Tetrahedron Letters,Vol.23,No.1,pp 87-90,1982 0040-4039/82/010087-04$03.00/0
Printed in Great Britain

PALLADIUM-CATALYZED ALLYLIC OXIDATION OF OLEFINS BY t-BUTYL HYDROPEROXIDE AND TELLURIUM(IV) OXIDE

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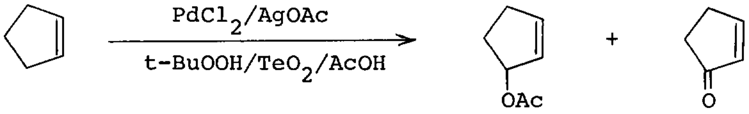
Summary: Treatment of several cyclic olefins, β-pinene, allylbenzene, and estragole with palladium(II) salt in acetic acid in the presence of t-butyl hydroperoxide and tellurium(IV) oxide afforded mainly the corresponding allylic acetates. The reaction proceeded catalytically with palladium(II) salt, t-BuOOH working as a reoxidizing agent.

Recently, Mimoun et al. have reported a selective stoichiometric oxidation of terminal olefins to methyl ketones by $[t\text{-BuOOPdOCOR}]_4$ and also a palladium-catalyzed ketonization of terminal olefins by alkyl hydroperoxides.[1,2] In these novel reaction systems, however, no reaction occurred with cyclic olefins. In contrast, when we treated several cyclic olefins and allylbenzene derivatives with a catalytic amount of palladium(II) salt in acetic acid in the presence of t-butyl hydroperoxide, it was found that the corresponding allylic acetates were formed in a good yield and selectivity under very mild conditions. We report here these new findings. Although the combination of SeO_2 with t-BuOOH in CH_2Cl_2 has been devised for a catalytic allylic oxidation of olefins, it was not applicable to cycloolefins unfortunately.[3]

A heterogeneous mixture of cyclopentene(20 mmol), palladium(II) chloride (1 mmol), silver acetate(2 mmol), tellurium(IV) oxide(1 mmol), 70%-t-butyl hydroperoxide(10 mmol), and acetic acid(30 ml) was stirred at 25°C for 3 days. After usuan workup procedure (filtration of a small amount of balck precipitates, addition of aq. NaCl, extraction with $CHCl_3$, washing with aq. $NaHCO_3$, drying over Na_2SO_4) GLC analysis of the extract revealed the presence of 2-cyclopentenyl acetate(2) (6.83 mmol) and 2-cyclopentenone(3) (0.78 mmol) as products (eq. 1).

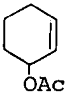
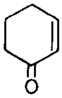
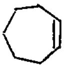
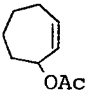
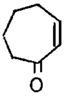
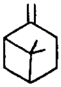
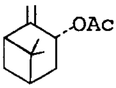
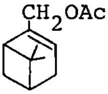


(1) (2) (3)

(1)

When a similar reaction was carried out in a mixed solvent of acetic acid(15 ml) and acetic anhydride(15 ml), the selectivity for the former product became higher. This palladium-catalyzed reaction can be applied well to cyclohexene, cycloheptene, and β-pinene, and the corresponding allylic acetates were obtained in 400-900% yields (based on $PdCl_2$ charged) together with α,β-unsaturated ketones as minor

Table 1. Reaction conditions and product yields[a]

Olefin	Reaction time(days)	Solvent	Product[b] and yield(mmol)[c]					
(1)	3	AcOH	(2)	6.83	(3)	0.78		
(1)	3	AcOH + Ac_2O	(2)	7.81	(3)	0.35		
	3	AcOH		8.83		2.41		
	3	AcOH + Ac_2O		6.47		0.45		
	6	AcOH		3.94		0.92		
	3	AcOH + Ac_2O		+		(63:37)		5.28
(4)	6	AcOH	(6)	6.64	(8)	0.89	(9)	1.26
(5)	6	AcOH	(7)	4.74[d]				

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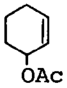
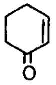
a) $PdCl_2$(1 mmol), AgOAc(2 mmol), TeO_2(1 mmol), t-BuOOH(10 mmol), olefin(20 mmol), and solvent(30 ml) were used. At 25°C. b) Authentic sample of each compound was commercial product or, when it is not available, prepared by the reported method. c) Determined by GLC. d) Two minor unidentified products[ca. 1/4 ~ 1/6 of (7) by peak area of GLC] were also formed.

products.[4] In all cases a saturated ketone (cyclopentanone, cyclohexanone etc.) was hardly obtained. Typical results are shown in Table 1.[5]

The reaction proceeded even without the addition of tellurium(IV) oxide, but the yields of allylic acetates were slightly lower. On the other hand, when much TeO_2 were added to the reaction system, the yields of those were also lower and it was revealed that the addition of an almost equal amount of TeO_2 to $PdCl_2$ gave reproducibly the best result for the formation of allylic acetates. A relation between the amount of TeO_2 added and the yield of the oxidation products from cyclohexene is shown in Table 2.

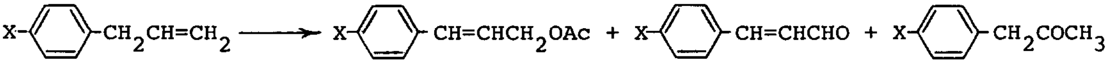
Table 2. Effect of the amount of TeO_2 added on the oxidation of cyclohexene.[a)]

TeO_2 (mmol)	 (mmol)	
0	6.79	2.29
1	8.83	2.41
2	7.65	2.13
5	7.66	2.18
10	5.16	2.03

a) Reaction conditions are the same to those in Table 1 by using AcOH as solvent. At 25°C for 3 days.

It is highly probable that a combination of $PdCl_2$ with AgOAc forms in situ a reactive species like palladium(II) acetate or $[PdCl(OAc)]_n$. In fact, when the reaction was carried out with commercial palladium(II) acetate in the place of $PdCl_2$-AgOAc, the same products were obtained. But in this case both the selectivity and the yields of allylic acetates were slightly lower and the experiments were not reproducible. Almost no reaction occurred when AgOAc was not used or NaOAc was used in the place of AgOAc.

Application of this reaction to linear olefins such as 1-octene and 1-decene resulted in a formation of methyl ketones as main products as has been observed by Mimoun et al. in a similar reaction with H_2O_2.[2] From allylbenzene(**4**) and p-methoxyallylbenzene (estragole)(**5**), on the other hand, cinnamyl acetate(**6**) and its p-methoxy derivative(**7**) were obtained as a major product respectively together with the corresponding aldehydes and methyl ketones(eq. 2)(Table 1).



(2)

(**4**): X=H
(**5**): X=MeO

(**6**): X=H
(**7**): X=MeO

(**8**): X=H

(**9**): X=H

However, from α- and β-methylstyrenes and anethole the dimeric compounds of these olefins were mainly formed and the expected allylic acetates were scarcely obtained.

The reaction may proceed via either π-allylic palladium complex or acetoxypalladation followed by dehydropalladation,[6] a Pd-hydride complex being reoxidized by t-BuOOH. The role of TeO_2 seems to be to accelerate this reoxidation step, although the oxide itself also works slightly as a reagent for allylic oxidation.[7]

References and Notes

1. H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, J. Am. Chem. Soc., **102**, 1047(1980).
2. M. Roussel and H. Mimoun, J. Org. Chem., **45**, 5387(1980).
3. M. A. Umbreit and K. B. Sharpless, J. Am. Chem. Soc., **99**, 5526(1977). When the reaction was carried out with SeO_2 in the place of $PdCl_2$/AgOAc under our reaction conditions, the expected allylic acetates were also formed. However, the yields were ca. 1/2~1/3 of those in the reactions with Pd(II).
4. p-Benzoquinone can be used as reoxidant as has been reported by Davidson et al., but the yield of 2-cyclohexenyl acetate was ca. 1/3 of that in the case of t-BuOOH as reoxidant under our reaction conditions: R. G. Brown and J. M. Davidson, J. C. S. (A), 1321(1971).
5. The reaction proceeded well even by reducing the amount of $PdCl_2$ to 1/10, though the selectivity for allylic acetate became lower: i.e., 2-cyclohexenyl acetate (4.18 mmol, 4180%) and 2-cyclohexenone(2.62 mmol, 5240%) were obtained in the reaction using cyclohexene(20 mmol), 70%-t-BuOOH(10 mmol), $PdCl_2$(0.1 mmol), AgOAc(0.2 mmol), and AcOH(30 ml) at 25°C for 3 days.
6. S. Wolfe and P. G. C. Campbell, J. Am. Chem. Soc., **93**, 1497(1971).
7. The following results of the oxidation (20°C, 4 days) of cyclohexene(20 mmol) in acetic acid(20 ml) in the presence of 70%-t-BuOOH(10 mmol) should be noted: the yield of 2-cyclohexenyl acetate[additives]; 0.17 mmol[TeO_2(1 mmol)], 6.15 mmol[$PdCl_2$(1 mmol)/AgOAc(2 mmol)], and 7.51 mmol[TeO_2(1 mmol)/$PdCl_2$ (1 mmol)/AgOAc(2 mmol)].

(Received in Japan 12 September 1981)