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SELECTIVE 1,4-DIACETOXYLATION OF CONJUGATED DIENES WITH TELLURIUM(IV) OXIDE

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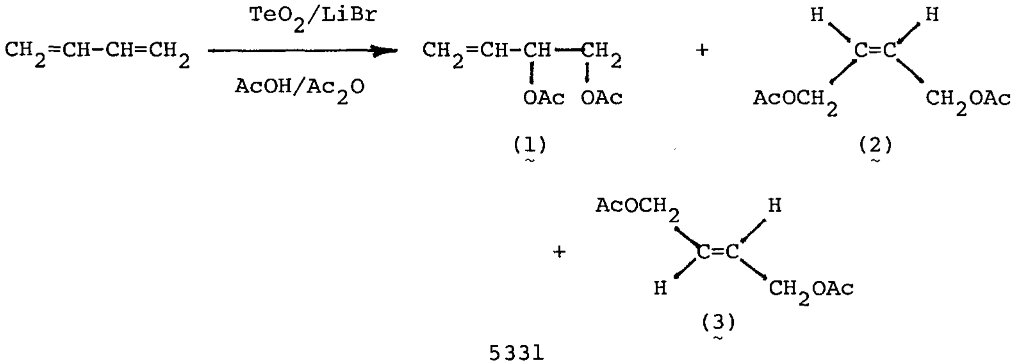
Summary: Oxidation of several linear conjugated dienes with tellurium(IV) oxide and lithium bromide in acetic acid affords an isomeric mixture of the corresponding diacetoxyalkenes (1,2- and 1,4-addition products), 1,4-isomer being highly selectively produced when the ratio of LiBr/TeO_2 is 5-10.

The production of butane-1,4-diol (leading to tetrahydrofuran) by the direct oxidation of buta-1,3-diene is industrially important and remarkable.[1] A key reaction in this process is the liquid phase selective acetoxylation of the diene to 1,4-diacetoxybut-2-ene. We now report a facile and new method for the selective 1,4-diacetoxylation of several conjugated dienes with tellurium(IV) oxide, lithium or sodium halide, and acetic acid, focusing on the oxidation of buta-1,3-diene.

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 under stirring in a glass pressure bottle. The reaction mixture was heterogeneous when LiBr/TeO_2=1, while it was homogeneous when its ratio is 5-10. Elemental tellurium was deposited as the reaction proceeded. After

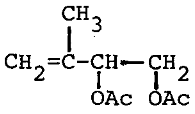


usual work up procedure (filtration, addition of aq. NaCl, extraction with $CHCl_3$, washing with aq. $NaHCO_3$, drying over Na_2SO_4, evaporation of $CHCl_3$) the organic products were treated with acetic anhydride/pyridine (80°C, 1 h) to convert the hydroxyl derivatives (small amounts) to the corresponding acetates, GLC analysis of which revealed that 3,4-diacetoxybut-1-ene(**1**), cis-1,4-diacetoxybut-2-ene(**2**), and its trans-isomer(**3**) are the products. The ratio of (**2**)+(**3**)(1,4-isomers) to (**1**)(1,2-isomer) and their yields depended profoundly on the ratio of $LiBr/TeO_2$. Thus, when the latter ratio is 1 or 5, the ratio of (**2**)+(**3**)/(**1**) is 0.49 or 9.0 respectively, and moreover the product yields are improved about five times in the latter case. This indicates that 1,4-isomers are formed highly selectively and in good yields when the ratio of $LiBr/TeO_2$ is 5. Since we confirmed separately that no interconversion between (**1**)-(**3**) occurred under these reaction conditions and an equilibrium distribution is reported to be 65/35 for (**2**)+(**3**)/(**1**),[1c] the observed product distribution is kinetically controlled. The isomer ratios of (**3**)/(**2**) are 84-88/12-16 in any case, the formation of trans-isomer being always favoured. The reaction proceeded rapidly at higher temperature, but lots of tarry compounds were produced and the ratio for 1,4-isomer became low at longer reaction time. Typical results are shown in Table. There seems to be no report on such highly selective synthesis of 1,4-isomer by the direct oxidation of buta-1,3-diene except Mitsubishi process using Pd/Te/C catalytic system and BASF method using $MnO_2/KBr/CuBr_2$.[1]

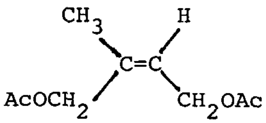
The reaction also proceeded with NaBr, LiCl and HBr in the place of LiBr, but the selectivity for 1,4-isomers was lower. Almost no reaction occurred by using LiF, LiI, NaCl, Br_2 and NH_4Br in the place of LiBr.

Application to other linear conjugated dienes afforded the corresponding isomeric diacetoxyalkenes: i.e., (**4**), (**5**) and (**6**) from isoprene and (**7**) and (**8**) from 2,3-dimethylbuta-1,3-diene. The selectivity for 1,4-isomers became higher in these cases as well when the ratio of $LiBr/TeO_2$ was larger. Typical results are also shown in Table.

In view of the results of the reactions of olefin[2] and acetylene[3] with TeO_2/LiX/AcOH and also the proposed mechanism of oxidation of buta-1,3-diene


$CH_2=C(CH_3)-CH(OAc)-CH_2OAc$

(4)



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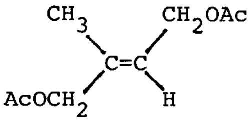

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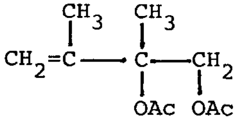
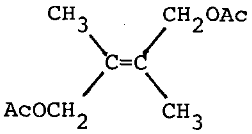

$CH_2=C(CH_3)-C(CH_3)(OAc)-CH_2OAc$

(7)



(8)

Table. Diacetoxyalkenes from conjugated dienes.[a]

Diene (mmol)	LiBr (mmol)	Temp (°C)	Time (h)	Yield[b] (mmol)	Isomer ratio[b] 1,2-:1,4-
Buta-1,3-diene					[(1):(2)+(3)]
25	5	125	20	1.27	[67:33]
25	25	125	20	6.10	[10:90]
25	50	125	20	3.65	[10:90]
25	5	155	5	4.37	[9:91]
25	25	155	10	4.08	[23:77]
10	25	125	20	4.49	[17:83]
25	25[c]	125	20	3.47	[26:74]
25	50[d]	125	20	3.07	[63:37]
Isoprene					[(4):(5)+(6)]
25	5	120	20	2.50[e]	[81:19]
25	25	95	48	3.85[e]	[20:80]
2,3-Dimethyl-buta-1,3-diene					[(7):(8)]
10	5	70	72	1.46	[37:63]
25	25	70	72	2.88[e]	[10:90]

a) TeO$_2$(5 mmol) and AcOH(18 ml)-Ac$_2$O(2 ml) were used. b) Determined by GLC. For the identification of products, see ref. 7. (2)/(3)=12~16/84~88. (5)/(6)= ca. 3/7. c) NaBr. d) LiCl. e) Isolated yield by column chromatography [SiO$_2$, hexane/ethyl acetate(5/1)].

with selenium dioxide,[4] it is probable that the reaction involves an electrophilic attack of tellurium(IV) species such as $Te(O)X^+$, $Te(OAc)_2X^+$, or TeX_3^+ etc. on one double bond followed by the attack of halide and/or acetate anion (halogeno- and/or acetoxytelluration). Then, the C-Te bond of the produced allylic or homoallylic tellurium(IV) compounds and also the C-X bond may be solvolyzed by acetic acid to give the products. It should be worth to refer that the reaction between $TeCl_4$ and buta-1,3-diene gave bis(4-chloro-2-butenyl)-tellurium dichloride in CCl_4[5] and 2,5-dihydrotellurophene 1,1-dichloride in acetonitrile,[6] respectively.

1. For example, (a) A. M. Brownstein and H. L. List, Hydrocarbon Processing, **56**, No.9, 159(1977). (b) L. F. Hatch and S. Matar, ibid., **57**, No. 8, 153 (1978). (c) P. R. Stapp, J. Org. Chem., **44**, 3216(1979).
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