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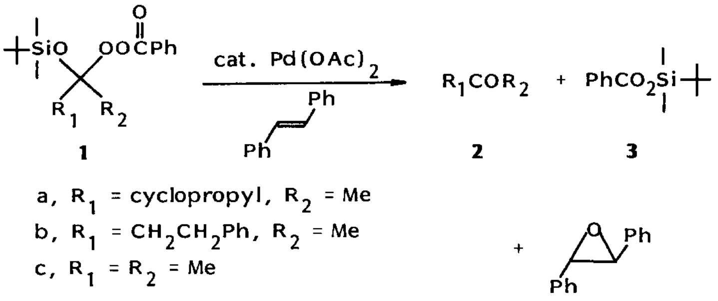
PALLADIUM(II)-CATALYZED EPOXIDATION OF OLEFINS WITH α-SILYLOXYALKYL PEROXYBENZOATES

Ryu Nagata, Teruo Matsuura, and Isao Saito*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University
Kyoto 606, Japan

Summary: A novel oxygen-atom-transfer reaction from α-silyloxyalkyl peroxybenzoate to olefins by palladium(II) catalyst to give epoxides has been described.

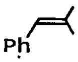
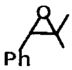
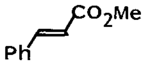
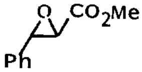
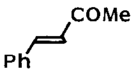
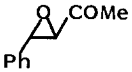
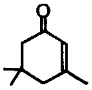
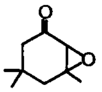
Our interest in generating dioxirane from silyl-protected Criegee peroxide adducts has led us to investigate a metal-catalyzed reaction of these peroxides. We now report a novel oxygen-atom-transfer reaction from α-silyloxyalkyl peroxybenzoates to olefins in the presence of palladium(II) catalyst to give epoxides under very mild conditions. In contrast to the thermal decomposition described in the preceding paper,[1] treatment of cyclopropyl-substituted peroxyester 1a[2] with a catalytic amount of $Pd(OAc)_2$ produces a reactive species that can transfer an oxygen atom to a range of olefins.



a, R_1 = cyclopropyl, R_2 = Me
b, R_1 = CH_2CH_2Ph, R_2 = Me
c, R_1 = R_2 = Me

When a solution of 1a (0.1 mmol) and *trans*-stilbene (1 equiv) in CD_2Cl_2 (0.4 mL) was stirred at room temperature in the presence of $Pd(OAc)_2$ (10 mol%) under nitrogen,[3] 1a was completely consumed within 8 h to give ketone 2 (95%), silyl ester 3 (76%) and *trans*-stilbene oxide (65%) as determined by ^{1}H-NMR. Surprisingly, formation of a Baeyer-Villiger type product was completely suppressed.[1,4] Peroxyester 1a was quite stable in the absence of $Pd(OAc)_2$ under the reaction conditions. The reaction of 1a with $Pd(OAc)_2$ (10 mol%) without *trans*-stilbene proceeded very slowly to result in the formation of 2 and 3 after 24 h, whereas addition of *trans*-stilbene to the reaction system remarkably accelerated the decomposition of 1a to give the *trans*-epoxide within 8 h. These observations suggest that the reaction of 1a

Table I. Oxidation of olefins by an Intermediate formed in $Pd(OAc)_2$-catalyzed decomposition of 1a[a]

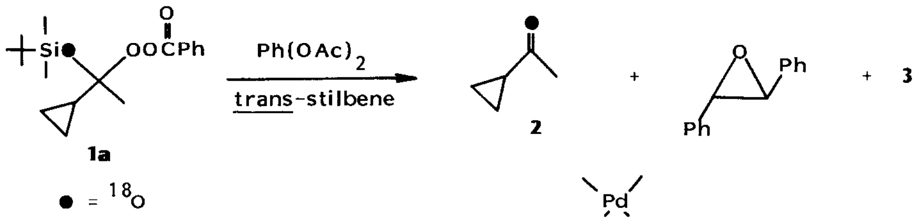
entry	olefin	reaction time (h)	product (yield %)
1		3	 (45)[b]  (50)[b]
2		5	 (88)[c]
3	*cis*-stilbene	8	*cis*-stilbene oxide (48)[b] *trans*-stilbene oxide (10)[b]
4		8	 (59)[b]
5		8	 (64)[b]
6		8	 (17)[c]
7		66	 (7)[d]
8		40	 (36)[d]
9		60	 (14)[d]  (4)[d]

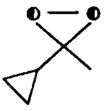
[a] Reaction was conducted at room temperature in dry CH_2Cl_2 containing 1a (250 mM), $Pd(OAc)_2$ (10 mol %) and olefin (250 mM). The reaction was stopped when 1a was completely consumed. [b] Determined by ^1H-NMR. [c] Isolated yield after column chromatography. [d] Determined by GLC.

with Pd(II) would first produce a reactive intermediate which then transfers an oxygen atom to stilbene to regenerate a Pd(II) species.

A wide variety of olefins were epoxidized under the conditions as illustrated in Table I.[5] Electron-rich olefins (entries 1∿3) and a weakly nucleophilic olefin (entry 4) were smoothly epoxidized, whereas electron-deficient olefins such as dimethyl fumarate or cyclopentenone were inert under the conditions. α,β-Unsaturated ketones which usually produce Baeyer-Villiger products upon oxidation with peracids[6] were epoxidized under the neutral conditions (entries 5 and 6). In the cases of terminal and internal olefins which are prone to form π-allylpalladium complexes, the epoxidation proceeded very slowly to give only low yields of epoxides (entries 7∿9). In fact, a π-allylpalladium complex prepared independently from (-)-β-pinene was not oxidized under the conditions.

When *trans* olefins were epoxidized, only *trans* epoxides were formed; however, *cis* olefins gave both *cis* and *trans* epoxides with the *cis* product predominating (entries 3 and 9). The lack of stereospecificity of the reaction suggests a stepwise mechanism with an intermediate which can rotate. In support of the stepwise mechanism, oxidation of 2,3-dimethyl-2-butene gave the expected epoxide together with pinacolone which presumably arises from the rearrangement via a cationic intermediate, *e.g.*, 4 (entry 1). When *trans*-stilbene was epoxidized with 1a containing ^{18}O-labelled silyloxy group (^{18}O enrichment 27%), the ^{18}O was not incorporated into the stilbene oxide at all with the fromation of ^{18}O-labelled 2 (^{18}O enrichment 27%). Here again, the participation of free dioxirane 5 or palladium-complexed dioxirane 6 as an intermediate was rigorously ruled out.

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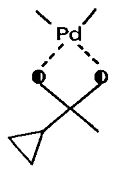

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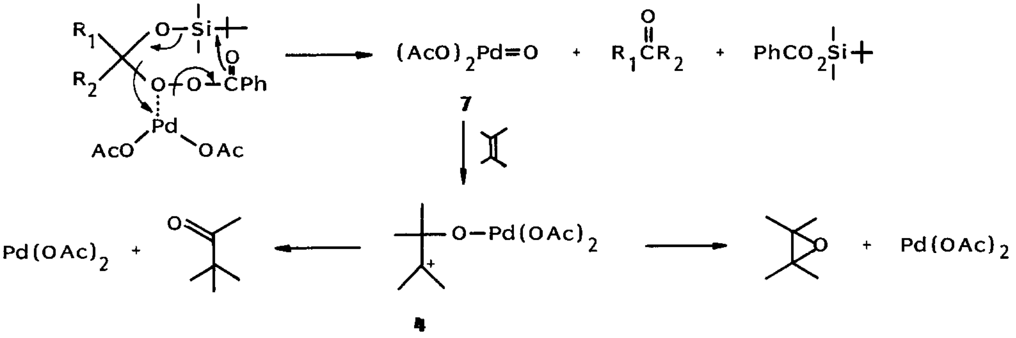
There has been reported several examples of oxidation of olefins with peroxides in the presence of palladium;[7] these include oxidation of terminal olefins to methyl ketones[7a,b] and allylic oxidation.[7d,e] However, the reactivity of our intermediate toward olefins is quite different from these species. Only example for successful epoxidation of olefins is the epoxidation of olefins in Pd(II)-catalyzed oxygenation of azibenzil.[8] In this case, however, epoxide formation is accompanied by oxidative cleavage of the double bond. In view of the considerably high affinity of acetal oxygen atom to Pd(II),[9] our observations are most reasonably explained by assuming a palladium(IV)-oxo species (7) as an oxygen-transfer reagent which would be formed by co-ordination of ketal peroxidic oxygen to Pd(II) followed by O-O cleavage and silyl migration as depicted in Scheme 1,[10] although an alternative possibility of the intervention of Pd(II)-peroxybenzoate species 8[11] cannot be ruled out rigorously.

Scheme 1



AcOPdOOCOPh

8

REFERENCES AND NOTES

(1) I. Saito, R. Nagata and T. Matsuura, Tetrahedron Lett., preceding paper in this issue.
(2) Epoxidation of olefins has been observed with 1b and 1c. However, production of a Baeyer-Villiger product is inevitable in the case of 1b. The use of 1c requires longer time and higher temperature.
(3) Other Pd(II) compounds such as Pd(OCOCF$_3$)$_2$ were found to be equally effective.
(4) I. Saito, R. Nagata and T. Matsuura, Tetrahedron Lett., 24, 1737 (1983).
(5) The following procedure is representative. To a solution of 1a (338 mg, 1 mmol) and 2-methyl-1-phenylpropene (132 mg, 1 mmol) in dry CH$_2$Cl$_2$ (4 mL) was added Pd(OAc)$_2$ (22 mg, 0.1 mmol) at room temperature. The mixture was stirred for 5 h under nitrogen. After evaporation the residue was chromatographed on silica gel to give β,β-dimethylstyrene oxide (130 mg, 88%).
(6) C. H. Hassal, Org. Reaction, 9, 73 (1957).
(7) (a) H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer and R. Weiss, J. Am. Chem. Soc., 102, 1047 (1980). (b) M. Roussel and H. Mimoun, J. Org. Chem., 45, 5387 (1980). (c) J. Tsuji, H. Nagashima and K. Hori, Chem. Lett., 257 (1980). (d) T. Hosokawa, S. Inui and S. Murahashi, ibid., 1083 (1983). (e) S. Uemura, S. Fukuzawa, A. Toshimitsu, and M. Okano, Tetrahedron Lett., 23, 87 (1982). (f) K. Jitsukawa, K. Kaneda and S. Teranishi, J. Org. Chem., 48, 389 (1983).
(8) H. S. Ryang and C. S. Foote, J. Am. Chem. Soc., 102, 2129 (1980).
(9) T. Hosokawa, Y. Imada and S. Murahashi, J. Chem. Soc. Chem. Comm., 1245 (1983).
(10) Iron(V)-, chromium(V)- and manganese(V)-oxo complexes are known to epoxidize olefins. See R. A. Scheldon and J. K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds", Academic Press, New York, 1981, p 152. For the proposal of Pd(IV)-oxo species, see ref. 7f.
(11) For an analogous species, see M. J. Y. Chen and J. K. Kochi, J. Chem. Soc. Chem. Comm., 205 (1977).

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