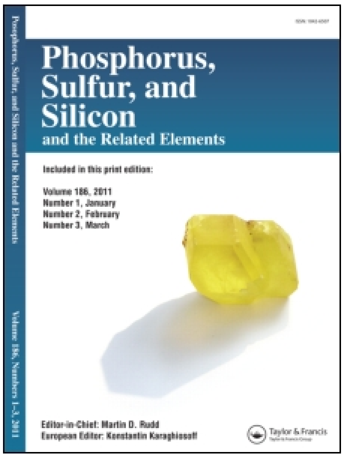

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CATALYTIC OXIDATION OF OLEFINS USING DIPHENYL DITELLURIDE

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To cite this Article Kambe, Nobuaki , Fujioka, Toyozo , Ogawa, Akiya , Miyoshi, Noritaka and Sonoda, Noboru(1988) 'CATALYTIC OXIDATION OF OLEFINS USING DIPHENYL DITELLURIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 38: 1, 167 — 175

To link to this Article: DOI: 10.1080/03086648808079711

URL: http://dx.doi.org/10.1080/03086648808079711

Phosphorus and Sulfur, 1988, Vol. 38, pp. 167–175
Reprints available directly from the publisher

CATALYTIC OXIDATION OF OLEFINS USING DIPHENYL DITELLURIDE

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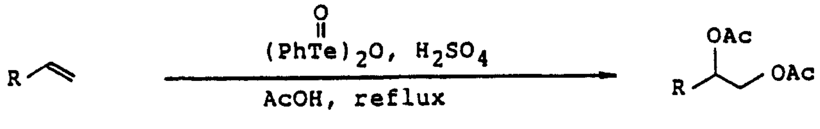
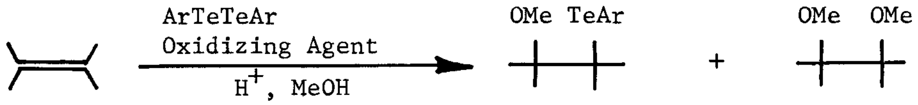
Abstract Reaction of aliphatic olefins with tert-butyl hydroperoxide and diaryl ditellurides in the presence of sulfuric acid in refluxing methanol gave methoxytellurenylation products with high regioselectivity having the arylturo group on the terminal carbon in the case of terminal olefins. The stereochemistry of the product from cyclohexene was trans. Under similar conditions, aromatic substituted olefins afforded vic-dimethoxyl compounds in the presence of a catalytic amount of diaryl ditelluride. In this reaction, molecular oxygen (or air) as well as peroxides and peracids were found to be effective as the oxidizing agent. The catalytic oxidation of olefins reported here proceeded in net syn fashion probably via anti methoxytellurenylation followed by displacement of the phenyltelluro group by a methoxy group with inversion.

INTRODUCTION

We have recently reported that olefins are oxidized with benzenetellurinic anhydride in refluxing acetic acid to give vic-diacetates.[1]



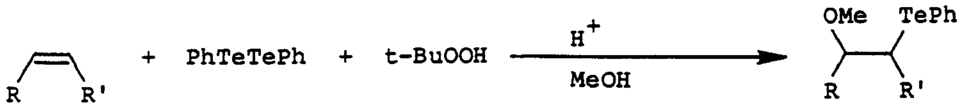
This reaction, based on the quantity of benzenetellurinic anhydride used, gives quantitative yields of diphenyl ditelluride. It is expected, therefore, that a similar oxidation may be achieved by the use of a catalytic amount of a ditelluride if selective oxidation of the ditelluride to the tellurinic acids can be carried out. Hence, the reaction of olefins with various oxidizing reagents in the presence of diaryl ditellurides was investigated. Aliphatic olefins were found to undergo methoxytellurenylation to give **b** in refluxing methanol in the presence of sulfuric acid. Under similar conditions, aromatic substituted olefins gave **c** in the presence of a catalytic amount of ditelluride. We report here some representative results of this new oxidation system of olefins.



a **b** **c**

OXIDATION OF ALIPHATIC OLEFINS

When aliphatic olefins were treated with t-butyl hydroperoxide in the presence of diphenyl ditelluride and sulfuric acid in refluxing methanol for 24 h, corresponding methoxytellurenylation products were obtained. This reaction proceeds with complete regioselectivity in the case of terminal olefins to give adducts in which phenyltelluro group are attached to the terminal carbon. Cyclohexene gave only the trans adduct. In the absence of sulfuric acid no reaction took place.



1 **2**

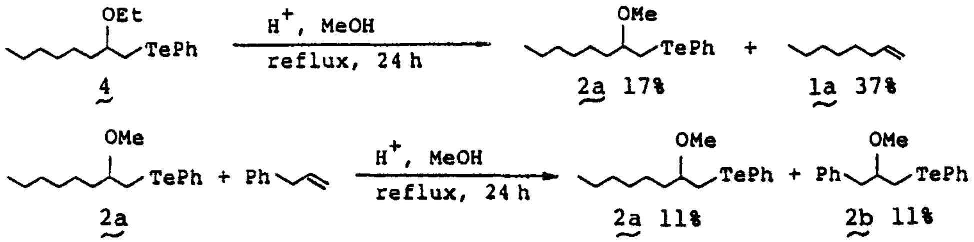
It is likely that there exists a rapid equilibrium process between the product **2**[2] and the starting material **1**, which is supported by the following facts. Treatment of 2-ethoxyoctyl

Table 1. Reaction of Aliphatic Olefins

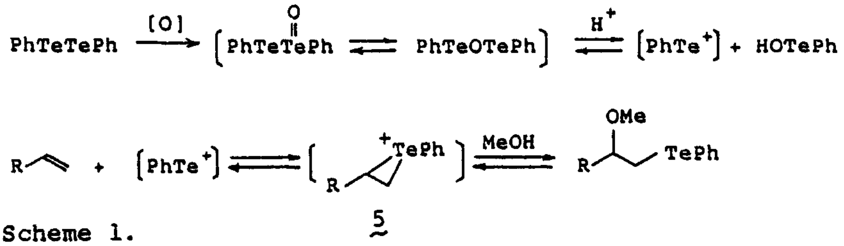
Olefin				Product[2]	
1	R	R'	mmol	2	mmol
1a	n-C_6H_{13}	H	1	2a	0.59
1b	$PhCH_2$	H	1	2b	0.73
1c	$-(CH_2)_4-$		3	2c	0.32

Conditions : PhTeTePh (1 mmol), H_2SO_4 (2 mmol), t-BuOOH (1 mmol), MeOH (10 ml), reflux, 24 h.

phenyl telluride 4[3] under the identical conditions afforded octene 1a and 2-methoxyoctyl phenyl telluride 2a in which ethoxy group in 4 was displaced by a methoxy group. In addition, a similar treatment of 2a in the presence of 3-phenylpropene gave equimolar amounts of corresponding adduct 2b and 2a.



The reaction may proceed through tellurenylation of olefins to give the active intermediate 5 which then undergoes methanolysis as shown in the following Scheme 1.



Scheme 1.

OXIDATION OF AROMATIC OLEFINS

We then examined similar oxidation of aromatic olefins. Under the identical conditions, styrene and p-methylstyrene gave corresponding vic-dimethoxy compounds 3d and 3e as the sole products. In the case of p-chlorostyrene, a small amount of methoxytellurenylation product 2f was obtained together with 3f. When the amount of sulfuric acid was reduced to 1/10, only 2d[2] was formed from styrene. In this reaction the use of a small amount of ethylene glycol was essential, since otherwise the reaction mixture was heterogeneous and the oxidation did not take place.

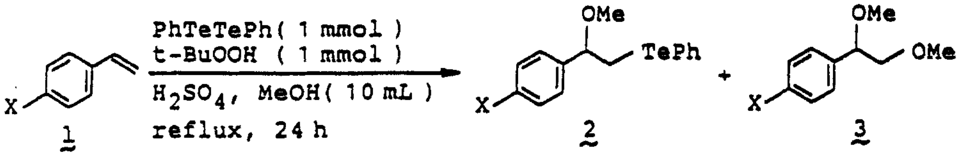


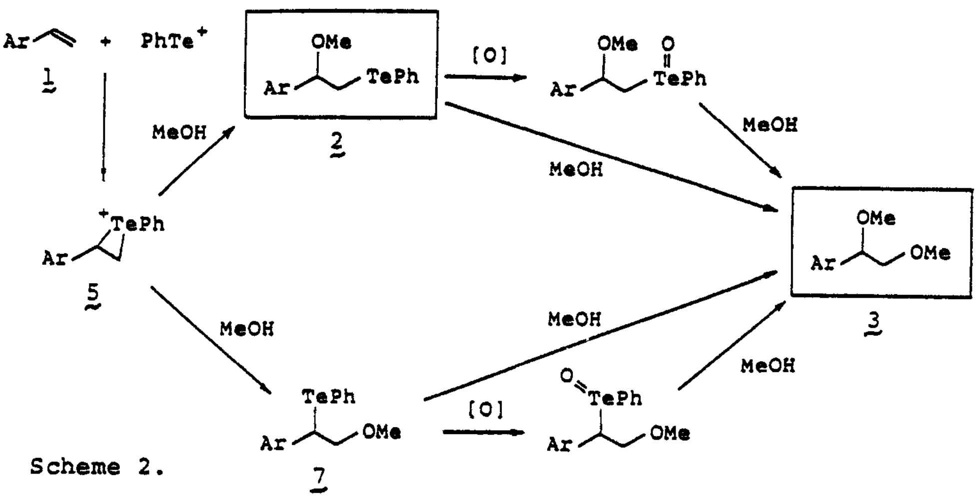
Table 2. Oxidation of Aromatic Olefins

olefin		H_2SO_4	yield in mmol(%)	
1	X (mmol)	mmol	2	3
1d	H (1)	2	0	0.73(73)
1d	H (2)	2	0	1.00(50)
1e	Me (1)	2	0	0.74(74)
1f	Cl (2)	2	0.05(2.5)	0.54(27)
1d*	H (1)	0.2	0.17(17)	0

* $HOCH_2CH_2OH$(0.5 mL) was added.

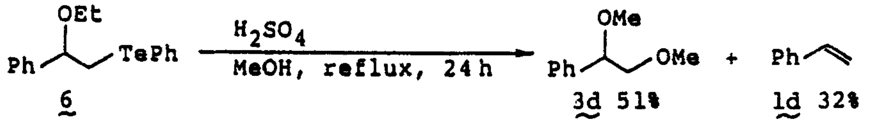
In Scheme 2 are shown some plausible paths of the present oxidation. Although isolation of the adduct 2 from this reaction system might suggest that 2 could be an intermediate, the following results may rule out the direct conversion process from 2 to 3 through simple displacement of phenyltelluro group with methoxy group.

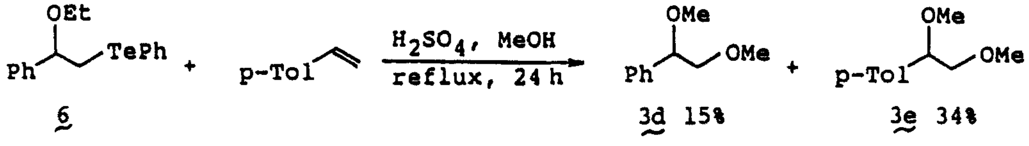
Treatment of 2-ethoxy-2-phenylethyl phenyl telluride 6[4] under the identical conditions afforded only 3d and styrene. A

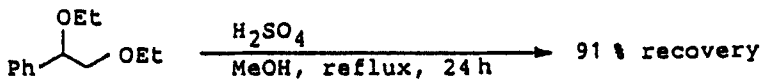


Scheme 2.

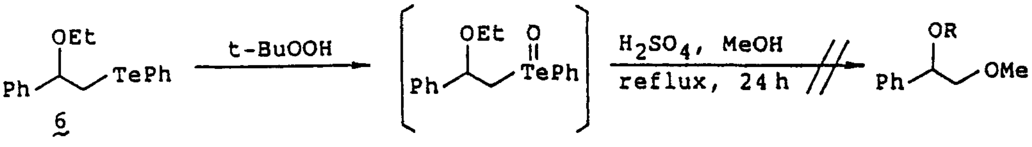
similar reaction of 6 in the presence of p-methylstyrene gave 3d and 3e. These results indicate a rapid equilibrium between 2 and the starting olefin 1 as in the case of aliphatic olefins. The treatment of α,β-diethoxystyrene under the identical conditions resulted in no displacement of methoxy by ethoxy and only starting material was recovered.



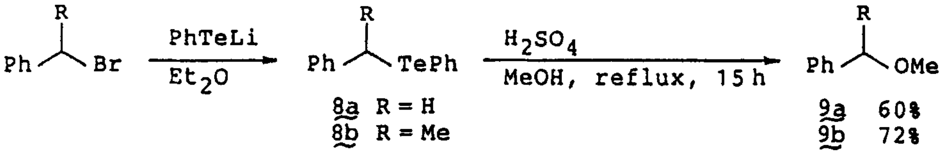


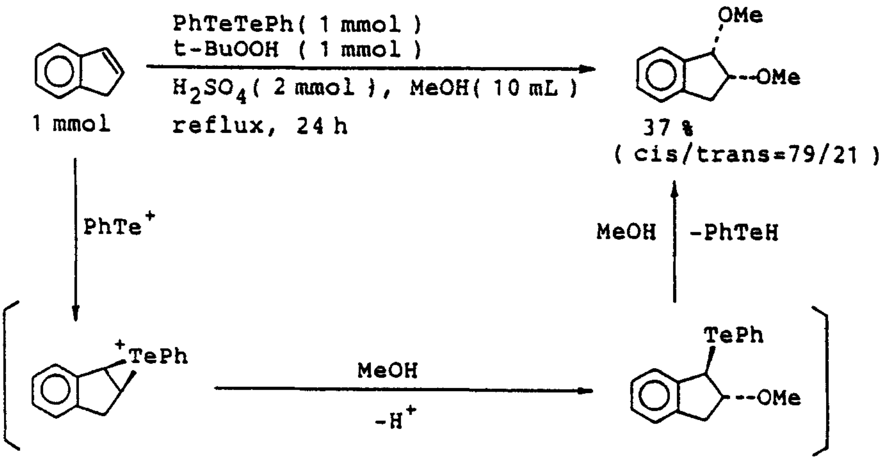


When 6 was oxidized with a stoichiometric amount of t-butyl hydroperoxide under similar conditions, any displacement products (R = Me or Et in the following Eq.) could not be detected in the resulting mixture. This fact eliminates the possibility that tellurium in the leaving group should have a higher oxidation state like that in telluroxides or tellurones.



These results have led us to suggest the intermediacy of adduct 7 which is the regioisomer of 2. In order to confirm this possibility, 8a and 8b, model compounds of 7, were subjected to methanolysis under the same conditions, and it was found that phenyltelluro group attached to benzylic carbon was easily displaced by methoxy group under these conditions.



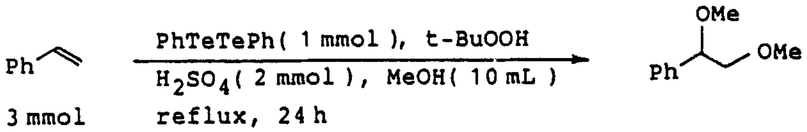


Scheme 3.

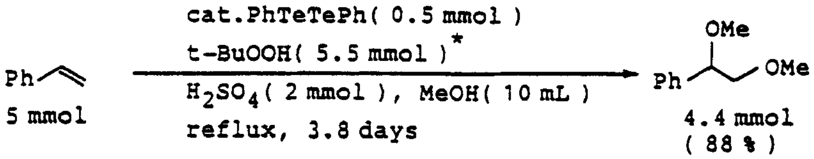
The stereochemistry of this reaction has been examined by use of indene. The major product had cis configuration, and this could be explained by the proposed reaction path; i.e., trans methoxytellurenylation following by inversion in methanolysis as shown in Scheme 3.

CATALYTIC USE OF DIARYL DITELLURIDES

Similar oxidation of aromatic olefins was found to proceed by use of a catalytic amount of diaryl ditellurides. It should be noted that the oxidation did not take place when more than three equivalents of t-butyl hydroperoxide to the ditelluride used was added in one portion. This problem has been overcome by the stepwise addition of the reagent as shown below. Similar oxidation proceeded by use of bis(p-methylphenyl) ditelluride and bis-(p-methoxyphenyl) ditelluride. The reaction was slightly faster with the former and slower with the latter than in the case of diphenyl ditelluride.

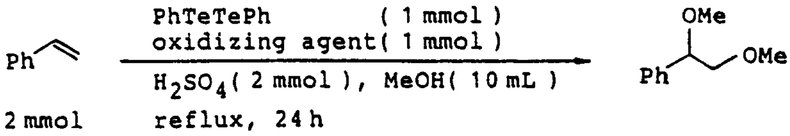


t-BuOOH(mmol)	yield(mmol)
1.0	1.0
2.0	1.9
3.0	0



* 1 mmol + 0.5 mmol X 9 times

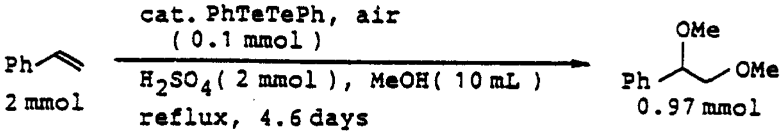
From similar reactions carried out using a limited amount of different oxidizing reagents, it was found that molecular oxygen as well as hydrogen peroxide and 3-chloroperoxybenzoic acid could also be used as an efficient oxidizing agent.

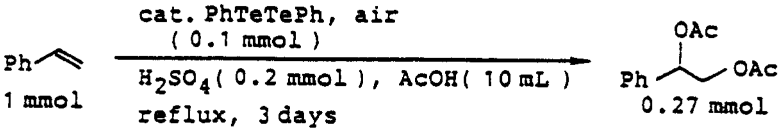


entry	oxidizing agent	yield(mmol)*
1	t-BuOOH	1.01
2	H_2O_2	1.01**
3	mCPBA	0.81
4	$Cu(OAc)_2$	0.10
5***	O_2	1.03

* GLC yield. ** Isolated yield.
*** O_2(0.45 mmol), 48 h.

Examples of air oxidation of styrene are shown below. Use of methanol and acetic acid as the solvent afforded corresponding vic-dimethoxy compound and vic-diacetate, respectively.





ACKNOWLEDGMENT

This work was supported in part by a grant-in-aid from the Ministry of Education, Science, and Culture, Japan.

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1) N. Kambe, T. Tsukamoto, N. Miyoshi, S. Murai, and N. Sonoda, Chem. Lett., 269(1987). For related tellurium and selenium chemistry, see references cited therein.

2) Products 2a-d were obtained in pure form from the resulting mixture by dilution with ether (50 ml), neutralization with potassium carbonate, and filtration followed by radial layer chromatography (silica gel, pentane/ether); 2a : ^{1}H NMR(270MHz, $CDCl_3$) δ 7.74-7.70(m, 2H), 7.25-7.11(m, 3H), 3.36(qu, 1H, 5.4Hz), 3.28(s, 3H), 3.10(d, 1H, 5.4Hz), 3.09(d, 1H, 5.4Hz), 1.57(br, 2H), 1.30-0.80(m, 11H); ^{13}C NMR(67.8MHz, $CDCl_3$) δ 138.5, 129.0, 127.4, 112,1, 81.1, 56.6, 35.0, 31.7, 29.3, 25.3, 22.6, 14.6, 14.1; MS(70eV, m/e, ^{130}Te), 350(M^+); Anal. Calcd for $C_{15}H_{24}OTe$: C, 51.78; H, 6.95. Found: C, 51.90; H, 7.08. 2b : ^{1}H NMR(60MHz, CCl_4) δ 7.75-7.45(m, 2H), 7.20-6.90(m, 8H), 3.53(qu, 1H, 6.0Hz), 3.25(s, 3H), 2.95(d, 2H, 6.0Hz), 2.85(d, 2H, 6.0Hz); ^{13}C NMR (22.5MHz, $CDCl_3$) δ 138.2, 129.7, 129.1, 128.5, 127.8, 126,6, 112.2, 82.5, 57.1, 41.3, 14.1; MS(70eV, m/e, ^{130}Te), 356(M^+); Anal. Calcd for $C_{16}H_{18}OTe$: C, 54.30; H, 5.13. Found: C, 54.11; H, 5.17. 2c: ^{1}H NMR(270MHz, $CDCl_3$) δ 7.82(d, 2H, 5.4Hz), 7.40-7.10 (m, 3H), 3.54(dt, 1H, 4.0, 10.0Hz), 3.35(s, 3H), 3.25(dt, 1H, 4.0, 10.0Hz), 2.25-1.10(m, 8H); ^{13}C NMR(67.8MHz, $CDCl_3$) δ 141.0, 128.8, 127.8, 111.1, 84.4, 56.2, 33.8, 32.0, 31.4, 27.6, 23.9. 2d : ^{1}H NMR (60MHz, CCl_4) δ 7.80-7.40(m, 2H), 7.30-6.90(m, 8H), 4.37(dd, 1H, 5.2, 8.2Hz), 3.35(dd, 1H, 8.2, 11.1HZ), 3.20(s, 3H), 2.95(dd, 1H, 5.2, 11.1Hz); ^{13}C NMR (22.5MHz, $CDCl_3$) δ 140.9, 137.2, 128.0, 127.5, 126.9, 126.4, 125.4, 111.5, 83.3, 56.0, 16.4; MS(70eV, m/e, ^{130}Te), 342(M^+); Anal. Calcd for $C_{15}H_{16}OTe$: C, 53.01; H, 4.74. Found: C, 52.90; H, 4.84.

3) Reaction of 1-octene using ethanol as the solvent in the presence of 0.3 ml of ethylene glycol under similar conditions as in run 1 of Table 1 gave 4. The workup was just the same as mentioned above. 4 : ^{1}H NMR(270MHz, $CDCl_3$) δ 7.72(d, 2H, 7.6Hz), 7.30-7.10(m, 3H), 3.53-3.40(m, 3H), 3.11(d, 2H, 6.1Hz), 1.57(br, 2H), 1.40-1.20(br, 8H), 1.15(t, 3H, 6.7Hz), 0.90-0.80(br, 3H); ^{13}C NMR (67.8MHz, $CDCl_3$) δ 138.3, 129.0, 127.4, 112.2, 79.5, 64.4, 35.6, 31.8, 29.3, 25.4, 22.6, 15.5, 15.4, 14.1.

4) Reaction of 2-ethoxy-2-phenylethyl bromide with sodium benzenetellurolate prepared from diphenyl ditelluride and sodium borohydride in ethanol gave 6 in 46% yield. 6 : ^{1}H NMR (60MHz, CCl_4) δ 7.67-7.37(m, 2H), 7.25-6.83(m, 8H), 4.47(dd, 1H, 5.0, 8.0Hz), 3.38(dd, 1H, 8.0, 11.0Hz), 3.30(q, 2H, 7.0Hz), 3.00(dd, 1H, 5.0, 11Hz), 1.13(t, 3H, 7.0Hz); ^{13}C NMR(22.5MHz, $CDCl_3$) δ 141.5, 136.9, 127.7, 127.2, 126.5, 126.1, 125.1, 111.6, 81.3, 63.3, 16.7, 14.0; MS(70eV, m/e, ^{130}Te), 356(M^+); Anal. Calcd for $C_{16}H_{18}OTe$: C, 54.30; H, 5.13. Found: C, 54.06; H, 5.15.