Heteroaromatic Rings as Substituents. Part 5.[1] Evaluation of σ and σ^- Constants of 2-Selenienyl and 2-Tellurienyl Groups

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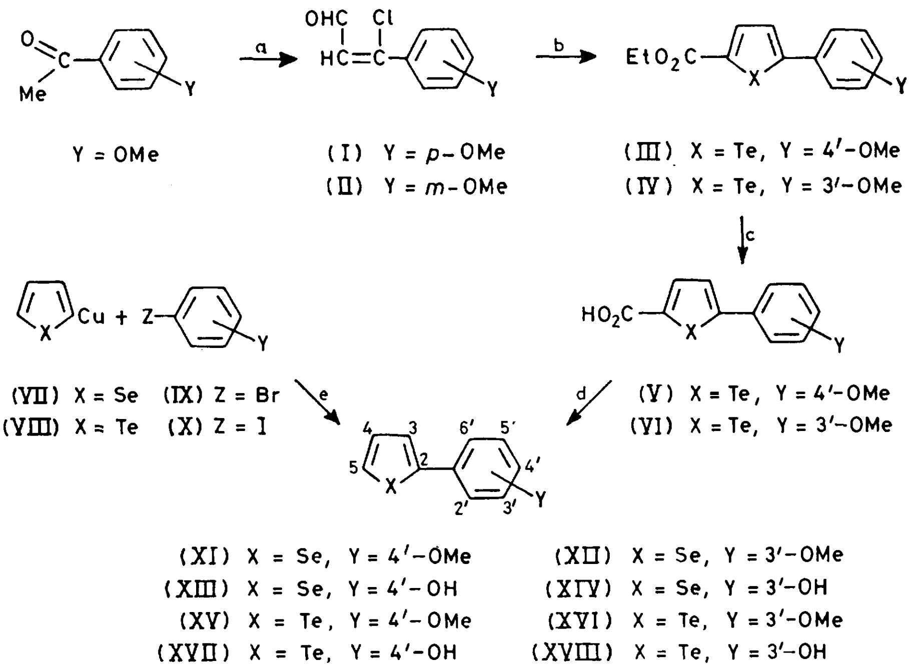
p- and *m*-2-selenienyl- and 2-tellurienyl-anisoles, *p*- and *m*-2-selenienyl- and 2-tellurienyl-phenols, and four 2,5-disubstituted tellurophens were synthesized and their structures established by ^{1}H n.m.r. and mass spectra. The σ^- and σ constants for *p*- and *m*-2-selenienyl and *p*- and *m*-2-tellurienyl were determined by the ionization reaction of monosubstituted phenols in 30% ethanol–water at 25 °C, by chemical shifts of the hydroxy-protons of phenols in DMSO, and by solvent chemical shifts of the methoxy-protons of anisoles. The 2-senenienyl and 2-tellurienyl groups are weakly, inductively electron-withdrawing and show greater ability to delocalize a negative charge by mesomeric effects. The results were compared with the substituent effects of 2-furyl and 2-thienyl.

CONTINUING our studies on tellurophen chemistry [2] and heteroaromatic rings as substituents [1,3] we were interested in evaluating the ability of 2-selenienyl and 2-tellurienyl groups to withdraw or release electrons according to the type of reaction. This effect is suitably measured by the three substituent constants, σ, σ^-, and σ^+.

The present paper reports the electronic effects of the *p*- and *m*-2-selenienyl and *p*- and *m*-2-tellurienyl groups for reactions in which there is not an important interaction between the substituent and the reaction site (σ constant) and for reactions in which the substituent interacts with a developing negative charge (σ^- constant).

Syntheses.—It has been reported [4] that the silylated reagents (IX and X; Y = *p*- or *m*-$OSiMe_3$) react with 2-furyl- and 2-thienyl-copper under Ullmann conditions to give aryl-heteroaryl compounds which may be easily desilylated to give the five hydroxy-containing products without isolation of intermediates. Attempts to prepare *p*- and *m*-2-selenienylphenols (XIII) and (XIV) following this procedure were unsuccessful. *p*- and *m*-2-selenienylanisoles (XI) and (XII) were prepared first by a modified Ullmann reaction [5] between 2-selenienylcopper (VII) and *p*- or *m*-iodoanisole (X; Y = *p*- or *m*-OMe) respectively in pyridine. The reaction yield is lower (15%) than that with 2-thienylcopper (55%) and it is further reduced by using the bromoanisoles.



SCHEME Reagents: a, $POCl_3$–DMF; b, $BrCH_2CO_2Et$–Na_2Te; c, KOH–H$^+$; d, copper chromite–quinoline; e, pyridine

A by-product of the reaction is 2,2′-diselenienyl (from 'dimerization' of 2-selenienylcopper) which was recognized by ^{1}H n.m.r. and mass spectra. The n.m.r. spectrum shows a double doublet at δ 7.60 (α-protons) and a multiplet at 7.05 (β-protons) respectively with J_o 5.0 and J_m 1.7 Hz. The mass spectrum shows a molecular ion (base peak), which can be easily computer-simulated using the stable isotopes of selenium, and an M — Se ion as the most important fragments.

Demethylation of (XI) and (XII) with sodium thioethoxide [6] (molar ratio methoxy-derivative : sodium thioethoxide 1 : 3) in dimethylformamide (DMF) at 130° gives the phenols (XIII) and (XIV) in high yield.

TABLE 1 [a]

^{1}H N.m.r. chemical shifts (δ) and coupling constants (J) of selenienyl- and tellurienyl-phenols and -anisoles [a]

Compound	H-3	H-4	H-5	H-2′	H-3′	H-4′	H-5′	H-6′	Additional data
(III)	7.65 (d)	8.35 (d)		7.35 (d)	6.77 (d)		6.77 (d)	7.35 (d)	OMe (3.77, s); CH_2 (4.25, q); Me (1.35, t); $J_{3.4}$ 4.2; $J_{2.3}$ 8.0; $J_{CH_2,Me}$ 6.0
(IV)	7.68 (d)	8.27 (d)		6.90 (m)		6.90 (m)	6.90 (m)	6.90 (m)	OMe (3.72, s); CH_2 (4.25, q); Me (1.32, t); $J_{CH_2,Me}$ 6.2
(V)	7.69 (d)	8.25 (d)		7.36 (d)	6.75 (d)		6.75 (d)	7.36 (d)	OMe (3.77, s); $J_{3.4}$ 4.2; $J_{2.3}$ 8.0
(VI)	8.05 (d)	8.37 (d)		7.15 (m)		7.15 (m)	7.15 (m)	7.15 (m)	OMe (3.80, s); $J_{3.4}$ 4.2
(XI)	7.13 (m)	7.13 (m)	7.65 (dd)	7.33 (d)	6.70 (d)		6.70 (d)	7.33 (d)	OMe (3.75, s); $J_{4.5}$ 5.5; $J_{3.5}$ 1.5; $J_{2.3}$ 8.0
(XII)	7.10 (m)	7.10 (m)	7.65 (dd)	7.10 (m)		6.60 (m)	7.10 (m)	7.10 (m)	OMe (3.78, s); $J_{4.5}$ 5.5; $J_{3.5}$ 1.5
(XIII)	7.23 (m)	7.23 (m)	7.76 (dd)	7.35 (d)	6.73 (d)		6.73 (d)	7.35 (d)	OH (4.95, s); $J_{4.5}$ 5.5; $J_{3.5}$ 1.5; $J_{2.3}$ 8.0
(XIV)	7.15 (m)	7.15 (m)	7.78 (dd)	7.15 (m)		6.65 (m)	7.15 (m)	7.15 (m)	OH (5.27, s); $J_{4.5}$ 5.5; $J_{3.5}$ 1.5
(XV)	7.55 (m)	7.55 (m)	8.50 (dd)	7.25 (d)	6.70 (d)		6.70 (d)	7.25 (d)	OMe (3.75, s); $J_{4.5}$ 6.9; $J_{3.5}$ 1.4; $J_{2.3}$ 8.0
(XVI)	7.65 (m)	7.65 (m)	8.60 (m)	6.90 (m)		6.90 (m)	6.90 (m)	6.90 (m)	OMe (3.77, s)
(XVII)	7.60 (m)	7.60 (m)	8.64 (dd)	7.30 (d)	6.75 (d)		6.75 (d)	7.30 (d)	OH (5.45, s); $J_{4.5}$ 6.8; $J_{3.5}$ 1.4; $J_{2.3}$ 8.0
(XVIII)	7.73 (m)	7.73 (m)	8.75 (m)	7.05 (m)		7.05 (m)	7.05 (m)	7.05 (m)	OH (5.40, s)

[a] For numbering system see Scheme. $CDCl_3$ was used as solvent except for carboxylic acids whose spectra were recorded in DMSO. Concentration was *ca.* 60—100 mg ml^{-1}. δ Values from internal Me_4Si. J in Hz. Multiplicity: s = singlet; d = doublet; dd = double doublet; t = triplet; q = quartet; m = multiplet.

The preparation of *p*- and *m*-2-tellurienylanisoles (XV) and (XVI) *via* tellurienylcopper derivatives failed, so that the synthesis of these compounds was achieved by the Cagniant [7] procedure, based on the condensation of a β-halogenocinnamaldehyde with sodium telluride and α-halogenoesters.

β-Chlorocinnamaldehydes (I) and (II) were obtained in good yield by Vilsmeier–Haack chloroformylation [8] of *p*- and *m*-methoxyacetophenone. The temperature of the reaction and the pH of the subsequent process of decomposition in ice–water must be carefully controlled. β-Chlorocinnamaldehydes (I) and (II) retain water which must be eliminated before condensation, but in the dry state they are quite unstable. The ^{1}H n.m.r. spectra (see Experimental section) are consistent with the structures and the chemical shifts of protons of formyl groups, δ 9.65 for (I) and 10.04 for (II), suggest a (Cl,CHO)-*cis* configuration.[9]

Condensation of (I) and (II) with sodium telluride and α-bromoethyl acetate in DMF gives 2-(*p*-methoxyphenyl)-5-carboxyethyltellurophen (III) and 2-(*m*-methoxyphenyl)-5-carboxyethyltellurophen (IV), respectively.

The ethyl esters (III) and (IV) were then hydrolysed to the corresponding acids (V) and (VI) which were decarboxylated with copper chromite in quinoline to *p*- and *m*-2-tellurienylanisole (XV) and (XVI).

The demethylation of (XV) and (XVI) to the corresponding phenols (XVII) and (XVIII) was a very difficult reaction. Compound (XVII) was obtained in 20% yield by treating (XV) with sodium thioethoxide in DMF with a molar ratio (XVII) : sodium thioethoxide of 1 : 8. The demethylation of (XVI) was achieved, after many attempts, by using, in large excess, boron trifluoride [10] in dichloroethane at —40 °C.

The structures of all compounds were established by ^{1}H n.m.r. and mass spectra. The signals (Table 1) were assigned by reference to previous data.[11] The main ions in the mass spectra contain the heteroatom and are readily identified due to the presence of a series of peaks with characteristic ratios due to the many stable isotopes of selenium or tellurium.[12] The following comments may be made: (i) the molecular ion is always the base peak; (ii) only for (XI) among the anisoles is there a significant presence of the $M - CH_3$ ion; (iii) the ethyl esters (III) and (IV) show a variety of ions in agreement with the fragmentation of aryl esters;[13] (iv) the main fragment in both carboxylic acids (V) and (VI) is the ion M — OH.

The σ Constants.—The most correct approach in determining the σ and σ^- constants is the ionization reaction of monosubstituted benzoic acids and phenols at 25 °C. Spectroscopic data were also used, but in this case a critical check is necessary before comparing the σ values with those from ionization reactions.

The ionization constants of 2-selenienyl- and 2-tellurienyl-phenols were determined (Table 2) at 25 °C in 30% ethanol–water (v/v). A reliable ρ value for this reaction in this solvent is available [3a] and σ^- constants for 2-selenienyl and 2-tellurienyl groups were calculated (Table 4) using the Hammett equation.

TABLE 2

pK_a Values of selenienyl- and tellurienyl-phenols in ethanol–water (3 : 7 v/v)

Phenol	No. of determinations	Average pK_a	Maximum deviations
p-2-Selenienylphenol (XIII)	3	10.10	0.02
m-2-Selenienylphenol (XIV)	2	10.26	0.02
p-2-Tellurienylphenol (XVII)	3	10.04	0.02
m-2-Tellurienylphenol (XVIII)	3	10.40	0.03

TABLE 3 [a]

Chemical shifts (δ) of hydroxy-protons in DMSO and methoxy-protons in CCl_4 and C_6H_6 of phenols and anisoles

Substituent	Phenol	Anisole (CCl_4)	Anisole (C_6H_6)
p-2-Furyl	9.54	3.76	3.30
m-2-Furyl	9.43	3.81	3.31
p-2-Thienyl	9.50	3.76	3.29
m-2-Thienyl	9.43	3.78	3.29
p-2-Selenienyl	9.52	3.75	3.28
m-2-Selenienyl	9.45	3.78	3.30
p-2-Tellurienyl	9.54	3.75	3.29
m-2-Tellurienyl	9.41	3.78	3.30
p-3-Thienyl	9.40	3.80	3.36
m-3-Thienyl	9.36	3.81	3.35

[a] Values from internal Me_4Si.

TABLE 4

σ and σ^- constants for 2-furyl, 2-thienyl, 2-selenienyl, and 2-tellurienyl groups from ionization and spectroscopic data

	Ionization		^1H n.m.r. [c]	
Substituent	σ	σ^-	σ	σ^-
p-2-Furyl	0.02 [a]	0.21 [a]	0.03	0.21
m-2-Furyl	0.06 [a]	0.11 [a]	0.09	0.13
p-2-Thienyl	0.05 [b]	0.19 [b]	0.04	0.18
m-2-Thienyl	0.09 [b]	0.11 [b]	0.08	0.13
p-2-Selenienyl		0.22	0.04	0.20
m-2-Selenienyl		0.16	0.06	0.15
p-2-Tellurienyl		0.25	0.03	0.21
m-2-Tellurienyl		0.10	0.06	0.12
p-3-Thienyl	−0.02 [b]	0.13 [b]	0.00	0.11
m-3-Thienyl	0.03 [b]	0.07 [b]	0.03	0.09

[a] Ref. 3*b*. [b] Ref. 3*a*. [c] Calculated by equations (1) and (2); the uncertainty is ±0.02 at a confidence level of 0.99.

Several authors [14] have observed that the chemical shifts of the hydroxy-protons of *meta*- and *para*-substituted phenols in DMSO can be correlated with the Hammett σ^- values.

An excellent linear correlation is observed (confidence level >0.999) and the equation (1) is obtained * by plotting reliable $\sigma_{m,p}^-$ values from the ionization of phenols (see Experimental section) *versus* recent [15] chemical shifts of the hydroxy-protons of 43 monosubstituted phenols in DMSO.

$$\sigma_{p,m}^- = 0.677\delta - 6.250 \ (r\ 0.988,\ s\ 0.062,\ n\ 43) \quad (1)$$

Tables 3 and 4 show the hydroxy chemical shifts of 2-furyl-, 2- and 3-thienyl-, 2-selenienyl-, and 2-tellurienyl-phenols in DMSO and the $\sigma_{p,m}^-$ values calculated by equation (1). The uncertainty of $\sigma_{p,m}^-$ is ±0.02 at 0.99 confidence level and the agreement with $\sigma_{p,m}^-$ values calculated by ionization constants is remarkably good.

As mentioned above the best approach in calculating the $\sigma_{p,m}$ constants is the 'classic' ionization reaction of substituted benzoic acids but at the present time there are difficulties in the synthesis of 2-selenienyl- and 2-tellurienyl-benzoic acids.

It is known [16] that benzene causes upfield shifts of the methoxy-resonances (relative to CCl_4 as solvent) in anisoles and the solvent shifts ($\Delta\delta = \delta_{CCl_4} - \delta_{C_6H_6}$) are in correlation with the Hammett $\sigma_{p,m}$ values. When literature data [16] for 28 *meta*- and *para*-monosubstituted anisoles are plotted against Hammett $\sigma_{p,m}$ values from ionization of benzoic acids, a very good linear correlation is observed (confidence level >0.999) and the equation (2) is obtained.†

$$\sigma_{p,m} = 1.655\Delta\delta - 0.733 \ (r\ 0.987,\ s\ 0.047,\ n\ 28) \quad (2)$$

Tables 3 and 4 give the methoxy-shifts in CCl_4 and benzene for 2-furyl-, 2- and 3-thienyl-, 2-selenienyl-, and 2-tellurienyl-anisoles and the $\sigma_{p,m}$ values calculated by equation (2). The uncertainty is ±0.02 at the 0.99 confidence level. A comparison (Table 4) with the $\sigma_{p,m}$ values of the 2-furyl and 2- and 3-thienyl groups calculated from the ionization reaction of benzoic acids is in good agreement, supporting the $\sigma_{p,m}$ values of 2-selenienyl and 2-tellurienyl. Our σ_p value for 2-selenienyl is in agreement, within experimental error, with that (σ_p 0.01) derived [17] from ionization of 5-substituted selenophen-2-carboxylic acids in 50% butylcellosolve–water (v/v) at 20 °C, but it is quite different from the value (σ_p −0.04) derived [18] from the i.r. stretching frequencies.

From the $\sigma_{p,m}$ and $\sigma_{p,m}^-$ values in this study and from a comparison with the corresponding σ values of the 2-furyl and 2-thienyl groups (Table 4) we conclude that: (i) 2-selenienyl and 2-tellurienyl are as weakly, inductively electron-withdrawing (positive σ_m) as 2-furyl and 2-thienyl but this is not essentially a polar effect of the heteroatom, because the effect of 2-furyl should be stronger than is observed; (ii) in the absence of important resonance interactions between the substituent and the reaction site, all four groups show an electron-releasing effect from the *para*-position as shown by the negative sign of ($\sigma_p - \sigma_m$) difference; (iii) σ_p^-, ($\sigma_p^- - \sigma_m^-$) and ($\sigma_p^- - \sigma_p$) show that 2-selenienyl and 2-tellurienyl easily delocalize a negative charge and the latter appears to show a higher ability than 2-furyl and 2-thienyl. These are the first reported data on the ability of the tellurophen ring to delocalize a negative charge.

EXPERIMENTAL

B.p.s and m.p.s are uncorrected. Light petroleum refers to the fraction with b.p. 40—60 °C and ligroin to that with b.p. 100—120 °C. ^1H N.m.r. spectra were recorded on a JEOL JNM-60 HI instrument. Mass spectra were recorded on a Varian MAT-311-A spectrometer; fragments containing selenium or tellurium are the main ions and are readily identified [12] due to the presence of a series of peaks with characteristic ratios due to the many stable isotopes of these elements; to simplify, only the base peak and $\%\Sigma_{70}$ of the main ions containing the heteroatom are reported. At *m/e* <70 there are no significant peaks.

p-2-*Selenienylanisole* (XI).—A 20% solution of n-butyllithium (7.5 ml) in dry ether (25 ml) was added under nitrogen to a stirred solution of selenophen (2.95 g) in dry

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* Previous equations were calculated using both a small number of substituents and some bisubstituted phenols; however the slope is not greatly different from that calculated in this study:
ref. 14*b* slope 0.650 (*r* 0.989, *s* 0.065, *n* 14)
ref. 14*c* slope 0.710 (*r* 0.997, *s* 0.031, *n* 22)
ref. 14*a* slope 0.700 (*r* 0.965, *s* 0.128, *n* 36)
For the data used in this study see Experimental section.

† Only qualitative observations have been reported for restricted numbers of substituents (ref. 16*a*, *n* 14 and 10; ref. 16*b*, *n* 13) and no least-squares computed equation was reported. For the data used in this study see the Experimental section.

ether (18.5 ml) at 0 °C. The mixture was left at room temperature for 1 h, diluted with dry ether (17 ml), and added dropwise and under nitrogen to a suspension of CuI (2.85 g) in dry ether (37 ml) at −10 °C. The suspension was stirred for 1 h at room temperature, the ether was distilled off, and pyridine (37 ml) and *p*-iodoanisole (3.5 g) were added. The mixture was stirred at 115 °C for 7 h, at room temperature for 10 h, and then diluted with water and extracted with ether. The extracts were washed with 10% HCl and water, dried (Na_2SO_4), and evaporated. The resulting oil was chromatographed on a column (silica gel) eluting with a gradient of light petroleum–ether (from 99 : 1 to 95 : 5). The first fraction gave 2,2′-diselenienyl (0.4 g), m.p. 45—46 °C (lit.,[19] 49 °C); δ ($CDCl_3$) 7.05 (4 H, m, β-H), 7.60 (2 H, dd, α-H, $J_{4.5}$ 5.0, $J_{3.5}$ 1.7 Hz); m/e 262 ($C_8H_6{}^{80}Se_2$ + $C_8H_6{}^{78}Se^{82}Se$, 100%), $\%\Sigma_{70}$ M^+ (46.8%), $M^+ - Se$ (11.60%).

The final fractions furnished pure compound (XI) (0.6 g), m.p. 108—109 °C, from light petroleum–chloroform (9 : 1); for ^1H n.m.r. see Table 1; m/e 238 ($C_{11}H_{10}{}^{80}Se$, 100%), $\%\Sigma_{70}$ M^+ (37.2%), $M^+ - Me$ (21.3%).

m-2-*Selenienylanisole* (XII).—Using the procedure for the preparation of (XI), we obtained a mixture of 2,2-diselenienyl and (XII) from which compound (XII) was easily separated by column chromatography in 20% yield, b.p. 115 °C at 0.2 mmHg; for ^1H n.m.r. see Table 1; m/e 238 ($C_{11}H_{10}{}^{80}Se$, 100%), $\%\Sigma_{70}$ M^+ (42.2%).

p-2-*Selenienylphenol* (XIII).—A solution of (XI) (0.375 g) in DMF (11 ml) was added over 30 min and under nitrogen to a stirred solution of sodium ethoxide (4.74 mmol) in dimethylformamide (DMF) (16.8 ml) and the mixture heated at 130 °C for 24 h. After cooling, the mixture was diluted with water and extracted with ether. The mother-liquors were acidified with 10% HCl, extracted with ether, and the extracts dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was chromatographed on a column (silica gel) eluting with light petroleum–ether (4 : 1) to give pure *compound* (XIII) (0.280 g), m.p. 133—134 °C [from ligroin–chloroform (1 : 1)], for ^1H n.m.r. see Table 1; m/e 224 ($C_{10}H_8O^{80}Se$, 100%), $\%\Sigma_{70}$ M^+ (63.4%) (Found C, 53.9; H, 3.8. $C_{10}H_8OSe$ requires C, 53.8; H, 3.6%).

m-2-*Selenienylphenol* (XIV).—Compound (XIV) was obtained in 80% yield using the procedure described for the *para*-isomer, m.p. 83—84 °C [from ligroin–chloroform (1 : 1)], for ^1H n.m.r. see Table 1; m/e 224 ($C_{10}H_8O^{80}Se$, 100%), $\%\Sigma_{70}$ M^+ (55.0%) (Found C, 53.8; H, 3.55. $C_{10}H_8OSe$ requires C, 53.8; H, 3.6%).

1-*Formyl*-2-*chloro*-2-(p-*methoxyphenyl*)*ethylene* (I).—DMF (115 g) was added dropwise to $POCl_3$ (198 g) at 5—8 °C. The mixture was stirred for 1 h and *p*-methoxyacetophenone (40 g), dissolved in a very small quantity of DMF, was added slowly at 0 °C. The mixture was stirred at 0 °C for 1 h, at room temperature for 30 min, and was then heated to 50—60 °C for 2 h. After cooling, the mixture was poured into a solution of ice–water and sodium acetate at pH 6. The pH must be kept constant during the decomposition. The yellow precipitate was filtered off, dried at room temperature under vacuum, and dissolved in benzene. The solution was concentrated *in vacuo* after removing water to give compound (I) (37 g), m.p. 60—62 °C (lit.,[20] 59—60 °C), δ ($CDCl_3$) 3.74 (3 H, s, OMe), 6.44 (1 H, d, C=CH, $J_{H,CHO}$ 6.5 Hz), 6.70 (2 H, d, *m*-H, $J_{m,o}$ 8.1 Hz), 7.50 (2 H, d, *o*-H, $J_{o,m}$ 8.1 Hz), 9.65 (1 H, d, CHO, $J_{CHO,H}$ 6.5 Hz). Compound (I) is not very stable after treatment with benzene and must be used as soon as possible.

1-*Formyl*-2-*chloro*-2-(m-*methoxyphenyl*)*ethylene* (II).—The procedure described for the *para*-isomer was used, giving the product in 71% yield, m.p. 40 °C, δ ($CDCl_3$) 3.76 (3 H, s, OMe), 6.50 (1 H, d, C=CH, $J_{H,CHO}$ 6.5 Hz), 7.00 (4 H, m, ArH), and 10.04 (1 H, d, CHO, $J_{CHO,H}$ 6.5 Hz).

2-(p-*Methoxyphenyl*)-5-*ethoxycarbonyltellurophen* (III).—Compound (I) (27 g) in DMF (100 ml) was added dropwise to stirred and cooled (0 °C) Na_2Te [from Na (7.5 g) and Te (18 g)] [21] in DMF (150 ml). The mixture was stirred at 0 °C for 1 h and at room temperature for 45 min. α-Bromoethyl acetate (24 g) in DMF (50 ml) was then added dropwise at 0 °C and under stirring. The mixture was stirred at 0 °C for 1.5 h and at room temperature for 1 h. The mixture was poured into a solution of ice–water and sodium acetate (pH 6) and extracted with ether. The solvent was removed *in vacuo* and the residue extracted with hot light petroleum and ligroin. The residue, after elimination of the solvent, was crystallized from ethanol to give pure *compound* (III) (6 g), m.p. 115—116 °C, for ^1H n.m.r. see Table 1, m/e 360 ($C_{14}H_{14}O_3{}^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (33.6%), $M^+ - C_2H_4$ (3.1%), $M^+ - OEt$ (20.0%), and $M^+ - CO_2 - C_2H_4$ (3.6%) (Found C, 46.8; H, 4.05. $C_{14}H_{14}O_3Te$ requires C, 47.0; H, 3.95%).

2-(m-*Methoxyphenyl*)-5-*ethoxycarbonyltellurophen* (IV)—The procedure described for (III) was used, giving the *product* in 10% yield, m.p. 46—47 °C (from ethanol), for ^1H n.m.r. see Table 1, m/e 360 ($C_{14}H_{14}O_3{}^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (12.2%), $M^+ - C_2H_4$ (0.6%), $M^+ - OEt$ (12.1%), and $M^+ - CO_2 - C_2H_4$ (2.8%) (Found C, 46.95; H, 3.9. $C_{14}H_{14}O_3Te$ requires C, 47.0; H, 3.95%).

2-(p-*Methoxyphenyl*)*tellurophen*-5-*carboxylic Acid* (V).—A solution of (III) (6 g) in ethanol (150 ml), water (50 ml), and NaOH (0.744 g) was refluxed for 2.5 h. After cooling the mixture was extracted with ether, acidified with 10% H_2SO_4, and extracted again with ether. The extracts from the acid solution were washed with saturated brine, dried (Na_2SO_4), and evaporated to give (V) (3.0 g), m.p. 233—235 °C (from ethanol), for ^1H n.m.r. see Table 1, m/e 332 ($C_{12}H_{10}O_3{}^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (43.8%) and $M^+ - OH$ (11.0%).

2-(m-*Methoxyphenyl*)*tellurophen*-5-*carboxylic Acid* (VI).—The procedure described for (V) was used, giving the product in 87% yield, m.p. 159—160 °C (from ethanol), for ^1H n.m.r. see Table 1, m/e 332 ($C_{12}H_{10}O_3{}^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (40.7%) and $M^+ - OH$ (18.8%).

p-2-*Tellurienylanisole* (XV).—A mixture of (V) (2.7 g) and copper chromite catalyst (0.1 g) in quinoline (16 ml) was refluxed for 3 h and after cooling filtered through a short column filled with neutral alumina. The solvent was evaporated under reduced pressure to give (XV) (1.9 g), m.p. 111—112 °C (from ligroin), for ^1H n.m.r. see Table 1, m/e 288 ($C_{11}H_{10}O^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (47.4%).

m-2-*Tellurienylanisole* (XVI).—The procedure described for the *para*-isomer gave (XVI) in 80% yield, m.p. 38—39 °C (from light petroleum), for ^1H n.m.r. see Table 1; m/e 288 ($C_{11}H_{10}O^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (31.9%).

p-2-*Tellurienylphenol* (XVII).—Compound (XV) (0.4 g) in DMF (9 ml) was added under nitrogen to a stirred solution of sodium thioethoxide (11 mmol) in DMF (9 ml) and the mixture heated at 80 °C for 14 h. After cooling, the mixture was diluted with water and extracted with ether. The mother-liquor was acidified (10% HCl), extracted with ether, and the extracts dried (Na_2SO_4) and concentrated *in vacuo*. The residue was chromatographed on a column (silica gel) eluting with light petroleum–diethyl ether (4 : 1) to give pure (XVII) (0.1 g), m.p. 158—160 °C [from ligroin–chloroform (1 : 1)], for ^1H n.m.r. see Table 1; *m/e* 274 ($C_{10}H_8O^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (33.4%) (Found C, 44.25; H, 3.05. $C_{10}H_8OTe$ requires C, 44.2; H, 2.95%).

m-2-*Tellurienylphenol* (XVIII).—A solution of BBr_3 (0.525 g) in dichloroethane (5 ml) was added to a solution of (XVI) (0.5 g) in dichloroethane (10 ml) cooled at −40 °C. A further amount of BBr_3 (0.315 g) in dichloroethane (3 ml) was added after 30 min at −40 °C. The mixture was allowed to stand at room temperature for 10 h and then diluted with water and extracted with ether. The extracts were washed with $NaHCO_3$ solution, dried (Na_2SO_4), and evaporated to give (XVIII) (0.050 g) which was purified by column chromatography (silica gel) eluting with light petroleum–ethyl ether (4 : 1); m.p. 78—80 °C [from ligroin–chloroform (1 : 1)], for ^1H n.m.r. see Table 1; *m/e* 274 ($C_{10}H_8O^{130}Te$, 100%), $\%\Sigma_{70}$ M^+ (28.5%) (Found C, 44.1; H, 3.1. $C_{10}H_8OTe$ requires C, 44.2; H, 2.95%).

Ionization Constants.—The apparatus and the procedure were those previously described.[3a] The pK_a values are non-thermodynamic (apparent) dissociation constants and are the average of 2—3 independent determinations.

^1H *N.M.R. Spectra.*—The chemical shifts of hydroxy- and methoxy-protons were recorded as described [15a, 16a] and the values (Table 3) were reproducible to ±0.6 Hz. Additional data used to calculate equation (2) were: *m*-bromoanisole δ (CCl_4) 3.76, δ (C_6H_6) 3.11; *m*-iodoanisole δ (CCl_4) 3.82, δ (C_6H_6) 3.17.

Linear Regression.—Equation (1) was calculated using the following substituents: *p,m*-NO_2, *p,m*-CN, *p,m*-Br, *p,m*-Cl, *p,m*-I, *p,m*-F, *p,m*-SMe,[22] *p,m*-$CONH_2$, *p,m*-CF_3,[23] *p,m*-Bu^t, *p*-SO_2Me,[24] *m*-SO_2Me, *p*-COMe, *m*-COMe,[15b] *p*-CO_2Me, *m*-CO_2Me,[15b] *m*-Me, *p*-OMe, *m*-OMe,[15b] *p*-OH, *p*-NH_2, *p*-CHO,[25] *m*-CHO, *p*-C_6H_5,[26] *p*-C_2H_5, *p*-$N{=}NC_6H_5$, *p,m*-OC_6H_5, *p*-COC_6H_5,[27] *m*-COC_6H_5, *p*-CO_2Et,[24] *m*-CO_2Et, H. The chemical shifts of hydroxy-protons were taken from ref. 15 and σ constants from ref. 28 except for those substituents for which more recent and reliable values (reference in parentheses) are available.

Equation (2) was calculated using the following substituents: *p,m*-NO_2, *p,m*-CO_2H, *p,m*-CHO, *p,m*-Br, *p,m*-I, *p,m*-Cl, *p,m*-SMe, *p,m*-OMe, *p,m*-Me, *p,m*-NH_2, *p*-SH, *p*-C_6H_5, *p*-NMe_2, *p*-OH, *p*-Bu^t, *p*-CN, *m*-CH_2OH, H. The chemical shifts of methoxyl protons were taken from refs. 16*a* and *b* except for *m*-Br and *m*-I (this study). The σ constants were taken from ref. 28. For *p*-OCH_3, *p*-NH_2, *p*-NMe_2, and *p*-OH, $\sigma_p{}^n$ [25] instead of σ_p values were used because it is known [29] that when strong resonance donors are not able to resonance directly with the side chain, they depart from a correlation involving $\sigma_{p,m}$ values because the σ scale is defined using the ionization of benzoic acids in which the so-called 'through conjugation' is present. In our case direct resonance between the hydrogens of methyl group and the phenyl ring is ruled out because of the insulating effect of the carbon atom.

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