophen-2-yl-lithium with acetaldehyde. Methyl 5-acetyltellurophen-2-carboxylate (10) was obtained in good yield by acetylation of the ester (3) with acetic anhydride under Friedel-Crafts conditions. Alkaline hydrolysis of the product (10) gave the acid (11). Structures (9)—(11) were supported by spectroscopic data (n.m.r. and i.r.).

Our results show that tellurophen is a typical heteroaromatic five-membered ring: it undergoes electrophilic and nucleophilic reactions, and is more reactive at the 2- than at the 3-position. However, the following observations show that the presence of the tellurium atom induces significant differences from furan, thiophen, and

selenophen: (a) tellurophen is very sensitive to mineral acids and in the presence of halogens gives addition products<sup>2a</sup> at position 1; (b) we were not able to obtain the desired products by nitration of compounds (1)—(3) with nitric acid-acetic acid under the usual conditions; (c) attempted conversion of the acetyl group of (10) into a carboxylic group *via* a halogenoform reaction was unsuccessful; and (d) alkylation (and arylation) of the tellurophen-2-yl-lithium with ethyl bromide (and bromobenzene) gave unsatisfactory results.

TABLE 6

Substituent effects on the chemical shifts of ring protons in substituted tellurophenes in  $\text{CDCl}_3$

Substituents			$\Delta\tau_3$	$\Delta\tau_4$	$\Delta\tau_5$
2-	5-				
$\text{CO}_2\text{H}$	H	(2)	0.81	0.13	0.47
$\text{COMe}$	H	(8)	0.53	0.18	0.45
H	H	(1)	0	0	0
$\text{CH(OH)Me}$	H	(9)	-0.36	-0.11	-0.10
$\text{CO}_2\text{H}$	Me	(7)	0.58	-0.40	
$\text{CO}_2\text{Me}$	$\text{COMe}$	(10)	0.81	0.54	
$\text{CO}_2\text{H}$	$\text{COMe}$	(11)	0.91	0.56	

We now describe the effect of substituents on chemical shifts (see Table 6). An electron-withdrawing substituent at C-2 shifts the ring-proton signals to low field

<sup>14</sup> F. S. Fawcett and H. E. Rasmussen, *J. Amer. Chem. Soc.* 1945, **67**, 1705; W. E. Haines, R. V. Helm, C. W. Baily, and J. S. Ball, *J. Phys. Chem.*, 1954, 270.

<sup>15</sup> Yu. K. Yur'ev, *J. Gen. Chem. (U.S.S.R.)*, 1946, **16**, 851.

<sup>16</sup> G. Horvath and A. I. Kiss, *Spectrochim. Acta*, 1967, 921.

<sup>17</sup> A. Bellotti and L. Chierici, *Gazzetta*, 1960, **90**, 1125; L. Chierici and G. Pappalardo, *ibid.*, 1958, **88**, 453.

<sup>18</sup> J. M. Read, jun., C. T. Mathis, and J. H. Goldstein, *Spectrochim. Acta*, 1965, **21**, 85.

( $\Delta\tau$  positive), whereas an electron-donating substituent tends to shift the signals to high field ( $\Delta\tau$  negative). The largest shift is shown by the 3-proton signal, because of electronic and anisotropic effects. A similar situation is observed in 2,5-disubstituted derivatives. The results are in agreement with those<sup>11,12</sup> for derivatives of furan and thiophen.

It seems that the additivity rule for multiple substitution also applies to derivatives of tellurophen. Use of the procedure of Morizur and Pascal<sup>12b</sup> yields values of  $\tau$  1.23 and 1.56 respectively for the 3- and 4-protons of the 5-acetyltellurophen-2-carboxylic acid (11), in good agreement with the data in Table 5.

#### EXPERIMENTAL

Ligroin refers to light petroleum with b.p. 100–120°. I.r. spectra were recorded with a Perkin-Elmer model 257 instrument and u.v. spectra with a Beckman DKW instrument. N.m.r. spectra were recorded with Varian A-100 or Jeol JNM-60 HL spectrometers.

**Tellurophen (1).**—A four-necked flask (2 l) (A) equipped with a mechanical stirrer, a gas inlet tube, and a potassium hydroxide guard tube was purged with dry nitrogen, and liquid ammonia (1.2 l) was distilled from sodium into the flask cooled in a solid carbon dioxide-acetone bath at  $-55^\circ\text{C}$ . Sodium (14.6 g) followed by tellurium (36.5 g) was then added in portions under nitrogen with stirring; stirring was continued at  $-55^\circ$  for a further 2 h and then the ammonia was evaporated off (*ca.* 10–12 h) under nitrogen. To the white sodium telluride thus obtained, dry deaerated methanol (1.1 ml) was added; the mixture was stirred until the solid dissolved. A current of nitrogen was then bubbled into the violet solution for 4 h to evaporate the residual ammonia. The butadiyne was prepared separately in a three-necked flask (B) fitted with a mechanical stirrer, a gas inlet, and a condenser connected (Pyrex tubes) through a trap to a column (40  $\times$  2.5 cm) filled with anhydrous calcium chloride. The apparatus (B) was purged with dry nitrogen. A solution of a potassium hydroxide (169 g) in distilled, deaerated water (1.7 l) and a solution of 1,4-dichlorobut-2-yne (173 g) in dioxan (169 ml) were added. Systems (A) and (B) were connected and flushed with a slow current of dry nitrogen. The solution in (B) was then heated under reflux with vigorous stirring and the butadiyne was bubbled into (A), which was cooled at  $0^\circ\text{C}$ . After 20 min the ice-bath was removed from (A) and the heating of (B) was continued for 2 h. The black precipitate which formed was filtered off and the resulting yellow methanolic solution was diluted with water (3 l) and extracted with ether (4  $\times$  1 l). The extracts were washed with saturated sodium chloride solution, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated at 18 mmHg and  $0-5^\circ$ . The residue was distilled\* at 100 mmHg to give pure (g.l.c.) tellurophen (1) (24.5 g) (see Tables 1–4) (Found: C, 26.65; H, 2.3.  $\text{C}_5\text{H}_4\text{Te}$  requires C, 26.7; H, 2.4%). Tellurophen (1) (0.5 g) was treated with a methanolic solution of bromine to give an insoluble orange precipitate (1,1-dibromotellurophen), m.p.  $125^\circ$  (decomp.) [lit.,<sup>2a</sup>  $125^\circ$  (decomp.)].

**Tellurophen-2-carboxylic Acid (2).**—A 20% solution of n-butyl-lithium in hexane (60 ml) was added dropwise under nitrogen to a stirred solution of tellurophen (1) (20 g) in dry ether (150 ml). At the end of the exothermic reaction, the

\* At the end of distillation decomposition sometimes occurred; in which case the distillation had to be repeated.

mixture was stirred for 45 min at room temperature and then poured (under nitrogen) into a slurry of dry ether (400 ml) and crushed solid carbon dioxide (300 g). After evaporation of the  $\text{CO}_2$  and addition of water (300 ml), the aqueous layer was separated, acidified with dilute  $\text{H}_2\text{SO}_4$  and cooled to  $5^\circ\text{C}$ . The yellow precipitate was filtered off and crystallized from ligroin (charcoal) to give the acid (2) (9.3 g), m.p.  $110-111^\circ$ ,  $\nu_{\text{max}}$  (Nujol)  $1660\text{ cm}^{-1}$  (C=O); n.m.r. data in Table 5 (Found: C, 26.9; H, 1.9.  $\text{C}_5\text{H}_4\text{O}_2\text{Te}$  requires C, 26.8; H, 1.9%).

**Methyl Tellurophen-2-carboxylate (3).**—The acid (2) (10 g) was treated with ethereal diazomethane to give the ester (3) (10 g), pure by g.l.c., b.p.  $118-120^\circ$  at 13 mmHg,  $n_D^{24}$  1.6358,  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ )  $1700\text{ cm}^{-1}$  (C=O) (Found: C, 30.2; H, 2.7.  $\text{C}_6\text{H}_6\text{O}_2\text{Te}$  requires C, 30.3; H, 2.7%).

**Tellurophen-2-carbaldehyde (5).**—Tellurophen (1) (4 g) was metallated with a 20% solution of n-butyl-lithium in n-hexane (10.4 ml) under nitrogen as before, and to the stirred solution *N*-methylformanilide (3 g) in ether (4 ml) was added dropwise. The mixture was heated under reflux for 1 h and then poured into concentrated HCl (4.5 ml) mixed with crushed ice. The organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were washed with 0.01N-HCl, followed by sodium hydrogen carbonate solution, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated *in vacuo*. To the residue was added a small amount of ethanol and then a saturated solution of sodium hydrogen sulphite (30 ml), and the whole was thoroughly mixed, and left for 40 min. Water (50 ml) was added and the solution was extracted with ether. To the aqueous layer an excess of sodium carbonate was added. The re-generated aldehyde was extracted with ether and worked up as usual to give pure (g.l.c.) aldehyde (5) (1.1 g), b.p.  $90-92^\circ$  at 2 mmHg,  $\nu_{\text{max}}$  (film)  $1655\text{ cm}^{-1}$  (C=O) (Found: C, 28.7; H, 2.15.  $\text{C}_5\text{H}_4\text{OTe}$  requires C, 28.9; H, 2.1%).

**Tellurophen-2-ylmethanol (4).**—The ester (3) (0.850 g) in dry ether (15 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.14 g) in dry ether (15 ml) at  $0^\circ$ . The mixture was then stirred for 40 min at  $0^\circ$  and then for 2.5 h at room temperature. Ice and dilute sodium hydroxide were added and the mixture was worked up as usual. The residual oil was chromatographed over alumina (gradient elution with light petroleum-ether) to give alcohol (4) (0.200 g) (pure by g.l.c.),  $\nu_{\text{max}}$  (film)  $3330\text{ cm}^{-1}$  (OH) (Found: C, 28.7; H, 3.1.  $\text{C}_5\text{H}_6\text{OTe}$  requires C, 28.68; H, 3.1%). An identical product (i.r. and g.l.c.) was obtained by similar reduction of tellurophen-2-carbaldehyde (5).

**2-Methyltellurophen (6).**—(a) Tellurophen (1) (8 g) in dry ether (40 ml) was metallated with a 20% solution of n-butyl-lithium in n-hexane (21 ml). Freshly distilled dimethyl sulphate (5 ml) in dry ether (20 ml) was added dropwise with stirring. The mixture was stirred for 24 h, cooled, and then dilute sodium hydroxide was added. The organic layer was separated and the mother liquor extracted with ether. The combined extracts were washed with saturated sodium chloride solution, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated *in vacuo* to give a mixture (7.5 g) of tellurophen (1) (24.5%), 2-methyltellurophen (6) (75%), and a minor component (0.5%; 3-methyltellurophen probably) in order of increasing retention times on g.l.c. The 2-methyltellurophen was purified by fractional distillation; b.p.  $108-110^\circ$  at 100 mmHg (Found: C, 30.85; H, 3.3.  $\text{C}_5\text{H}_6\text{Te}$  requires C, 30.9; H, 3.3%).

(b) A solution of tellurophen-2-carbaldehyde (5) (0.400 g),

hydrazine hydrate (85%; 0.60 ml), and ethylene glycol (8 ml) was heated at 140° for 20 min. The solution was cooled to 50–60°, then potassium hydroxide (0.4 g) was added and the mixture was heated at 90–100° for 20 min, cooled, and extracted with ether. The extract was washed with dilute hydrochloric acid and then worked up as usual to give 2-methyltellurophen (6) (0.150 g), identical with the sample prepared by alkylation.

*5-Methyltellurophen-2-carboxylic Acid* (7).—Following the described procedure for the acid (2), the 2-methyltellurophen (6) was carboxylated to the *methyl-acid* (7) (35%) m.p. 149–150° (from water), n.m.r. data in Table 5 (Found: C, 30.2; H, 2.7.  $C_8H_8O_2Te$  requires C, 30.3; H, 2.7%).

*2-Acetyltellurophen* (8).—A solution of tin(IV) chloride (0.3 g) in acetic anhydride (9 g) was added dropwise and with stirring to tellurophen (1) (6 g) at –10°. The mixture was left at room temperature for 3 h and was then poured into a solution of sodium hydrogen carbonate and extracted with ether. The usual work-up gave a residual oil which was chromatographed on alumina [eluant light petroleum-ether (3:1)] to give *2-acetyltellurophen* (8) (2 g) (pure by g.l.c.), b.p. 134–136° at 15 mmHg,  $n_D^{24}$  1.6687,  $\nu_{max}$  (film) 1645  $cm^{-1}$  (C=O),  $\lambda_{max}$  (n-hexane) 211 ( $\epsilon$  8600), 232 (7400), and 346 nm (3800), n.m.r. data in Table 5 (Found: C, 32.4; H, 2.8.  $C_8H_8OTe$  requires C, 32.4; H, 2.9%).

*1-(Tellurophen-2-yl)ethanol* (9).—Tellurophen (1) (4 g) was metallated in dry ether (20 ml) as before. The mixture was cooled to –15° and a solution of acetaldehyde (3 ml) in dry ether (10 ml) was added dropwise with stirring. The mixture was stirred for 3 h at room temperature, poured into ice-water, and extracted with ether, and the product was worked up as usual to give the *alcohol* (9) (3 g) (pure by g.l.c.), b.p. 133–135° at 15 mmHg,  $n_D^{26}$  1.6307,  $\nu_{max}$  (film) 3480  $cm^{-1}$  (OH), n.m.r. data in Table 5 (Found: C, 32.1; H, 3.9.  $C_8H_8OTe$  requires C, 32.1; H, 3.85%).

Reduction of the ketone (8) with lithium aluminium

hydride, as described for the ester (3), gave the alcohol (9), identical (i.r. and g.l.c.) with the sample previously prepared.

*Methyl 5-Acetyltellurophen-2-carboxylate* (10).—To a stirred solution of tin(IV) chloride (30.2 ml;  $d$  2.22) in benzene (35 ml) at 0°, was added a solution of the ester (3) (9 g) in acetic anhydride (4.6 ml) at a suitable rate to maintain the temperature below 5°. The mixture was then stirred at 5° for 30 min, at room temperature for 1 h, and then at 50–55° for 18 h, poured into ice-hydrochloric acid, and extracted with benzene. The extracts were washed with a saturated solution of sodium hydrogen carbonate and then water, dried ( $Na_2SO_4$ ), and evaporated *in vacuo*. The residue, chromatographed on alumina [eluants light petroleum and light petroleum-ether (1:1)] gave the *keto-ester* (10) (4.5 g), m.p. 80–81°,  $\nu_{max}$  ( $CHCl_3$ ) 1706 ( $CO_2Me$ ) and 1665  $cm^{-1}$  (COMe), n.m.r. data in Table 5 (Found: C, 34.2; H, 3.1.  $C_8H_8O_3Te$  requires C, 34.3; H, 3.1%).

*5-Acetyltellurophen-2-carboxylic Acid* (11).—To a solution of the foregoing ester (10) (1.1 g) in ethanol (95%; 30 ml), *N*-sodium hydroxide (8.0 ml) was added and the mixture was heated under reflux for 1.5 h. The cooled solution was then extracted with ether, and the aqueous layer was acidified with dilute sulphuric acid and extracted with ether. The latter ethereal solution was worked up as usual to give the *acid* (11) (1 g), m.p. 190–191° (from water),  $\nu_{max}$  (Nujol) 1690 ( $CO_2H$ ) and 1655  $cm^{-1}$  (COMe), n.m.r. data in Table 5 (Found: C, 31.6; H, 2.5.  $C_7H_8O_3Te$  requires C, 31.6; H, 2.4%). Treatment of the ester (11) (0.1 g) with ethereal diazomethane gave the starting keto-ester (10).

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