Liquid-phase 1,4-Diacetoxylation of Conjugated Dienes with Tellurium(IV) Oxide and Alkali Metal Halides

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Oxidation of buta-1,3-diene, isoprene, and 2,3-dimethylbuta-1,3-diene with tellurium(IV) oxide and lithium bromide in acetic acid affords an isomeric mixture of the corresponding diacetoxyalkenes (1,2- and 1,4-addition products). The product yield and selectivity for 1,4-isomers are high [up to 61% (based on TeO_2) and 1,4-/1,2- = 90/10 respectively in the case of buta-1,3-diene] when an excess of LiBr is employed ($LiBr/TeO_2$ = 5—10). The reaction also proceeds in the presence of NaBr, KBr, LiCl, HBr, or I_2 in the place of LiBr, but both the selectivity for 1,4-isomers and the product yield are lower. The reaction hardly occurs using LiF, LiI, NaCl, Br_2, and NH_4Br as a halogen source. The reaction proceeds catalytically with respect to TeO_2 to some extent when a re-oxidant such as H_2O_2 or t-BuOOH is used. In the cases of 2,5-dimethylhexa-2,4-diene, cyclopenta-1,3-diene, cyclohexa-1,3-diene, and cyclo-octa-1,3-diene the results are unsatisfactory in either the product yield or the selectivity for 1,4-isomers. Halogeno- and/or acetoxy-telluriation of a diene followed by acetolysis of the produced C–X (X = halogen) and C–Te bonds are proposed as one of the possible reaction pathways.

The production of butane-1,4-diol is industrially important because of its wide use as a starting material for a variety of organic compounds such as polybutylene terephthalate resin, tetrahydrofuran, and polyurethane.[1] Recently, a new process for its production was developed and commercialized, which involves a liquid-phase direct oxidation of buta-1,3-diene with molecular oxygen in acetic acid in the presence of a supported solid catalyst consisting essentially of elemental palladium.[1a,b,2] A key reaction in this process is a selective diacetoxylation of the diene to 1,4-diacetoxybut-2-ene. There are many non-transition and transition metal salts which can oxidize alkenes to diols and/or their derivatives in a liquid phase (*i.e.*, Hg, Tl, Pb, Mn, Co, Cu, Pd, Os, Pt, Au, Se, *etc.*).[3] Patents of oxirane's ethylene glycol process based on direct oxidation of ethylene indicate that a catalytic system of tellurium oxide–bromine compounds works well for the reaction of oxygen with ethylene in acetic acid.[4] It has been reported that a combination of tellurium(IV) oxide and a lithium halide or iodine can be used to oxidise some alkenes to diacetoxyalkanes in acetic acid.[4b,5] We have applied this oxidation procedure to several conjugated dienes and have found a convenient new method for selective 1,4-diacetoxylation of the dienes.[5,6] We describe here the results, focusing especially on the oxidation of buta-1,3-diene, and discuss the reaction pathway briefly. It is worth noting that these reaction conditions are also known to be effective for the oxidation of some nitrogen compounds[7] and aromatic compounds.[8]

Results and Discussion

A mixture of buta-1,3-diene (10—50 mmol), tellurium(IV) oxide (5 mmol), lithium bromide (5—50 mmol), and acetic acid (18 ml)–acetic anhydride (2 ml) was heated at 125 °C and stirred in a glass pressure bottle. The reaction mixture was heterogeneous when the mol ratio $LiBr/TeO_2$ = 1, while it was homogeneous when the ratio was 5—10. Elemental tellurium was deposited as a black precipitate as the reaction proceeded. After the normal work-up procedure, the organic products were treated with acetic anhydride–pyridine to convert the hydroxy derivatives (variable amounts) into the corresponding acetates, g.l.c. analysis of which revealed that they consisted of 3,4-di-acetoxybut-1-ene (1), *cis*-1,4-diacetoxybut-2-ene, and *trans*-1,4-diacetoxybut-2-ene (3), reaction (1). The oxidation did not occur at all in the absence of tellurium(IV) oxide or lithium
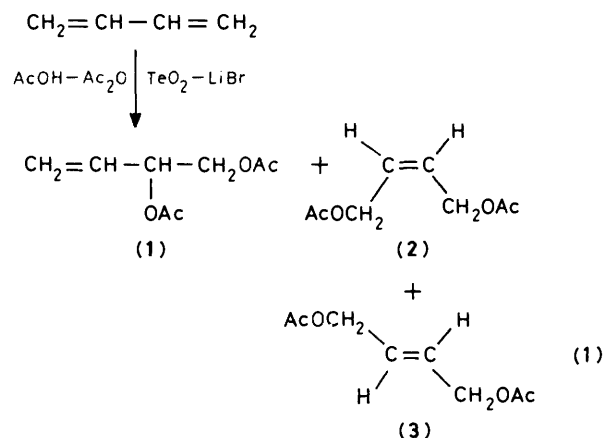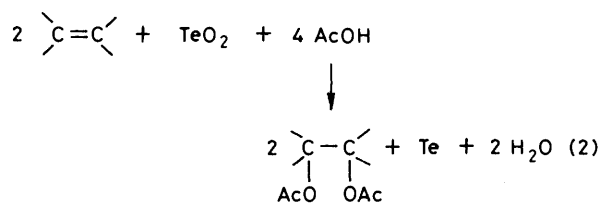

bromide. The isomer ratio of (2) + (3) (1,4-isomers) to (1) (1,2-isomer) as well as their yields depended profoundly on the ratio of LiBr to TeO_2. Thus, when the latter ratio is 1 or 5, the ratio of 1,4-isomers/1,2-isomer is 0.49 or 9.0 respectively, and more-over the product yields were improved about five times in the latter case. This result indicates that 1,4-isomers are formed highly selectively and in good yields when the ratio $LiBr/TeO_2$ is *ca.* 5—10, preferably 5. Since it was confirmed separately that no interconversion occurred between the diacetates (1), (2), and (3) under these reaction conditions and that the equilibrium distribution has been reported to be 65/35 for 1,4-isomers/1,2-isomer,[3b] the observed product distribution should be kinetic-ally controlled. The isomer ratios (3)/(2) are 82—88/12—18, the *trans*-isomer being always the major one. The reaction pro-ceeded even at 95 °C, but slowly. At higher temperatures (*i.e.*, 150—170 °C) considerable quantities of tarry compounds were produced and the proportions of 1,4-isomers were reduced for longer reaction times. Results are summarized in Table 1. There seem to be no reports on such a highly selective synthesis of the 1,4-isomer by the direct oxidation of buta-1,3-diene except that of the Mitsubishi process using a Pd–Te–C catalytic system and the BASF method using MnO_2–KBr–$CuBr_2$.[1,2] It is worth noting that the ratio 1,4-isomers/1,2-isomer = 4.0 was obtained in a similar oxidation of buta-1,3-diene in acetic acid using SeO_2, LiBr, and 1,4-dibromobut-2-ene.[3b]

The reaction also proceeded in the presence of either NaBr,

KBr, LiCl, HBr, or I_2 in the place of LiBr, but the selectivity for 1,4-isomers was lower. The reaction hardly occurred using LiF, LiI, NaCl, Br_2, or NH_4Br as a halogen source. Typical results are also listed in Table 1.

Considering the stoicheiometry shown in reaction (2), 2

$$2 \ \text{C}=\text{C} \ + \ TeO_2 \ + \ 4 \ AcOH$$

$$\downarrow$$

$$2 \ \text{C}-\text{C} \ + \ Te \ + \ 2 H_2O \quad (2)$$
$$\text{AcO} \quad \text{OAc}$$

equiv. of diacetoxyalkane corresponds to 1 equiv. of TeO_2 in a stoicheiometric reaction. When an oxidizing agent such as H_2O_2 or t-BuOOH was added to the reaction system, more than 2 equiv. of diacetoxybutenes were formed in the reaction using 1 equiv. of TeO_2. This means that a low-valent tellurium species such as Te^{II} or Te^0 can be re-oxidized to a Te^{IV} species by the oxidant under the reaction conditions, the reaction being catalytic with respect to TeO_2 to some extent. The best yield (239% based on TeO_2 charged) was obtained almost without affecting the isomer ratio when 10 equiv. of H_2O_2 (to 1 equiv. of TeO_2) were added to the reaction system (Table 1).

Application to other linear conjugated dienes such as isoprene and 2,3-dimethylbuta-1,3-diene resulted in the formation of a mixture of expected isomeric diacetoxyalkenes, i.e., compounds (4)—(6) from isoprene and (7) and (8) from 2,3-dimethylbuta-1,3-diene, while the oxidation of 2,5-dimethylhexa-2,4-diene afforded only the 1,2-isomer (9) in low yield (<7% based on TeO_2) under various conditions examined. In the former two cases the best result of both the product yield and the selectivity for the 1,4-isomer was obtained when the ratio $LiBr/TeO_2$ was ca. 5 as in the case of buta-1,3-diene. In all cases considerable quantities of tarry compounds were produced in the reaction at higher temperature. It was confirmed separately that almost no interconversion occurred between (4), (5), and (6) and also between (7) and (8) under these reaction conditions. The oxidation of cyclic conjugated dienes such as cyclopenta-1,3-diene and cyclohexa-1,3-diene similarly gave the isomeric diacetoxycycloalkenes (10)—(13) and (14) and (15) respectively, but in these cases the isomer ratio of the

(4)

(5)

(6)

(7)

(8)

(9)

(10)   (11)   (12)   (13)

(14)   (15)
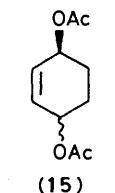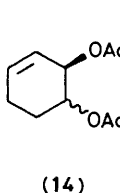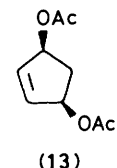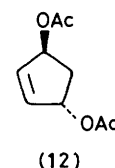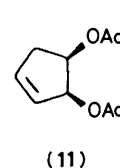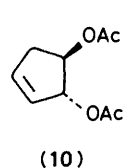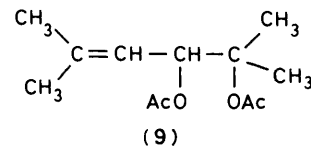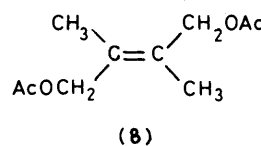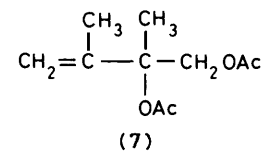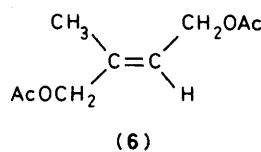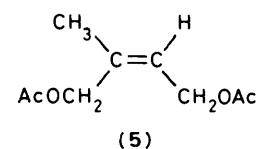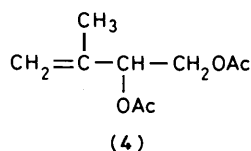
products (1,4-/1,2-) was hardly affected by changing the ratio $LiBr/TeO_2$ and so the detailed study was not carried out. From cyclo-octa-1,3-diene only small amounts of many unidentified compounds were produced. Results are shown in Table 2.

Since tellurium(IV) oxide itself is poorly soluble in acetic acid, LiBr should produce some soluble tellurium(IV) compounds such as $Te(O)(OAc)X$, $Te(O)X_2$, $Te(O)(OAc)_2$, and $Te(OAc)_yX_{4-y}$ ($y = 0$—4) under the present reaction conditions, making the solution homogeneous. Considering the
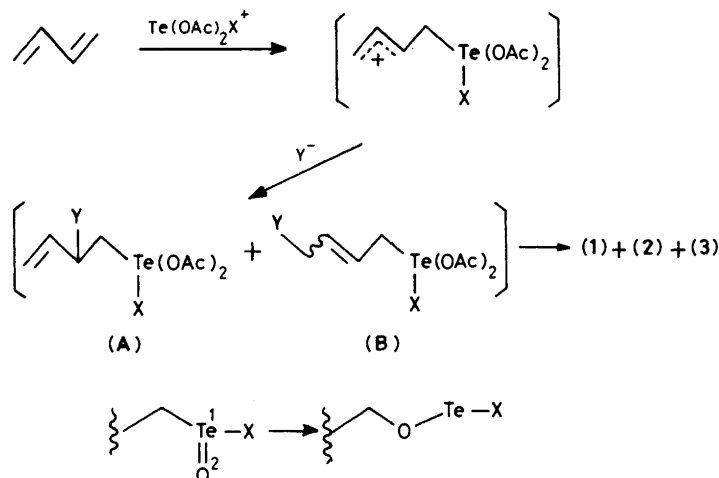

Scheme 1. X = halogen, Y = OAc, halogen

Table 1. Diacetoxybutenes from buta-1,3-diene[a]

Buta-1,3-diene (mmol)	TeO$_2$ (mmol)	Halogen source (mmol)		Reaction temp. (°C)	Reaction time (h)	Product yield[b] (mmol) (1) + (2) + (3)	Isomer ratio[b,c] 1,2-:1,4- [(1):(2) + (3)]
25	5	LiBr	5	125	20	1.27	67:33
25	5	LiBr	10	125	20	3.21	25:75
25	5	LiBr	25	125	5	5.37	11:89
25	5	LiBr	25	125	20	6.10	10:90
25	5	LiBr	50	125	20	3.87	11:89
25	5	LiBr	25	155	2	3.46	9:91
25	5	LiBr	25	155	5	4.37	9:91
25	5	LiBr	25	155	10	4.08	23:77
25	5	LiBr	25	95	20	1.98	18:82
10	5	LiBr	25	125	20	4.49	17:83
50	5	LiBr	25	125	20	6.80	10:90
25	0	LiBr	25	120	20	0	—
25	5	—		120	20	0	—
25	5	LiCl	25	125	20	2.08	55:45
25	5	LiCl	50	125	20	3.07	63:37
25	5	LiI	50	120	5	0.27	100:0
25	5	LiF	50	120	5	0	—
25	5	I$_2$	5	125	20	3.55	80:20[d]
25	0	I$_2$	5	125	20	0	—
50	5	NH$_4$Br	50	120	20	0	—
25	5	HBr	5	120	20	0.75	90:10
25	5	KBr	50	120	20	1.53	38:62
25	5	Br$_2$		120	20	0	—
25	5	NaCl	50	120	20	0.22	86:14[e]
25	5	NaBr	25	125	20	3.67	38:62
25	5	NaBr	50	125	20	3.87	32:68
10[f] H$_2$O$_2$ 20	1	LiBr	20	125	20	2.49	33:67
10[f] H$_2$O$_2$ 10	1	LiBr	20	125	20	4.77	16:84
10[f] t-BuOOH 10	1	LiBr	20	125	20	2.74	9:91
10[f] t-BuOOH 20	1	LiBr	10	125	20	2.00	32:68
10[f] t-BuOOH 20	1	LiBr	10	155	5	1.27	32:68

[a] Carried out in a glass pressure bottle. Solvent: AcOH (18 ml)–Ac$_2$O (2 ml). [b] Determined by g.l.c. [c] (2)/(3) 12—18/82—88. [d] (2)/(3) 9/91. [e] (2)/(3) 23/77. [f] Solvent: AcOH (10 ml)–Ac$_2$O (10 ml).

results of the reaction of olefins[4b,5] and acetylenes[9] with TeO$_2$–LiX–AcOH and also the proposed mechanism for the oxidation of buta-1,3-diene with SeO$_2$,[3c] we propose that the present reaction involves an electrophilic attack of some cationic tellurium(IV) species on one double bond followed by the attack of halide and/or acetate anion (halogeno- and/or acetoxy-telluriation of the double bond) as shown in Scheme 1 [Te(OAc)$_2$X$^+$ and buta-1,3-diene were chosen as a matter of convenience]. Here, TeX$_4$ or TeX$_3$$^+$ (X = halogen) does not seem to be involved in a main reaction pathway, since we confirmed separately that the treatment of buta-1,3-diene with commercial TeBr$_4$ in acetic acid under reflux for 5 h afforded hardly any of the expected diacetoxybutenes. The C–Te bond and the C–Y (Y = halogen) bond of the produced homoallylic and allylic tellurium(IV) compounds [(A) and (B)] may be solvolysed by acetic acid to give compounds (1)—(3). An intramolecular acetolysis of the C–Te bond in (A) or (B) may also be possible as proposed in the case of SeO$_2$ oxidation of buta-1,3-diene.[3c] A 1,2-tellurium–oxygen shift at (A) or (B) [Te(O)X instead of Te(OAc)$_2$X] may give the C–O–Te derivative[10] (Scheme 1) and its hydrolysis during the work-up procedure may produce hydroxy compounds. Although such intermediates as (A) and/or (B) could not be isolated, the possibility of occurrence of such an oxytelluriation of olefins in this reaction system was confirmed by the isolation of a new organotellurium compound (17) from o-allylphenol (Scheme 2) via treatment with TeO$_2$ and LiBr in acetic acid at reflux temperature to afford the intermediate (16) in good yield; the Te^{IV} species was reduced to the telluride (17).[11,*] This type of
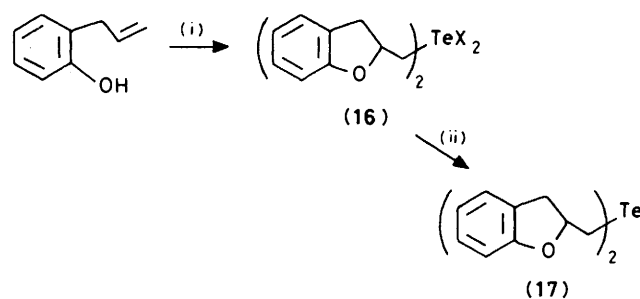
Scheme 2. X = Br, OH, OAc, etc. Reagents: (i) TeO$_2$–LiBr, AcOH; (ii) aqueous Na$_2$S$_2$O$_3$

intramolecular oxytelluriation has been fully investigated by Bergman and Engman under similar reaction conditions using TeO$_2$ and LiCl.[12]

It should also be noted that both diacetates, (2) and (3), were formed from 2,5-dihydrotellurophene(2,5-dihydrotellurole)-1,1-dichloride (18), prepared from buta-1,3-diene and TeCl$_4$ in acetonitrile,[13] in ca. 50% yield when the mixture was heated in acetic acid in the presence of TeO$_2$ and LiBr, the diester (2) being the major product (Scheme 3). This fact suggests that a dihydrotellurophene-type compound such as (C) might also be

* Compound (16) was actually isolated as a mixture of several compounds with different kinds of group X (as determined by [1]H n.m.r. and mass spectra).

Table 2. Diacetoxyalkenes from several conjugated dienes[a]

Diene (mmol)	TeO$_2$ (mmol)	LiBr (mmol)	Reaction temp. (°C)	Reaction time (h)	Product yield[b] (mmol)	Isomer ratio[b,c] 1,2-:1,4-
Isoprene					(4) + (5) + (6)	
25	5	25	70	72	2.33	31:69
25[d]	5	25	95	48	3.85	20:80
25[d]	5	25	100	20	2.47	26:74
25	5	25	100	20	3.43	30:70
25	5	5	100	20	2.16	77:23
25[d]	5	50	100	20	2.96	33:67
2,3-Dimethylbuta-1,3-diene					(7) + (8)	
10	5	5	70	72	1.46	37:63
25	5	5	60	48	1.05	38:62
10[d]	5	25	70	72	1.79	16:84
25	5	25	70	72	2.88	10:90
25	5	50	70	72	0.53	~0:100
25	5	25	70	24	1.19	14:86
25[d]	5	25	100	48	0.15	~0:100
2,5-Dimethylhexa-2,4-diene					(9)	
10	5	5	70	72	0.50	
20[e]	10	10	120	20	1.30	
Cyclopenta-1,3-diene					(10) + (11) + (12) + (13)	
10[e]	5	5	50	20	0.50 (5:40:31:24)	45:55
10[e]	5	5	120	2	1.01 (15:28:28:29)	43:57
Cyclohexa-1,3-diene					(14) + (15)	
10[e]	5	5	50	24	3.60[f]	
5[e]	5	5	120	18	2.15[f]	

[a] Carried out in a glass pressure bottle. Solvent: AcOH (18 ml)–Ac$_2$O (2 ml) except where otherwise stated. [b] Determined by g.l.c. [c] (5)/(6) 27—31/69—73. [d] Solvent: AcOH (36 ml)–Ac$_2$O (4 ml). [e] Solvent: AcOH (10 ml)–Ac$_2$O (1 ml). [f] Isolated yield. An exact isomer ratio could not be determined by g.l.c. because of inseparable peaks.
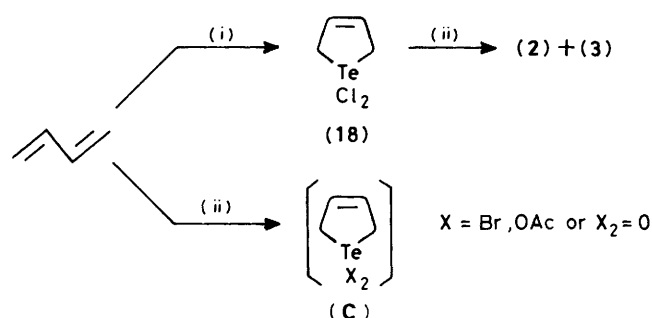
Scheme 3. *Reagents:* (i) TeCl$_4$, CH$_3$CN; (ii) TeO$_2$–LiBr, AcOH

a possible intermediate in the present diacetoxylation reaction, but that it is not involved in the main reaction pathway. A reasonable explanation for the large effect of the ratio LiBr/TeO$_2$ on the ratio 1,4-isomers/1,2-isomer is still obscure.

Experimental

^{1}H N.m.r. spectra were recorded using a JEOL JNM-GX 400 (400 MHz) instrument in CDCl$_3$ with Me$_4$Si as internal standard. I.r. spectra were taken with a Hitachi EPI-S2

spectrophotometer. G.l.c. analyses were carried out using a Shimadzu 4CMPF apparatus with EGSS-X(15%)–Chromosorb-W (1 and 3 m), Apiezon-L(30%)–Celite (3 m), and PEG 6000(25%)–Chromosorb-W (3 m) columns (N$_2$ as carrier gas). Mass spectra were recorded on a JEOL JMN-01SG spectrometer.

All commercial organic solvents and organic and inorganic compounds were used without further purification. The diacetoxyalkenes (1)—(15) were prepared separately by the reported method[14] for authentic samples for g.l.c. analysis.

Oxidation of Buta-1,3-diene with TeO$_2$ *and* LiBr *in Acetic Acid.*—The following example is a typical experimental procedure for the oxidation of a diene. A mixture of TeO$_2$ (0.80 g, 5 mmol), LiBr (2.17 g, 25 mmol), acetic acid (18 ml), and acetic anhydride (2 ml) was placed in a glass pressure bottle (Taiatsu Glass Ind. Co. Ltd.; content 50 ml) with a magnetic stirring bar. The bottle was chilled to *ca.* −20 °C and to it was added chilled liquid buta-1,3-diene (1.35 g, 25 mmol). The resulting suspension was heated on an oil-bath (120—130 °C) and stirred for 20 h, during which time the mixture became a yellow homogeneous solution and gradually turned to a blackened suspension. The mixture was cooled and the solids were filtered off. The filtrate was treated with brine and then extracted with CHCl$_3$ (50 ml × 3). The extract was washed successively with aqueous NaHCO$_3$ and brine, and then dried over MgSO$_4$. G.l.c. analysis

of the extract revealed the presence of the diacetates (1)—(3) and some minor compounds. Evaporation of the solvent left an oily residue, the i.r. spectrum of which showed strong absorptions due to hydroxy and acetoxy groups, and the residue was treated with acetic anhydride (3 ml) in pyridine (7 ml) at 80 °C for 1 h. G.l.c. analysis of the pyridine solution using ethyl cinnamate as internal standard revealed the presence of compounds (1) (0.61 mmol), (2) (0.71 mmol), and (3) (4.78 mmol) [total 1.05 g, 6.10 mmol; (1):(2) + (3) 10:90].

Treatment of Buta-1,3-diene with TeBr$_4$.—A mixture of TeBr$_4$ (Strem Chemicals) (2.24 g, 5 mmol), buta-1,3-diene (1.35 g, 25 mmol), acetic acid (18 ml), and acetic anhydride (2 ml) was placed in a pressure bottle and the resulting yellow suspension was heated at 120—125 °C as above. It turned quickly into a black suspension and after 5 h the mixture was worked up as above (black precipitates 0.40 g). G.l.c. analysis of the pyridine solution using ethyl cinnamate as internal standard revealed the presence of diacetates (1) (0.03 mmol), (2) (0.01 mmol), (3) (0.11 mmol) [total 0.15 mmol; (1):(2) + (3) 20:80].

Isolation of Bis-[(2,3-dihydrobenzofuran-2-yl)methyl] Telluride (17).—A heterogeneous mixture of *o*-allylphenol (2.64 g, 20 mmol), TeO$_2$ (1.60 g, 10 mmol), LiBr (0.86 g, 10 mmol), acetic acid (20 ml), and acetic anhydride (5 ml) was stirred at reflux temperature for 2 h. The mixture was cooled and the grey solids were filtered off. The filtrate was treated with water and extracted with CHCl$_3$ (50 ml × 3). The extract was combined with CHCl$_3$ washings of the solid and the chloroform solution was washed successively with aqueous NaHCO$_3$, aqueous Na$_2$S$_2$O$_3$, and brine, and dried over MgSO$_4$. Evaporation of the solvent left an orange solid which was recrystallized from hexane–CHCl$_3$ (9:1) to afford white crystals of the pure telluride (17) (2.40 g, 61%), m.p. 132—133 °C; δ_H (400 MHz) 2.93 (2 H, dd, J 15.62 and 7.32 Hz), 3.01 (2 H, dd, J 12.21 and 7.33 Hz), 3.12 (2 H, dd, J 12.21 and 5.86 Hz), 3.36 (2 H, dd, J 15.63 and 9.28 Hz), 4.97—5.04 (2 H, m), 6.73 (2 H, d, J 7.82 Hz), 6.83 (2 H, t, J 7.32 Hz), and 7.07—7.13 (4 H, m); $v_{max.}$(KBr disk) 1 595s, 1 481s, 1 460s, 1 412, 1 360, 1 330, 1 317, 1 238s, 1 227s, 1 170, 1 151, 1 099, 1 018, 988, 936s, 924s, 869, 857, 797, 744s, and 713 cm^{-1}; *m/z* 392, 394, and 396 (Found: C, 54.3; H, 4.61. C$_{18}$H$_{18}$O$_2$Te requires C, 54.9; H, 4.57%).

Treatment of the Tellurophene (18) *with Acetic Acid.*—A pale yellow heterogeneous mixture of compound (18) [0.50 g, 2 mmol; m.p. 190 °C (decomp.)],[13] TeO$_2$ (5 mmol), LiBr (5 mmol), and acetic acid (30 ml) was treated as described above. G.l.c. analysis of the CHCl$_3$ extract using ethyl cinnamate as internal standard revealed the presence of 1,4-dichlorobut-2-ene (0.1 mmol), compounds (1) (trace), (2) (0.72 mmol), and (3) (0.33 mmol), and small amounts of six unidentified compounds.

References
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