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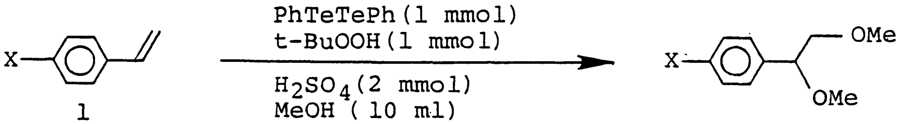
Oxidation of Aromatic Olefins Catalyzed by Diaryl Ditellurides

Nobuaki KAMBE,* Toyozo FUJIOKA, Akiya OGAWA, Noritaka MIYOSHI, and Noboru SONODA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Diaryl ditellurides were found to have unique catalytic activity for oxidation of aromatic olefins with a variety of oxidizing reagents in methanol or in acetic acid to give vic-dimethoxyl or vic-diacetoxyl compounds, respectively. Molecular oxygen (or air) as well as organic peroxides and peracids can be employed as the oxidizing reagents in this new oxidation system.

We have recently reported that olefins are oxidized with benzenetellurinic anhydride in acetic acid to vic-diacetates and proposed that benzenetellurenic acid derivatives formed in situ play an important role as the active species in this oxidation.[1] Since a quantitative amount of diphenyl ditelluride was obtained from the resulting mixture of this reaction, it was expected that similar oxidation should proceed by use of a catalytic amount of a ditelluride if selective oxidation of ditellurides to tellurenic acid derivatives could be attained. Now we wish to report that styrenes undergo oxidation in methanol or in acetic acid in the presence of a catalytic amount of a diaryl ditelluride under controlled addition of various oxidizing reagents.[2]

As preliminary experiments, we carried out reactions using stoichiometric amount of diphenyl ditelluride and tert-butyl hydroperoxide. In refluxing methanol, styrene and p-methylstyrene gave corresponding vic-dimethoxyl compounds 2 in 73% and 74% isolated yields, respectively, in the presence of sulfuric acid as an acid catalyst. In the absence of sulfuric acid, the oxidation did not take place.



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1 mmol

2a : X = H 73%

2b : X = Me 74%

The reactions were examined using a limited amount of various oxidizing reagents (see Table 1). The product 2a was obtained in almost

Table 1. Oxidation of Styrene with Various Oxidizing Reagents in Methanol[a]

Oxidizing reagent	Yield of 2a/mmol[b]
t-BuOOH	1.00
H_2O_2	1.01[c]
MCPBA	0.81
O_2[d]	1.03

a) Styrene(2 mmol), PhTePh(1 mmol), oxidizing reagent(1 mmol), H_2SO_4(2 mmol), MeOH(10 ml), reflux, 24 h. b) GLC yield. c) Isolated yield. d) Molecular oxygen (0.45 mmol), 48 h.

quantitative yield based on the reagent in every case. Interestingly, molecular oxygen acts quite efficiently.$^{3)}$

These successful results prompted us to examine the catalytic use of ditellurides in this system. But we encountered a problem that the oxidation did not take place when more than three equivalents of oxidizing reagent to ditelluride was added in one portion to the reaction mixture, although use of less than three equivalents of the reagent gave quantitative amount of product (Table 2, runs 1-3). This problem has been overcome by continuous or periodical addition of the oxidizing reagent into the reaction mixture. Some representative results are presented in runs 4-6. tert-Butyl hydroperoxide gave a satisfactory result. What should be emphasized is that the catalytic oxidation proceeded by the use of air as the oxidizing agent. When acetic acid was employed as the solvent, the corresponding diacetate was obtained (run 6). Similar oxidation took place in the presence 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.

Table 2. Catalytic Oxidation of Styrene$^{a)}$

Run	Styrene	Ph_2Te_2	Oxidizing reagent	H_2SO_4	Solvent	Time	Product	
	mmol	mmol	(mmol)	mmol			mmol	Yield/%$^{b)}$
1	3	1.0	$\underline{\text{t-BuOOH(1.0)}}$$^{c)}$	2.0	MeOH	24 h	1.0	100
2	3	1.0	$\underline{\text{t-BuOOH(2.0)}}$$^{c)}$	2.0	MeOH	24 h	1.9	95
3	3	1.0	$\underline{\text{t-BuOOH(3.0)}}$$^{c)}$	2.0	MeOH	24 h	0	0
4	$\underline{5}$	0.5	t-BuOOH(5.5)$^{d)}$	2.0	MeOH	3.8 d	4.4	88
5	$\underline{2}$	0.1	Air$^{e)}$	2.0	MeOH	4.6 d	0.97	49
6	$\underline{1}$	0.1	Air$^{e)}$	0.2	AcOH	3 d	0.27$^{f)}$	27

a) In refluxing solvent(10 ml). b) Isolated yield based on the limited amount of substance which is indicated by an underline. c) Added in one portion. d) Added periodically (1 mmol + 0.5 mmol X 9 times). e) Slowly bubbled continuously. f) The product is phenyl-1,2-ethanediol diacetate.

Indene was oxidized under similar conditions to 1,2-dimethoxyindane with cis/trans ratio of 79/21 which is quite similar to the cis/trans ratios of products obtained by oxidation of olefins with benzenetellurinic acid in acetic acid.$^{1)}$

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References

1) N. Kambe, T. Tsukamoto, N. Miyoshi, S. Murai, and N. Sonoda, Chem. Lett., 1987, 269.

2) Reaction of olefins with disulfides or diselenides in the presence of oxidizing reagent results in oxysulfenylation or oxyselenenylation. See, T. Hori and K. B. Sharpless, J. Org. Chem., 43, 1689(1978); M. Shimizu, R. Takeda, and I. Kuwajima, Tetrahedron Lett., 1979, 419 and 3461; B. M. Trost, M. Ochiai, and P. G. McDougal, J. Am. Chem. Soc., 100, 7103(1978); N. Miyoshi, Y. Ohno, K. Kondo, S. Murai, and N. Sonoda, Chem. Lett., 1979, 1309.

3) Ditellurides are known to be oxidized with oxygen, but the product has not been fully characterized. For example, see: H. D. K. Drew, J. Chem. Soc., 1926, 223; G. T. Morgan and R. E. Kellett, ibid., 1926, 1080.

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