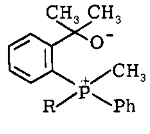
chemical shift values observed for **5** and **6** (δ −78.7 and −65.4) are, however, typical[9] of pentacoordinate phosphorus compounds (phosphoranes) rather than tetracoordinate phosphonium salts such as structure **19**. Consequently, we conclude that structures **5** and **6**, rather than **19**, are dominant for these compounds but with considerable polarization of the hypervalent C–P–O bond. The large P–O dipole is, however, not near to the rigidly oriented ortho proton in **5** or **6** so we do not find the downfield shift seen for the related proton in **4**.



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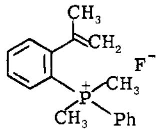

20, $\delta_{^{31}P}$ 17.6

One example of an acid-catalyzed dehydration was observed. Treatment of **5** with anhydrous HF in $CDCl_3$ gave a 3:2 mixture of the salts **15** and **20**. It may well be that **15** undergoes acid-catalyzed dehydration, giving **20**.

Acknowledgment. This work was supported in part by a grant to J.C.M. from the National Cancer Institute (No. HEW PHS CA 13963) and by instrumentation for mass spectrometry provided by NIH Grants CA 11388 and GM 16864. We wish to thank Professor M. R. Wilcott, III, for helpful discussion and the Alexander von Humboldt Stiftung for an award to J.C.M.

Synthesis of 2,5-Dihydrotellurophene—A New Heterocyclic Compound[24]

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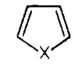
Contribution from the Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden.

Received August 28, 1980

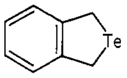
Abstract: 2,5-Dihydrotellurophene 1,1-dichloride was isolated in 62% yield when $TeCl_4$ was heated in acetonitrile with an excess of butadiene. Isoprene and 2,3-dimethylbutadiene reacted similarly affording the 3-methyl- and the 3,4-dimethyl-substituted 2,5-dihydrotellurophene 1,1-dichlorides which were easily reduced with aqueous Na_2S to the corresponding 2,5-dihydrotellurophenes. 2,5-Dihydrotellurophene could be converted to its 1,1-dibromide and 1,1-diiodide, respectively, by treatment with Br_2 and I_2. Treatment with XeF_2 afforded the 1,1-difluoride and oxidation with H_2O_2 similarly afforded 2,5-dihydrotellurophene 1-oxide, which was not isolated. The double bond of 2,5-dihydrotellurophene 1,1-dichloride was inert to treatment with Br_2 or Cl_2, probably due to an interaction, either steric or electronic, with the $TeCl_2$ group.

The unsaturated five-membered heterocycles 3-pyrroline (**1a**) and 2,5-dihydrofuran (**1b**) have long been known. The former[1] was obtained by reduction of pyrrole (**2a**), and the latter was formed by dehydrohalogenation of 3-bromotetrahydrofuran.[2] 2,5-Dihydrothiophene (**1c**) was one of the reduction products from thiophene (**2b**) when treated with sodium in liquid ammonia.[3]

1a, X = NH
1b, X = O
1c, X = S
1d, X = PCl_3
1e, X = GeI_2
1f, X = $SiCl_2$
1g, X = Te
1h, X = Se



2a, X = NH
2b, X = S
2c, X = Te
2d, X = Se



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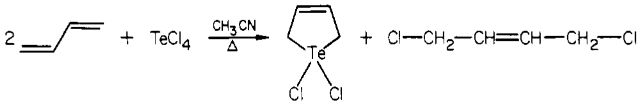
Scheme I



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(9) On the other hand, the corresponding dehydrogenated compound, tellurophene (**2c**), has been extensively studied[9a,b] and reviewed.[9c] Derivatives of the fully hydrogenated system has also been described.[9d] (a) Lohner, W.; Praefcke, K. *Chem. Ber.* **1978**, *111*, 3745. (b) Barton, T. J.; Roth, R. W. *J. Organomet. Chem.* **1972**, *39*, C66. (c) Fringuelli, F.; Marino, G.; Taticchi, A. *Adv. Heterocycl. Chem.* **1977**, *21*, 119. (d) Albeck, M.; Tamary, T. *J. Organomet. Chem.* **1979**, *164*, C23.

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(11) (a) A mass spectrum of compound **7** prepared according to Funk and Weiss[11b] indicated the presence of small amounts of a dimeric species. However, ^1H and ^{13}C NMR data seems to fit with structure **7**. (b) Funk, H.; Weiss, W. *J. Prakt. Chem.* **1954**, [4] *273*, 33.

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(20) In a preliminary experiment it was found that treatment of 2,5-dihydrotellurophene 1,1-dichloride (**4**) with dimethylamine in refluxing acetonitrile caused separation of elemental tellurium. The organic material obtained after filtration and evaporation of the solvent contained several products, including tellurophene (**2c**). 1,4-Bis(dimethylamino)-2-butene could not be detected.

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More recently the analogous 1,1,1-trichlorophospholine (**1d**)[4] and 1,1-diiodogermacyclo-3-pentene (**1e**)[5] were synthesized from butadiene and PCl_3 and GeI_2, respectively, by using a cheletropic reaction. Furthermore, 1,1-dichlorosilacyclo-3-pentene (**1f**) was obtained from 3,4-dichloro-1-butene over an alloy of Si–Cu at 300 °C.[6]

In the tellurium series the aromatic tellurophene (**2c**) is a well-known compound[7] as well as a number of its derivatives, including 2,5-dihydrobenzo[*c*]tellurophene (**3**), obtained from sodium telluride and α,α'-dibromo-*o*-xylene.[8]

In this paper we would like to report about the synthesis and reactions of 2,5-dihydrotellurophene (**1g**), a hitherto unknown[9] heterocyclic compound.

Results and Discussion

We have found that $TeCl_4$ adds reproducibly to butadiene in refluxing acetonitrile forming 2,5-dihydrotellurophene 1,1-dichloride (62% yield) and 1,4-dichloro-2-butene, according to Scheme I.

When the reaction was carried out in toluene, the yield could be improved to 95%, but unfortunately the reaction was not reproducible in this solvent, often depositing large amounts of elemental tellurium.

The reaction between $TeCl_4$ and butadiene was earlier studied by Arpe and Kuckertz[10] under somewhat different reaction conditions. They reported the formation of bis(4-chloro-2-butenyl)tellurium dichloride (**5**), when butadiene was introduced into a 30% suspension of $TeCl_4$ in CCl_4 at 20–60 °C. Compound **5** separated as a yellow oil and was crystallized from CCl_4 and characterized by elemental analysis and ^1H NMR and IR spectroscopy.

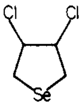
We have found that compound **5** can be converted into 2,5-dihydrotellurophene 1,1-dichloride (**4**), when refluxed in toluene for 1 h. Compound **5** is therefore likely to be an intermediate on the reaction pathway from butadiene to the heterocyclic tellurium dichloride **4**, e.g., through a hexacoordinated tellurium species (not isolable), that should be expected to readily undergo a reductive elimination.

$(Cl{-}CH_2{-}CH{=}CH{-}CH_2)_2{-}TeCl_2$

5

The selenium isologue of compound **4**, **6**, is to the best of our knowledge not described in the literature. Treatment of $SeOCl_2$ or $SeCl_4$ with butadiene in refluxing acetonitrile yielded a number of selenium-containing compounds but not compound **6**. 2,5-Dihydroselenophene (**1h**) is also an unknown compound that was not formed from a product claimed[11] to be 3,4-dichlorotetrahydroselenophene (**7**) on attempted dehalogenation with zinc in HOAc. Neither could the purported compound **7** be dehydrohalogenated to give selenophene (**2d**) upon treatment with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).

6



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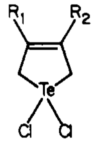
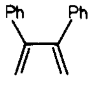
When $TeCl_4$ was refluxed in acetonitrile with isoprene or 2,3-dimethylbutadiene, the corresponding methyl-substituted 2,5-dihydrotellurophene dichlorides **8a** and **8b** could be obtained in 46 and 53% yield, respectively. 2,3-Diphenylbutadiene (**9**) did not react with $TeCl_4$ under the same reaction conditions and *cis*-2,*trans*-4-hexadiene (**10**) produced large amounts of elemental tellurium.



8a, $R_1 = H, R_2 = CH_3$
8b, $R_1 = CH_3, R_2 = CH_3$



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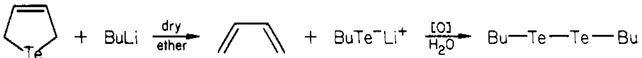
Scheme II



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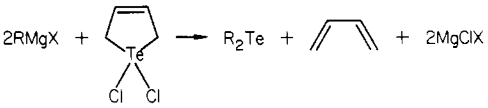
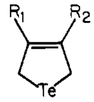
Scheme III

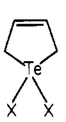


R (% yield): phenyl (70), 4-methylphenyl (88), 4-methoxyphenyl (60)

Reduction of the three crystalline dichlorides **4**, **8a**, and **8b** with aqueous Na_2S afforded the 2,5-dihydrotellurophenes **1g**, **11a**, and **11b**, respectively, all foul-smelling unstable oils that slowly deposited elemental tellurium upon standing. When 2,5-dihydrotellurophene (**1g**) was treated in CCl_4 with an equivalent amount of Br_2 or I_2, it was converted to the 1,1-dibromide (**12a**) and 1,1-diiodide (**12b**), respectively. The 1,1-difluoride **12c** was similarly prepared by treatment with XeF_2 in CH_2Cl_2.



11a, $R_1 = H, R_2 = CH_3$
11b, $R_1 = CH_3, R_2 = CH_3$



12a, X = Br
12b, X = I
12c, X = F

The ^1H NMR spectrum of 2,5-dihydrotellurophene showed the same "deceptively simple" pattern as was first observed for the corresponding oxygen and sulfur isologues (**1b** and **1c**).[12] Due to very small values of the coupling constants, the spectrum consists of only two somewhat broadened peaks with an integral ratio 1:2, as recently analyzed in detail for compounds **1b** and **1c**.[13] The mass spectra (70 eV) of compounds **4**, **8a**, and **8b** all contain a Te_2^+ fragment, (base peak for **4**) probably formed by decomposition in the mass spectrometer (compounds **4**, **8a**, and **8b** all melt with decomposition). Furthermore, all three compounds exhibited loss of Cl_2 in the mass spectrum and no molecular peaks could be observed at 70 eV.

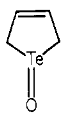
When 2,5-dihydrotellurophene was treated in dry ether at room temperature with 1 equiv of butyl lithium, a ring-opening reaction took place, according to Scheme II. Aqueous work up in the presence of air afforded dibutyl ditelluride (**13**) as the only product.

Treatment of the dichloride **4** with at least 2 equiv of a Grignard reagent caused evolution of butadiene and formation of a diaryltelluride in good yield according to Scheme III. 2-Thienyllithium similarly afforded di-2-thienyl telluride in 79% yield. We conclude that this route should be considered when a small amount of a specific telluride is required cleanly and rapidly. Conventional reactions using Grignard reagents and Te (or $TeCl_4$) are hampered by the fact that mixtures of mono- and ditellurides are often obtained. Furthermore, the yields are often unsatisfactory.[14]

Photolysis of 3-methyl-2,5-dihydrotellurophene (**11a**) in ethanol at 300 nm readily caused separation of elemental tellurium and formation of isoprene. The a priori expected product,[8] 1-methylcyclobutene (**14**), could not be detected.

14

In order to synthesize 2,5-dihydrotellurophene 1-oxide (**15**), we treated compound **1g** in tetrahydrofuran with hydrogen peroxide (35% aqueous) in a manner analogous to the preparation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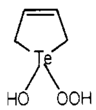
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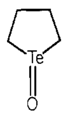
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of 2,5-dihydrothiophene 1-oxide from 2,5-dihydrothiophene.[15] A white precipitate immediately separated that was readily soluble in aqueous $NaHCO_3$, but the material exploded violently[16] upon attempted isolation. The explosive compound is probably a hydroperoxide of some kind, e.g., compound **16**, formed as a byproduct from 2,5-dihydrotellurophene 1-oxide and a small excess of H_2O_2. When the aqueous $NaHCO_3$ solution was neutralized with hydrochloric acid and extracted several times with CH_2Cl_2, 2,5-dihydrotellurophene 1,1-dichloride (**4**) could be isolated in 40% yield. A similar transformation of an oxide to a dichloride was studied by Morgan[17] for tetrahydrotellurophene 1-oxide (**17**).

2,5-Dihydrotellurophene 1,1-dichloride (**4**) was surprisingly inert to treatment with Br_2 or Cl_2 while the analogous 1,1-dibromogermacyclo-3-pentene and 1,1-dichlorosilacyclo-3-pentene (**1f**) were readily halogenated when treated with Br_2 and Cl_2, respectively.[18,19] This lack of reactivity may be due either to steric factors or an interaction through space of the tellurium atom with the π bond, pulling electrons from it and thus rendering it less susceptible to an electrophilic attack. The relatively strong shifts of the olefinic protons of the 1,1-dihalogenides (Table I), as compared with the parent compound **1g**, supports the latter view, although no relevant NMR data are available from the literature for reference purposes.

In spite of the instability (the decomposition seems to be autocatalyzed by Te^0) of 2,5-dihydrotellurophene (**1g**) peaks corresponding to the parent ion, *m/e* 184 (^{130}Te) could be recorded by mass spectroscopy (20 eV). The fragmentation pattern around *m/e* 182 reveals that dehydrogenation to *m/e* 182 (^{130}Te) does occur. Interestingly the spectrum (20 eV) of the much more stable chlorine adduct (**4**) showed strong peaks at *m/e* 184 and 182 and exhibited the highest peaks around *m/e* 258 (Te_2^+) and the parent ion peak around *m/e* 252. In contrast the highest peaks in the spectrum (20 eV) of the bromine adduct (**12a**) were recorded at *m/e* 292 ($TeBr_2^+$, ^{130}Te, ^{81}Br) and *m/e* 263 (M – Br, ^{130}Te, ^{81}Br), which might be compared with the spectrum[9a] of the bromine adduct of tellurophene, which exhibits the highest peak at *m/e* 261 (M – Br).

Pyrolysis of 2,5-dihydrotellurophene 1,1-dichloride (**4**) at 250 °C, resulted in formation of elemental tellurium and 1,4-dichloro-2-butene as the main products. We are presently trying to introduce ligands other than halogens, e.g., cyanide or amines,[20] that could migrate from tellurium to carbon at elevated temperatures, yielding 1,4-disubstituted 2-butenes.

Experimental Section

Elemental analyses were performed by Centrala Analyslaboratoriet, Uppsala, Sweden. All melting points were uncorrected. NMR spectra were recorded on a Bruker WP 200 instrument and a Varian EM-360 instrument. Infrared spectra were obtained by using a Perkin-Elmer 257 instrument. Mass spectra were obtained with an LKB 9000 mass spectrometer. $TeCl_4$ was a Merck product and 1,3-butadiene, isoprene, and 2,3-dimethylbutadiene were obtained from Fluka. XeF_2 was purchased from PCR Research Chemicals, Inc.

2,5-Dihydrotellurophene 1,1-Dichloride (4). 1,3-Butadiene was bubbled through a stirred suspension of $TeCl_4$ (10.0 g, 0.037 mol) in acetonitrile (150 mL) at room temperature until all material had dissolved (30 min). The temp. was then slowly raised to reflux. The solution gradually darkened, and after 45 min the bubbling of butadiene was stopped and the reflux continued for another 4 h. The filtered solution was evaporated to give a semisolid which could be crystallized from a small amount of acetonitrile yielding 5.8 g (62% yield) of compound **4**, mp 194–195 °C dec.

When the reaction was performed in toluene instead of acetonitrile, the yield could be improved to 95% in a small-scale preparation (1.0 g of $TeCl_4$. However, the reaction was not reproducible in this solvent, often depositing large amounts of elemental tellurium when the reaction mixture was brought to reflux: mass spectrum (70 eV), *m/e* (relative intensity, only peaks stronger than 10% of the base peak above *m/e* 100) 260 (53), 258 (95), 256 (100), 254 (70), 219 (14), 217 (10), 200 (20), 198 (15), 184 (80), 182 (81), 180 (53), 165 (26), 163 (20), 130 (58), 128 (60), 126 (35); mass spectrum (20 eV); *m/e* (relative intensity, only peaks stronger than 8% of the base peak above *m/e* 130) 260 (16), 258 (26), 256 (28), 254 (19), 252 (12), 250 (9), 221 (18), 219 (47), 217 (44), 215 (31), 202 (27), 200 (42), 198 (36), 196 (25), 184 (100), 182 (100), 180 (72), 165 (53), 163 (50), 61 (28); IR (KBr) 3030 (w), 2965 (w), 2920 (w), 1630 (m), 1395 (w), 1390 (m), 1380 (m), 1330 (m), 1110 (w), 1100 (m), 960 (m), 780 (w), 665 (s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 58.33, 129.41; ^1H NMR ($CDCl_3$, Me_4Si) δ 4.53 (s, 4 H), 6.41 (s, 2 H). Anal. ($C_4H_6Cl_2Te$) C, H, Cl, Te.

Table I. ^1H and ^{13}C NMR Data for 2,5-Dihydrotellurophene and Its 1,1-Dihalogenides

compd	halogen	^1H δ_{CH}	^1H δ_{CH_2}	^{13}C δ_{CH}	^{13}C δ_{CH_2}
1g		5.70	4.02	133.14	10.59
12c	F	6.49	3.93	129.29	53.98
4	Cl	6.41	4.53	129.41	58.33
12a	Br	6.30	4.73	129.77	56.88
12b	I	6.12	4.83		

2,5-Dihydrotellurophene (1g). 2,5-Dihydrotellurophene 1,1-dichloride (0.65 g, 2.6 mmol) was shaken with a mixture of ethyl ether and $Na_2S·9H_2O$ (5% aqueous) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound **1g** as a light yellow oil with obnoxious odor: 0.39 g, 84% yield; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 10.59, 133.14; ^1H NMR ($CDCl_3$, Me_4Si) δ 4.02 (s, 4 H), 5.70 (s, 2 H); mass spectrum (20 eV), *m/e* (relative intensity, only peaks stronger than 5% of the base peak above *m/e 45*) 184 (15), 182 (17), 180 (12), 178 (9), 130 (21), 128 (20), 126 (12), 54 (100), 53 (92), 52 (19), 51 (34), 50 (35).

2,5-Dihydrotellurophene 1,1-Dibromide (12a). When Br_2 (0.50 g, 3.1 mmol) dissolved in CCl_4 (5 mL) was poured into a solution of 2,5-dihydrotellurophene (0.50 g, 2.8 mmol) in CCl_4 (15 mL), the yellow dibromide **12a** (1.00 g, 88% yield) was immediately precipitated and filtered off: mp 189–190 °C (acetonitrile); IR (KBr) 3030 (w), 2920 (w), 1635 (w), 1630 (m), 1400 (w), 1390 (m), 1380 (m), 1330 (m, 1310 (w), 1095 (m), 955 (m), 775 (w), 660 (s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 56.88, 129.77; ^1H NMR ($CDCl_3$, Me_4Si) δ 4.73 (s, 4 H), 6.30 (s, 2 H); mass spectrum (20 eV), *m/e* (relative intensity, only peaks stronger than 15%, except the $TeBr_2$ peak, of the base peak above *m/e* 45) 292 (5) 290 (11), 288 (14), 263 (31), 261 (50), 259 (44), 211 (33), 209 (53), 207 (45), 184 (91), 182 (100), 180 (65), 179 (34), 178 (27), 130 (38), 128 (40), 126 (26), 82 (41), 81 (18), 80 (41), 79 (18).

2,5-Dihydrotellurophene 1,1-Diiodide (12b): When I_2 (0.41 g, 1.61 mmol) dissolved in CCl_4 (10 mL) was poured into a solution of 2,5-dihydrotellurophene (0.29 g, 1.58 mmol) in CCl_4 (15 mL), the brown diiodide **12b** (0.63 g, 90% yield) was immediately precipitated and filtered off: mp 154–155 °C; IR (KBr) 1630 (m), 1380 (m), 1375 (m), 1330 (m), 1200 (w), 1155 (w), 1100 (m), 1085 (w), 960 (m), 775 (w), 650 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 4.83 (s, 4 H), 6.12 (s, 2 H).

2,5-Dihydrotellurophene 1,1-Difluoride (12c). XeF_2 (0.32 g, 1.89 mmol) was added to a stirred solution of 2,5-dihydrotellurophene (0.34 g, 1.87 mmol) in dry CH_2Cl_2 (25 mL) kept at –78 °C. Evaporation of the solvent afforded 0.40 g (97% yield) of compound **12c** as a white solid: mp 156–157 °C dec; (rapidly from ethanol). IR (KBr) 2980 (w), 2930 (w), 1630 (m), 1525 (m), 1395 (m), 1345 (m), 1125 (w), 1100 (m), 955 (m), 670 (s); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 53.98, 129.29; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.93 (s, 4 H), 6.49 (s, 2 H). Anal. ($C_4H_6F_2Te$) C, H, F.

3-Methyl-2,5-dihydrotellurophene 1,1-Dichloride (8a). Isoprene (2.4 g, 35.3 mmol) was added at room temperature to a suspension of $TeCl_4$ (2.0 g, 7.4 mmol) in acetonitrile (60 mL) and stirred for 30 min when the temperature was slowly raised to reflux, The solution gradually darkened, and after 3 h of reflux it was filtered from a small amount of elemental tellurium and evaporated to give an oil which could be crystallized from CCl_4. The yield of the white compound **8a** was 0.90 g, 46%: mp 147–148 °C dec; mass spectrum, *m/e* (relative intensity, only peaks stronger than 10% of the base peak above *m/e* 100) 260 (10), 258 (16), 256 (17), 254 (13), 198 (100), 197 (12), 196 (98), 195 (10), 194 (62), 193 (27), 192 (19), 183 (17), 181 (17), 179 (10), 130 (33), 128 (31), 126 (19); IR (KBr) 2960 w), 2930 (w), 2910 (w), 2850 (w), 1650 (m), 1430 (m), 1395 (s), 1370 (w), 1300 (w), 1200 (m), 1110 (w), 1100 (m), 1035 (w), 1015 (w), 840 (w), 740 (s); ^1H NMR ($CDCl_3$, Me_4Si) δ 2.0 (s, 3 H), 4.4 (s, 4 H), 6.2 (s, 1 H). Anal. ($C_5H_8Cl_2Te$) C, H.

3-Methyl-2,5-dihydrotellurophene (11a). 3-Methyl-2,5-dihydrotellurophene 1,1-dichloride was shaken thoroughly with a mixture of ethyl ether and excess $Na_2S·9H_2O$ (5% aqueous) until all material had dissolved. Drying ($CaCl_2$) and evaporation of the organic phase yielded compound **11a** as a foul-smelling light yellow oil in almost quantitative yield: ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ 8.57, 13.16, 18.45, 127.51, 142.39; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.82 (s, 3 H), 3.91 (s, 4 H), 5.55 (s, 1 H).

3,4-Dimethyl-2,5-dihydrotellurophene 1,1-Dichloride (8b). 2,3-Dimethyl-1,3-butadiene (2.4 g, 29.3 mmol) was added at room temperature to a suspension of TeCl$_4$ (2.0 g, 7.4 mmol) in acetonitrile (60 mL) and stirred for 30 min when the temperature was slowly raised to reflux. The solution gradually darkened, and after 3 h of reflux it was filtered from a small amount of elemental tellurium and evaporated to give a semisolid which could be crystallized from acetonitrile. The yield of compound **8b** was 1.1 g, 53%: mp 215–216 °C dec; mass spectrum *m/e* (relative intensity, only peaks stronger than 30% of the base peak above *m/e* 100) 260 (34), 258 (63), 256 (63), 254 (45), 212 (38), 210 (39), 147 (39), 145 (37), 138 (74), 136 (100), 134 (84), 130 (34), 122 (37), 121 (66), 119 (53), 109 (34), 107 (66), 105 (50); IR (KBr) 2980 (w), 2960 (w), 2920 (w), 2910 (w), 1655 (m), 1430 (m), 1385 (s), 1375 (m), 1365 (m), 1120 (w), 1110 (w), 985 (w), 900 (w), 780 (s); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.9 (s, 6 H), 4.3 (s, 4 H). Anal. (C$_6$H$_{10}$Cl$_2$Te) C, H.

3,4-Dimethyl-2,5-dihydrotellurophene (11b). 3,4-Dimethyl-2,5-dihydrotellurophene 1,1-dichloride was shaken thoroughly with a mixture of ethyl ether and excess Na$_2$S·9H$_2$O (5% aqueous) until all material had dissolved. Drying (CaCl$_2$) and evaporation of the organic phase yielded compound **11b** as a foul-smelling light yellow oil in almost quantitative yield: ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 1.6 (s, 6 H), 4.0 (s, 4 H).

Preparation of Diaryltellurides from 2,5-Dihydrotellurophene 1,1-Dichloride (4). General Procedure. 2,5-Dihydrotellurophene 1,1-dichoride (0.50 g, 1.98 mmol) was added at room temperature to a stirred ether solution (50 mL) of *a* millimole of the appropriate Grignard reagent. A slow gas evolution could immediately be observed, and the stirring was continued for another hour at room temperature when the reaction mixture was poured into a saturated solution of NH$_4$Cl (50 mL). The organic phase was separated and the aqueous phase extracted once with ethyl ether (50 mL). The combined ether extracts were washed with water, dried (CaCl$_2$), and evaporated to yield an oil or a semisolid of the corresponding diaryltelluride. The following diaryltellurides were prepared according to the general procedure.

Diphenyl Telluride (*a* = 6.4 mmol): yield 0.04 g (70%). The compound is an oil and was isolated as diphenyltellurium dichloride by treatment with Cl$_2$ gas in CCl$_4$ (10 mL) at room temperature; mp 159–160 °C (lit.[21] 159 °C).

Bis(4-methylphenyl) Telluride (*a* = 4.09 mmol): yield 0.54 g (88%); mp 66 ° (lit.[22] 69–70 °C).

Di-2-thienyl telluride was prepared according to the general procedure except that 2-thiethyllithium was employed instead of the Grignard reagent and that the reaction mixture was refluxed 30 min after addition of the tellurium dichloride **4** (*a* = 5.3 mmol): yield 0.46 g (79%); mp 49–50 °C (lit.[23] 50.5 °C).

Reaction of 2,5-Dihydrotellurophene with H$_2$O$_2$. H$_2$O$_2$ (35% aqueous, 0.20 g, 2.05 mmol) was added dropwise to a stirred solution of 2,5-dihydrotellurophene (0.36 g, 1.98 mmol) in THF (15 mL) at 0 °C. The white precipitate that immediately separated was filtered off and dried, but the material exploded violently upon attempted weighing.

In another identical experiment it was found that the precipitate could be dissolved by addition of NaHCO$_3$ (5% aqueous, 50 mL) to the THF suspension. Neutralization of this solution with HCl (2 M aqueous) followed by several extractions with CH$_2$Cl$_2$ afforded 2,5-dihydrotellurophene 1,1-dichloride (**4**) 0.20 g (40%), identical with the compound described above. When H$_2$SO$_4$ (2 M, aqueous) was used instead of HCl in the neutralization, no organic material could be extracted from the aqueous phase.

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The Synthesis of Megaphone

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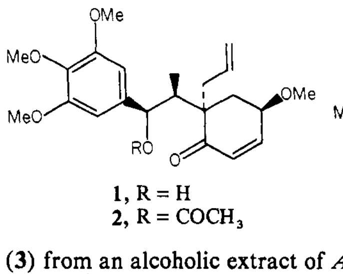
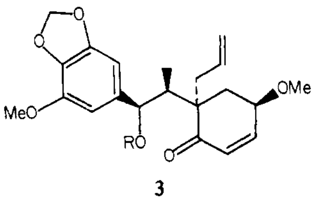
Abstract: Condensation of 4,4,5-trimethoxy-2-[3-[(methylsulfonyl)oxy]propyl]-2,5-cyclohexadien-1-one (**7**) with 1,2,3-trimethoxy-5-(1-(*Z*)-propenyl)benzene in dichloromethane, in the presence of 1 equiv of stannic chloride, gave (2β,3β,3aα)-3,3a-dihydro-5-methoxy-3-methyl-3a-[3-[(methylsulfonyl)oxy]propyl]-2-(3,4,5-trimethoxyphenyl)-6-(2*H*)-benzofuranone (**6**). Subsequent regio- and stereoselective hydrogenation of the 4,5 double bond with 5% Rh on carbon gave a single dihydro derivative **5**. Elimination of methanesulfonic acid with the use of Sharpless' method followed by reduction of the carbonyl group and rearrangement gave racemic megaphone (**1**) characterized by its naturally occurring acetate (**2**).

In the course of an extensive search for antitumor agents among plant metabolites the late S. M. Kupchan and his co-workers isolated megaphone (**1**), megaphone acetate (**2**), and megaphyllone (**3**) from an alcoholic extract of *Aniba megaphylla Mez*, (*Lauraceae*).[1] These neolignans[2] exhibit "inhibitory activity, in vitro, against cells derived from human carcinoma of the nasopharynx (KB)".[3] Both gross structure and stereochemistry of megaphone (**1**) were deduced tentatively from chemical and spectroscopic data. An X-ray crystallographic analysis confirmed the conclusions reached and established the molecular conformation, as well as the absolute stereochemistry. The first total synthesis of megaphone (**1**) and its acetate (**2**) is described in this paper.



1, R = H
2, R = COCH$_3$



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Retrosynthetic analysis suggested that megaphone (**1**) could be synthesized by reduction of the vinylogous ester **4**, which in turn could be prepared from mesylate **5**. The latter should be available from the selective hydrogenation of the cyclohexadienone **6** which might result from an acid-catalyzed condensation of the *p*-benzoquinone ketal **7** with 1,2,3-trimethoxy-5-(1-(*Z*)-propenyl)benzene.[4,5] This approach (Scheme I) appeared at-

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(1) Kupchan, S. M.; Stevens, K. L.; Rohlfing, E. A.; Sickles, B. R.; Sneden, A. T.; Miller, R. W.; Bryan, F. R. *J. Org. Chem.* **1978**, *43*, 586–590.

(2) Review: Gottlieb, O. R. In "Progress in the Chemistry of Organic Natural Products"; Herz, W.; Grisebach, H.; Kirby, G. W., Eds.; Springer-Verlag/Wien: Austria, 1978, Vol. 35, pp 1–72.

(3) The KB activity was assayed under the auspices of the National Cancer Institute. **1**, **2**, and **3** showed cytotoxicity against KB cell culture at 1.70, 1.75, and 2.55 μg/mL, respectively.

(4) Büchi, G.; Mak, C.-P. *J. Am. Chem. Soc.* **1977**, *99*, 8073–8075.

(5) Mak, C.-P. Ph.D. Dissertation, Massachusetts Institute of Technology, 1978.

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