Nuclear Magnetic Resonance of Aromatic Heterocycles. XII.

Synthesis, ^1H and ^{13}C NMR Parameters of some 2-Substituted Tellurophenes

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The synthesis of 2-chloro-, 2-bromo-, and 2-iodotellurophene is reported. Di-2-tellurienyl telluride was unexpectedly obtained in two attempts to synthesise 2-nitrotellurophene. The ^1H and ^{13}C NMR parameters of the chloro, bromo, iodo, methyl, *N,N*-dimethylcarbox-amido, and 1-acetyethyl derivatives have been determined. The substituent-induced shifts are discussed in comparison to those of the corresponding furan, thiophene, and selenophene derivatives.

In a previous investigation, the NMR parameters of six 2-substituted tellurophenes (CHO , COCH_3 , COOH , COOCH_3 , SCH_3 , CH_2OH) were compared with those of the corresponding furans, thiophenes, and selenophenes.¹ However, four of the substituents contained carbonyl groups so this set was not considered to be representative enough for a more detailed discussion of the substituent-induced shifts of the four five-membered chalcogen heterocycles. In particular substituents with $-\text{I} + \text{M}$ effects (the halogens) and with very strong electron-attracting (nitro) and very strong electron-donating effects (*e.g.* methoxy) were missing.

We have now partially overcome the difficulties in synthesising 2-substituted tellurophenes containing such substituents.

The halo derivatives of tellurophenes cannot be obtained by reactions with halogens as 1,1-addition products are formed.²

Recently, very convenient methods for obtaining halo and nitro derivatives of furan, thiophene, and selenophene were reported. The 2- and 3-chloro compounds of these heterocycles were prepared by treating the corre-

sponding lithio derivatives with hexachloroethane.³ 2-Iodo- and 2-nitrothiophene were obtained by nucleophilic attack of nitrite ion on di-2-thienyliodonium chloride.⁴

Applying this method to 2-lithiotellurophene at low temperature, 2-chloro- and 2-bromotellurophene were obtained in fair yields. The separation from unreacted starting material and tetrahaloethylene could, however, not be achieved by distillation. The pure compound was therefore obtained by treating the crude reaction mixture with a chloroform solution of bromine and by reducing the resulting 1,1-dibromide derivative with sodium hydrogen sulfite.

The 2-fluoro derivatives of thiophene and selenophene have been obtained through the reaction of the 2-lithio derivatives with perchloryl fluoride.^{5,6} Unfortunately, attempts to prepare 2-fluorotellurophene with this method were without success.

In order to obtain both 2-iodo- and 2-nitrotellurophene, crude di-2-tellurienyl-iodonium salt, obtained through the reaction of 2-lithiotellurophene with *trans*-1-chloro-2-dichloriodoethylene, was treated with sodium nitrite in dimethylformamide. 2-Iodotellurophene was obtained as expected, but no product with the expected properties of 2-nitrotellurophene could be isolated. 2-Iodotellurophene was also obtained, but in lower yield, by decomposing the iodonium salt in dimethylformamide without the presence of sodium nitrite. The only compound besides 2-iodotellurophene that could be isolated was crystalline di-2-tellurienyl tel-

Scheme 1.

luride, whose structure was confirmed both by spectroscopic and analytical data and by an authentic synthesis. This compound was also obtained during another attempt to prepare 2-nitrotellurophene by reacting 2-lithiotellurophene with ethyl nitrate. Probably, 2-lithiotellurophene is partly decomposed under the influence of ethyl nitrate to give tellurium, which reacts with 2-lithiotellurophene, and the resulting intermediate is converted to di-2-tellurienyl telluride *via* the ditelluride. This reaction sequence, outlined in Scheme 1, is in accordance with the reaction route proposed for the synthesis of diaryl telluride.⁷

Di-2-tellurienyl telluride was indeed readily obtained by treating 2-lithiotellurophene with tellurium, whereupon the reaction mixture was hydrolysed with water.

In addition, the NMR spectra of 2-methyl-,⁸ 2-(*N,N*-dimethylcarboxamido)-,⁹ and 2-(α -acetoxy)ethyl-¹⁰ tellurophene were studied. The syntheses of these compounds have been described previously.

¹H NMR SPECTRA

The ¹H NMR spectra of the 2-substituted derivatives studied in this paper were recorded in deuterioacetone solutions, and the NMR parameters are collected in Table 1. The assignments of the chemical shifts were based on results from previous studies,^{1,11} and on the assumption that substituent effects in tellurophene are analogous to those in the other five-membered heterocycles. As shown in Table 1, the coupling constants fall in well-defined intervals with the same relative order as in thiophene and selenophene, but the magnitudes of the coupling constants are somewhat larger in the tellurophene derivatives compared to the sulfur- and selenium-containing heterocycles. Furthermore, the halo-substituted derivatives increase the intervals for the proton-proton couplings in the tellurphene series.

By plotting J_{45} and J_{34} of the halo-substituted derivatives¹²⁻¹⁴ against the electronegativity of the heteroatom (3.5, 2.5, 2.4, and 2.1 for O, S, Se, and Te, respectively), good correlations were obtained, while the correlation coefficient for J_{35} was much lower. The coupling constants were taken from Refs. 3, 13, 15, 16, and Table 1.

In attempts to correlate the proton substituent-induced shifts of the halo derivatives¹²⁻¹⁴ against the electronegativity of the heteroatom, it was only the 3- and 5-positions of the chloro derivatives that gave acceptable correlation coefficients (0.95 and 0.99, respectively).

Table 1. ¹H NMR chemical shifts (δ), coupling constants (Hz), and shifts relative to the α - and β -protons for some 2-substituted tellurophenes, furans, thiophenes, and selenophenes at 60 MHz^a

Substituent	Hetero atom	H ₃	H ₄	H ₅	J_{34}	J_{35}	J_{45}	ΔH_3	ΔH_4	ΔH_5
Cl	Te	7.33	7.34	8.75	4.26	1.47	7.33	-0.46	-0.45	-0.22
Br	Te	7.72	7.41	8.91	4.27	1.49	7.28	-0.07	-0.38	-0.06
I	Te	8.11	7.32	9.13	4.06	1.54	7.10	+0.32	-0.47	+0.16
CH ₃	Te	7.23	7.47	8.64	3.90	1.26	7.14	-0.56	-0.32	-0.33
CON(CH ₃) ₂	Te	7.94	7.87	9.19	4.10	1.95	6.00	+0.15	+0.08	+0.22
"	O	6.97	6.55	7.68	3.45	0.80	1.80	+0.61	+0.19	+0.22
"	S	7.46	7.08	7.60	3.70	1.10	4.80	+0.36	-0.02	+0.20
"	Se	7.59	7.30	8.28	3.80	1.10	5.50	+0.26	-0.03	+0.18
CH(OCOCH ₃)CH ₃	Te	7.60	7.67	8.87	4.10	1.82	6.10	-0.19	-0.12	-0.10
"	O	6.36	6.36	7.46	-	-	-	0.00	0.00	0.00
"	S	7.06	6.93	7.31	3.60	1.90	4.80	-0.04	-0.17	-0.09
"	Se	7.22	7.14	8.00	3.80	2.10	4.60	-0.11	-0.19	-0.10

^a ¹H NMR shifts for the parent compounds are taken from Ref. 5.

In the tellurophene series, good correlations could be obtained between the electronegativity of the halo-substituents and the proton shifts (ΔH) for all positions except position 4. This behaviour was also observed in the other congener systems.¹²⁻¹⁴

¹³C NMR SPECTRA

The ¹³C NMR spectra were also recorded in deuterioacetone solutions, because all derivatives were soluble enough to give 20 % solutions and to enable use of the deuterium resonance as internal lock signal for the ¹³C measurements. All shifts were determined from the proton-decoupled spectra using TMS as an internal standard. The assignments of the ring carbons were made with the same procedure as in Ref. 1, based on the fact that the direct coupling for the α -carbons is larger than that for the β -carbons, and that the long-range couplings have the same relative order as in the 2-substituted thiophene and selenophene series, where the long-range coupling over three bonds (³*J*) is larger than that over two bonds (²*J*). It has, however, been demonstrated that 3-substituted thiophenes and selenophenes, as well as both 2- and 3-substituted furans, show exceptions to this rule.¹⁴ The resulting shifts are presented in Table 2, and the coupling constants in Table 3. For the iodo and methyl derivatives, the coupling constants are missing because there was a reaction between the substrate and TMS. In Table 4, the relative shifts,

which also show the expected substituent effects, are given. As the 2-(*N,N*-dimethylcarboxamido) and 2-(α -acetoxy)ethyl derivatives of furan, thiophene, and selenophene were not included in our comparative study of the ¹³C NMR parameters in furan, thiophene, and selenophene,¹⁴ their NMR parameters and relative shifts for all four congeners are also given in Tables 1, 2 and 4.

In our previous studies, the relative shifts of furan, selenophene, and tellurophene were plotted against those of thiophene for use in the prediction of the shifts of the less common heterocycles in this series, since those of thiophene are known.¹⁴ In equations (1)–(4), these relations for the carbons of tellurophene are presented, and in equations (5)–(7) those for the protons.

$$\Delta C_1^{\text{Te}} = 1.18 \quad C_1^{\text{S}} + 1.73 \quad (r = 0.99) \quad (1)$$

$$\Delta C_3^{\text{Te}} = 1.10 \quad C_3^{\text{S}} - 0.99 \quad (r = 0.95) \quad (2)$$

$$\Delta C_4^{\text{Te}} = 1.04 \quad \Delta C_4^{\text{S}} - 0.86 \quad (r = 0.78) \quad (3)$$

$$\Delta C_5^{\text{Te}} = 1.25 \quad \Delta C_5^{\text{S}} - 0.45 \quad (r = 0.95) \quad (4)$$

$$\Delta H_3^{\text{Te}} = 1.23 \quad \Delta H_3^{\text{S}} - 0.16 \quad (r = 0.98) \quad (5)$$

$$\Delta H_4^{\text{Te}} = 1.64 \quad \Delta H_4^{\text{S}} + 0.04 \quad (r = 0.91) \quad (6)$$

$$\Delta H_5^{\text{Te}} = 1.16 \quad \Delta H_5^{\text{S}} - 0.02 \quad (r = 0.97) \quad (7)$$

By comparing these equations for tellurophene with those in Refs. 1 and 14, where only six substituents, much more similar in character than the twelve in this paper, were included, it is found that the slopes of the carbon

Table 2. ¹³C NMR chemical shifts (ppm) for some 2-substituted tellurophenes, furans, thiophenes, and selenophenes at 25.142 or 15.0 MHz.

Substituent	Hetero atom	C ₂	C ₃	C ₄	C ₅	CH	CO	COCH ₃	N(CH ₃) ₂	CH ₃
Cl	Te	136.4	139.1	136.0	128.7					
Br	Te	110.0	142.6	137.4	131.5					
I	Te	68.9	149.2	139.4	135.0					
CH ₃	Te	144.6	137.5	136.8	124.9					22.6
CON(CH ₃) ₂	Te	146.6	138.4	138.4	132.6		168.2		38.4	
"	O	149.0	115.9	111.9	144.8		160.1		37.1	
"	S	139.6	129.8	127.3	129.8		164.0		38.0	
"	Se	146.1	131.6	130.6	135.6		165.2		38.1	
CH(OCOCH ₃)CH ₃	Te	152.7	134.8	137.4	127.1	21.3	170.2	73.4		24.3
"	O	154.6	108.4	111.0	143.4	20.9	170.1	65.3		18.5
"	S	145.6	125.9	127.3	125.9	21.0	170.0	67.8		22.3
"	Se	152.9	127.7	129.6	131.3	21.0	170.0	69.9		23.2

Table 3. ^{13}C NMR coupling constants (Hz) for some 2-substituted tellurophenes.

Substituent	$J(\text{C}_3-\text{H}_3)$	$J(\text{C}_4-\text{H}_4)$	$J(\text{C}_5-\text{H}_5)$	$J(\text{C}_5-\text{H}_4)$	$J(\text{C}_5-\text{H}_3)$	$J(\text{C}_4-\text{H}_3)$	$J(\text{C}_4-\text{H}_5)$	$J(\text{C}_5-\text{H}_3)$	$J(\text{C}_5-\text{H}_4)$
Cl	165.0	164.0	185.0	6.0	10.0	4.2	2.2	9.8	4.8
Br	166.0	164.0	187.0	5.8	10.5	4.6	2.5	10.9	4.3
$\text{CON}(\text{CH}_3)_2$	163.0	166.0	185.6	5.7	10.7	4.5	2.0	10.7	—
$\text{CH}(\text{OCOCH}_3)\text{CH}_3$	160.0	164.0	185.6	5.7	10.7	5.0	2.0	10.4	4.6

equations have decreased much more than the slopes of the proton equations. Only minor changes in the equations for the furan, thiophene, and selenophene shifts were observed when the 2-(*N,N*-dimethylcarboxamido) and 2-(α -acetoxy)ethyl substituents are included instead of methoxy, nitro, and cyano in the set of substituents previously studied.¹⁴

EXPERIMENTAL

2-Chlorotellurophene. To 4.0 g (0.022 mol) of tellurophene¹¹ in 30 ml of dry ether 13.6 ml of a 20 % solution of butyllithium in hexane was added dropwise under nitrogen at room temperature. When the addition was complete, the reaction mixture was stirred for 30 min, and then cooled to -70°C . At this temperature, a solution of 6.7 g (0.028 mol) of hexachloroethane in 34 ml of dry ether was added and the temperature was not allowed to rise above -60°C . The reaction mixture was kept at -70°C for 3 h, whereupon the cooling bath was removed. When the reaction mixture had reached room temperature, it was hydrolysed with ice water. Most of the organic layer was separated and the mother liquor was then acidified (HCl) and extracted with ether. The combined organic phases were washed with a solution of sodium hydrogen carbonate and dried over magnesium sulfate. After evaporation, the residual red oil was chromatographed on alumina using light petroleum ether (b.p. $40-60^\circ\text{C}$) as eluent; 2.5 g (53 %) of 2-chlorotellurophene b.p. $124^\circ\text{C}/80$ mmHg was obtained. (Found: C 22.34; H 1.39; Cl 16.59; m.wt. 218. Calc. for $\text{C}_4\text{H}_3\text{ClTe}$: C 22.44; H 1.41; Cl 16.55; m.wt. 214.1).

2-Bromotellurophene was prepared as described above for 2-chlorotellurophene from 2-lithiotellurophene (prepared from 10 g of tellurophene in ether and 28.0 g (0.056 mol) of hexabromoethane in 22 ml of dry ether and 120 ml of tetrahydrofuran. The crude product was treated with 150 ml of light petroleum and the solid material filtered off and the filtrate evaporated *in vacuo*. The resulting oil was distilled at 17 mmHg and the fraction boiling at $93-103^\circ\text{C}$ was collected. As this fraction did not consist of pure 2-bromotellurophene, it was diluted with 10 ml of chloroform and treated at 0°C dropwise with a solution of bromine in chloroform until a permanent brown colouring was obtained. The orange precipitate was filtered off, washed with cold chloroform and benzene and then treated with 100 ml of a saturated solution of sodium hydrogen sulfite with vigorous stirring. The mixture was extracted with ether and the combined ethereal phases were washed, dried and evaporated. The remaining oil was chromatographed on alumina by eluting with light petro-

Table 4. ^{13}C NMR shifts relative to the α - and β -carbons of the parent compounds (ppm) for some 2-substituted tellurophenes, furans, thiophenes, and selenophenes.^a

Substituent	Hetero atom	ΔC_2	ΔC_3	ΔC_4	ΔC_5
Cl	Te	9.1	1.1	-2.0	1.4
Br	Te	-17.3	4.6	-0.6	4.2
I	Te	-58.4	11.1	1.4	7.8
CH_3	Te	17.3	-0.5	-1.2	-2.4
$\text{CON}(\text{CH}_3)_2$	Te	19.3	0.4	0.4	5.4
"	O	5.4	5.6	1.4	1.2
"	S	14.0	2.5	0.0	4.2
"	Se	15.1	1.8	0.8	4.7
$\text{CH}(\text{OCOCH}_3)\text{CH}_3$	Te	25.4	-3.3	-0.6	-0.2
"	O	11.0	-2.0	0.7	-0.2
"	S	20.0	-1.4	0.0	0.3
"	Se	21.9	-2.1	-0.2	0.3

^a ^{13}C NMR shifts for parent compounds, see Ref. 5; however C_β for selenophene should be 129.8, cf. Ref. 13.

leum ether. Yield 5.0 g (44 %), b.p. 100 °C/17 mmHg. (Found: C 18.66; H 1.13; Br 31.10. Calc. for $\text{C}_4\text{H}_3\text{BrTe}$: C 18.58; H 1.16; Br 30.90).

2-Iodotellurophene. 2-Lithiotellurophene was prepared from 10 g (0.056 mol) of tellurophene¹¹ in 80 ml of dry ether and 27 ml of a 20 % solution of butyllithium in hexane and cooled to -70 °C, whereupon it was slowly added to 7.12 g (0.030 mol) of *trans*-1-chloro-2-dichloro-iodo ethylene¹⁷ in 50 ml of dry toluene at -70 °C. The reaction mixture was stirred at -70 °C for 3 h and then poured into ice-water. The precipitated iodonium salt was filtered off, washed with water, acetone, and ether, dried and immediately used in the next step.

5.6 g (0.011 mol) of ditellurienyl-iodonium salt and 4 g of sodium nitrite in 30 ml of anhydrous *N,N*-dimethylformamide were stirred at 60 °C for 5 h and at 100 °C for 1 h. After cooling, the mixture was diluted with water and extracted with ether. The combined ether phases were washed with water, dried over sodium sulfate and evaporated. The residue was chromatographed on alumina using light-petroleum as eluent. The first fractions contained 1.1 g of pure 2-iodotellurophene according to GLC and TLC analyses. (Found: C 15.23; H 1.10; I 41.03. Calc. for $\text{C}_4\text{H}_3\text{ITe}$: C 15.72; H 0.99; I 41.52).

Continuing the elution using benzene and more polar solvents such as ether and chloroform, no compounds with the physical properties of 2-nitrotellurophene could be observed. The only product that could be isolated was di-2-tellurienyl telluride (1.2 g).

Di-2-tellurienyl telluride. 2-Lithiotellurophene was prepared from 2.0 g (0.011 mol) of tellurophene in 15 ml of dry ether and 6 ml of 20 % butyllithium in hexane. 0.7 g of tellurium was added and the reaction mixture was stirred at room temperature under nitrogen for 2.5 h,

whereupon it was poured into ice-water. The organic material was extracted with ether and the combined ethereal phases dried and evaporated. The residual oil gave after column chromatography using a mixture of light petroleum and ether (7:3) 0.3 g of the product which was recrystallised from ligroin, m.p. 73–74 °C. ^1H NMR spectrum (CDCl_3): δ 8.15 (H-3), 7.62 (H-4), 9.16 (H-5); J_{34} 4.0 Hz, J_{35} 1.3 Hz, J_{45} 6.9 Hz. (Found: C 19.96; H 1.26; m.wt. 490. Calc. for $\text{C}_8\text{H}_4\text{Te}_2$: C 19.81; H 1.24; m.wt. 484.9).

2-Methyltellurophene was prepared as described in Ref. 11, 2-(α -acetoxy)ethyltellurophene in Ref. 10 and 2-(*N,N*-dimethylcarboxamido)-tellurophene and -selenophene in Ref. 9. 2-(*N,N*-Dimethylcarboxamido)furan, -thiophene were prepared according to the general procedure described in Ref. 18, giving products identical to those described in Refs. 18 and 19. 2-(α -Acetoxy)ethylfuran, -thiophene, and -selenophene were prepared from the parent compounds *via* the 2-acetyl derivatives in analogy with the procedures in Refs. 11 and 10, giving products identical with those described in Ref. 20.

The ^1H NMR spectra were obtained with a Varian A60 and a Jeol MH100 high resolution spectrometer. The ^{13}C NMR spectra were obtained either at 25.142 MHz on a Varian XL-100-15 spectrometer equipped with frequency sweep, proton wide band decoupler and Fourier transform operation or at 15.0 MHz with a Jeol JNM-60 spectrometer with a built-in Jeol 980A computer with 12 K memory.

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