CHEMISTRY LETTERS, pp. 269-272, 1987.

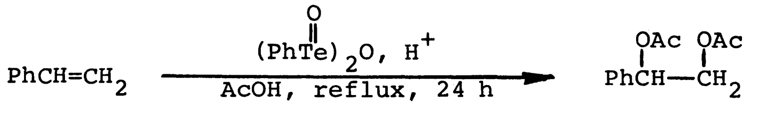
Oxidation of Olefins with Benzenetellurinic Anhydride

Nobuaki KAMBE,* Takashi TSUKAMOTO, Noritaka MIYOSHI, Shinji MURAI,
and Noboru SONODA*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Olefins were found to be oxidized by use of benzenetellurinic anhydride in acetic acid leading to vic-diacetates. Benzenetellurenic acid derivatives formed in situ are suggested as the active species. This diacetoxylation proceeds in net syn fashion probably via anti acetoxytellurenylation of the olefin followed by displacement of the phenyltelluro group by an acetoxy group with inversion.

It has already been reported that tellurones1) and telluroxides2-4) have a unique oxidizing ability toward some specific functional groups. On the other hand little is known about the reactivity of tellurinic acids and their anhydrides. Recently Barton has shown that arenetellurinic anhydrides are effective oxidizing reagents for the selective oxidation of thiols and hydroquinones.5) Brill has also demonstrated that polymer-bound tellurinic acid shows a remarkable catalytic activity for the epoxidation of olefins with hydrogen peroxide, in which some peroxy intermediates are generated from hydrogen peroxide and in situ formed tellurinic anhydride as the active oxidizing species.6) These reports prompted us to disclose our study on the oxidation of olefins with benzenetellurinic anhydride.7)

Benzenetellurinic anhydride8) is sparingly soluble in usual organic solvents except acetic acid, acetic anhydride and their congeners, so that the reaction was performed using acetic acid as the solvent. When the acetic acid solution of styrene and benzenetellurinic anhydride was refluxed for 24 h, the solution gradually turned red indicating the formation of diphenyl ditelluride. Usual workup gave corresponding vic-diacetate in 48% yield. In the presence of a catalytic amount of sulfuric acid, the yield was improved to 82% (Eq. 1). The reaction was slow at 100 °C, and did not proceed below 80 °C.



$$\mathrm{PhCH{=}CH_2} \xrightarrow[\mathrm{AcOH,\ reflux,\ 24\ h}]{(\mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Te}}})_2\mathrm{O},\ \mathrm{H}^+} \mathrm{Ph}\underset{}{\overset{\mathrm{OAc}}{\overset{|}{\mathrm{CH}}}}\!-\!\overset{\mathrm{OAc}}{\overset{|}{\mathrm{CH_2}}} \quad 82\% \qquad (1)$$

It was confirmed that there exists an induction period (about 5 h), which was shortened by the addition of a reducing reagent such as triphenylphosphine or sulfurous acid. Additionally diphenyl ditelluride was found to have a remarkable effect for shortening the induction period. These results suggest that the active species for the oxidation of the double bond is not benzenetellurinic anhydride itself but some reduced product of it. The effect of two additives, sulfuric acid and diphenyl ditelluride, is shown in Fig. 1, in which yield of vic-diacetate is plotted at the different reaction periods. In the absence of diphenyl ditelluride, S shape curve was obtained. This may indicate that the present reaction is subject to self-catalysis.

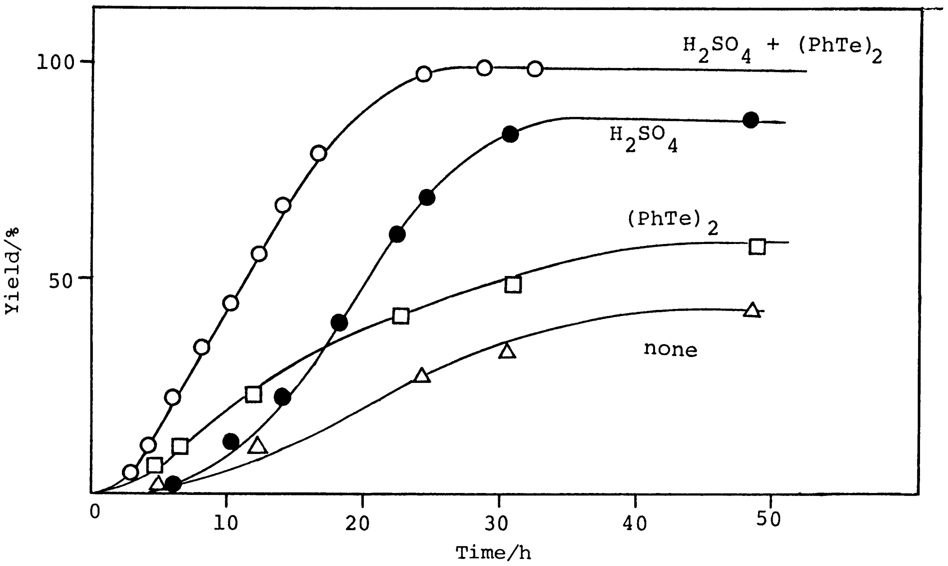
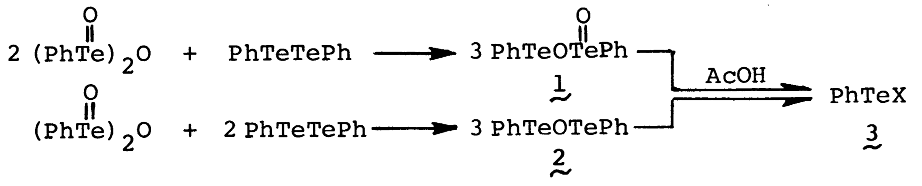


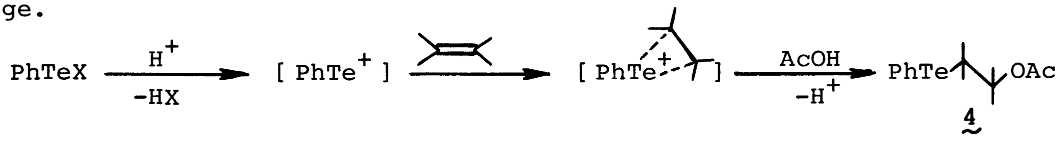
Fig. 1. Effect of additives in the reaction of styrene with benzenetellurinic anhydride in refluxing acetic acid.[9)]

From these observations, the following reaction path can be postulated. At first, benzenetellurinic anhydride is reduced to a benzenetellurenic acid derivative **1**, **2**, or **3**, which is likely to be the active species (Eq. 2). In the absence of reducing agent, the active species may be formed by oxidizing acetic acid used as the solvent.[10)] The latter process seems to be slow and may require the high temperature. The induction period observed is ascribable to this stage.



$$2\,(Ph\overset{O}{\overset{\|}{Te}})_2O + PhTeTePh \longrightarrow 3\,PhTeO\overset{O}{\overset{\|}{Te}}Ph\ (\mathbf{1})$$
$$(Ph\overset{O}{\overset{\|}{Te}})_2O + 2\,PhTeTePh \longrightarrow 3\,PhTeOTePh\ (\mathbf{2})$$
$$\mathbf{1},\ \mathbf{2} \xrightarrow{AcOH} PhTeX\ (\mathbf{3}) \qquad (2)$$

Then, **1**, **2**, or **3** reacts with olefin in acetic acid to give a 2-acetoxyalkyl phenyl telluride (**4**)[11-14)] (Eq. 3). The acid catalyst may play an important role in this stage.



(3)

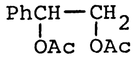
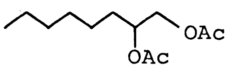
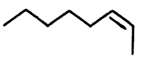
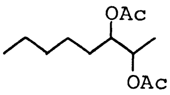
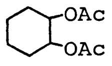
The final step of this reaction would be an acid catalyzed solvolysis of **4** to give vic-diacetate together with benzenetellurol (**5**),[15,16)] which would in turn reduce benzenetellurinic anhydride to **1** or **2** resulting in the acceleration of the reaction.

4 5

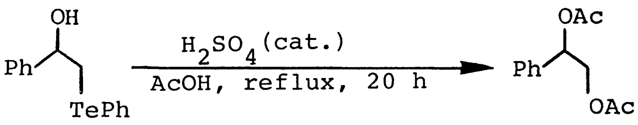
(4)

In Table 1 are summarized the results of diacetoxylation.17) Terminal olefins gave satisfactory yields of the products. The reaction of internal olefins was slow under the identical conditions. cis-2-Octene and cyclohexene gave corresponding cis adduct as the major product.

Table 1. Diacetoxylation of Olefins

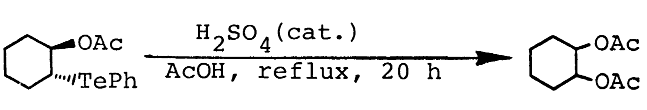
Olefin	Product	Yield/%
$PhCH=CH_2$	 $PhCH(OAc)—CH_2(OAc)$	82
		71
	 (erythro:threo = 71:29)	38
	 (cis:trans = 80:20)	38

In order to confirm the intermediacy of 4, related tellurium compounds 6 and 7 were synthesized19) and treated with sulfuric acid in refluxing acetic acid (reactions 5 and 6). These results show that displacement of phenyltelluro group with acetoxy group proceeds under these conditions. The reaction 6 indicates the inversion of the configuration at the carbon having the phenyltelluro group. Unexpected low yield of diacetate from 7 is probably due to reverse acetoxytellurenylation to give cyclohexene. The fact that a small amount of trans diacetate is formed from 7 may suggest that elimination of phenyltelluro group assisted by the adjacent acetoxy group in 7 competes with the direct displacement of phenyltelluro group with acetate. Solvolysis of 7 in the presence of benzenetellurinic anhydride under similar conditions did not improve the yield of diacetate. This result rules out a possibility that tellurium in the leaving group should have a higher oxidation state like that in telluroxides or tellurones.



6

52% (5)



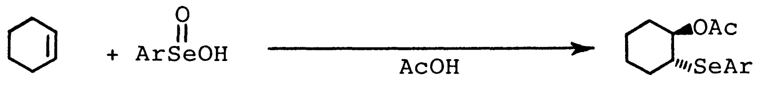
7

15% (6)

(cis:trans = 82:18)

References

1) L. Engman and M. P. Cava, J. Chem. Soc., Chem. Commun., 1982, 164.
2) D. H. R. Barton, S. V. Ley, and C. A. Meerholz, J. Chem. Soc., Chem. Commun., 1979, 755.
3) S. V. Ley, C. A. Meerholz, and D. H. R. Barton, Tetrahedron Lett., 21, 1785(1980).
4) S. V. Ley, C. A. Meerholz, and D. H. R. Barton, Tetrahedron, Supplement No. 1, 37, 213(1981).
5) D. H. R. Barton, J.- P. Finet, and M. Thomas, Tetrahedron, 42, 2319(1986).
6) W. F. Brill, J. Org. Chem., 51, 1149(1986).
7) A part of this work has been reported in the 13th Symposium on Organic Sulfur and Phosphorus Chemistry, Hiroshima, January 1985, Abstr., p. 57.
8) R. Thavornyutikarn and W. R. McWhinnie, J. Organomet. Chem., 50, 135(1973).
9) Benzenetellurinic anhydride (1 mmol), styrene (1 mmol), diphenyl ditelluride (1 mmol), sulfuric acid (0.1 mmol), acetic acid (15 ml).
10) We have already reported a similar oxyselenenylation using benzeneseleninic acid. See, N. Miyoshi, Y. Takai, S. Murai, and N. Sonoda, Bull. Chem. Soc. Jpn., 51, 1265(1978).



8

11) Corresponding selenium compound 8 was obtained in the reaction of olefin with benzeneseleninic acid; see Ref. 10. Several synthetic reactions have been reported in which the key reaction is the oxyselenenylation of olefins by in situ formed selenenic acid derivatives; see Refs. 12-14.
12) G. Höltzle and W. Jenny, Helv. Chim. Acta., 41, 593(1958).
13) T. Hori and K. B. Sharpless, J. Org. Chem., 43, 1689(1978).
14) M. Shimizu, R. Takeda, and I. Kuwajima, Tetrahedron Lett., 1979, 419 and 3461.
15) N. Ohira, Y. Aso, T. Otsubo, and F. Ogura, Chem. Lett., 1984, 853.
16) M. Akiba and M. P. Cava, Synthetic Commun., 14, 1119(1984).
17) A typical experiment is as follows. To a dry acetic acid solution (15 ml) of benzenetellurinic anhydride (2.1 mmol, 950 mg) were added styrene (2.0 mmol, 208 mg in 4 ml of AcOH) and sulfuric acid (98%, 0.2 mmol, 20 mg in 1 ml of AcOH). The mixture was gently refluxed for 24 h. As the reaction proceeded, the solution gradually turned red and deposition of a small amount of elemental tellurium was observed.18) After removal of tellurium (71 mg, 0.56 mmol) by filtration, the solvent was evaporated. The product was extracted into ether and dried over $MgSO_4$. Chromatography on silica gel gave vic-diacetate (363 mg, 82%) and 1-phenylethyl acetate (29 mg, 9%).
18) Arenetellurenyl halides disproportionate to give diarylteluium dihalides and elemental tellurium; W. L. Dorn, A. Knöchel, P. Schulz, and G. Klar, Z. Naturforsch., B, 31, 1043(1976).
19) D. L. J. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchen, C. G. Russell, A. Singh, C. K. Wong, and N. J. Curtis, J. Am. Chem. Soc., 102, 4438(1980). An attempt for acetylation of 6 failed under similar reaction conditions.

(Received October 24, 1986)