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REGIOSELECTIVE OXIDATION OF INTERNAL OLEFINS BEARING NEIGHBORING OXYGEN FUNCTIONS BY MEANS OF PALLADIUM CATALYSTS. A DIRECT PREPARATION OF γ-KETO ESTERS AND 1,4-DIKETONES FROM β,γ-UNSATURATED ESTERS AND KETONES

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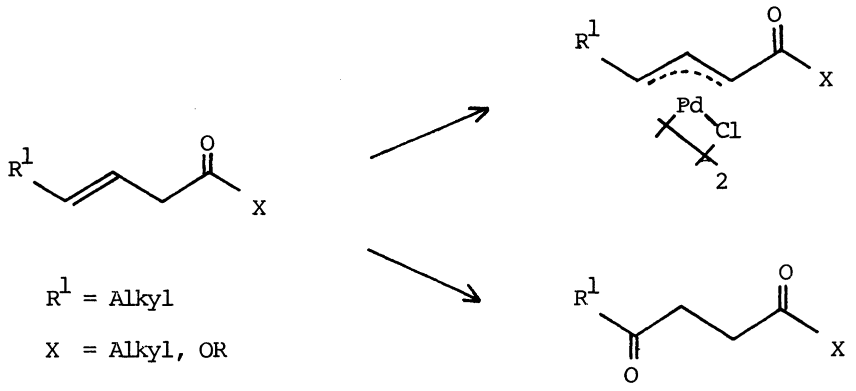
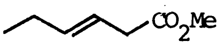
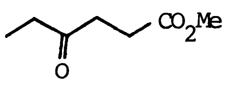
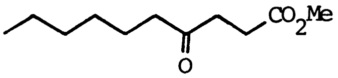
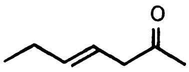
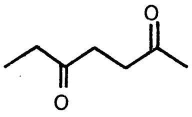
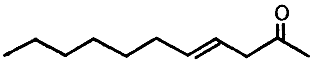
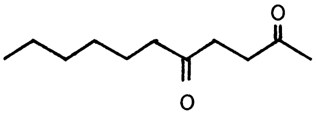
γ-Keto esters and 1,4-diketones were prepared by the palladium-catalyzed regioselective oxidation of β,γ-unsaturated esters and ketones. The best yields were obtained when the reaction was carried out using $PdCl_2/CuCl/O_2$ catalyst system in aqueous dioxane.

1,4-Dicarbonyl compounds are useful intermediates for the synthesis of five-membered ketone derivatives and their efficient synthesis is an important problem. In our preceeding paper,$^{1)}$ we have reported the highly regioselective oxidation of internal olefins bearing neighboring alkoxy or acetoxy group. The results lead us to study the effect of other oxygen functions on the regioselective oxidation of internal olefins. It is well-known that π-allylpalladium complexes are easily formed by the reaction of $PdCl_2$ with β,γ-unsaturated esters or ketones.$^{2)}$ An attempted oxidation of β,γ-unsaturated esters and ketones with $PdCl_2/CuCl/O_2$ catalyst system in aqueous DMF led to the π-allylpalladium complexes as the main reaction, and the oxidation of olefinic bond was hardly observed. However, we have found that in aqueous dioxane or aqueous THF the oxidation became the main reaction, giving γ-keto esters and 1,4-diketones, respectively, with high regioselectivity.$^{3)}$



In a typical example, $PdCl_2$ (18 mg, 0.1 mmol) and CuCl (99 mg, 1 mmol) were placed in a flask fitted with a rubber balloon filled with oxygen. Aqueous dioxane (dioxane : H_2O = 7 : 1, 1 mL) was added, and the suspension was stirred for 2 h at room temperature under oxygen atmosphere. Then, methyl 3-hexenoate (128 mg, 1 mmol) was added and the solution was heated at 50°C. After 12 h, the mixture was cooled and excess CH_2Cl_2 was added. Green paste formed was filtered off, and the filtrate

Table

Substrates	Products	Yields (%)
		52
		61
		45
		61

was dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (silica gel, hexane-ether) to give methyl 4-oxohexanoate (75 mg, 52%). Other β,γ-unsaturated esters and ketones also underwent the regioselective oxidation to give the corresponding γ-keto esters and 1,4-diketones. As shown in the table in all cases, no β-keto ester or 1,3-diketone was detected. At the end of the reaction, a considerable amount of π-allylpalladium complexes was formed.

γ-Keto esters and 1,4-diketones are useful intermediates for the preparation of cyclopentanedione and cyclopentenone, respectively, by base catalyzed cyclization.$^{4)}$ The regioselective oxidation presented in this paper provides a unique and efficient synthetic method of γ-keto esters and 1,4-diketones.

References

1) J. Tsuji, H. Nagashima, and K. Hori, Tetrahedron Lett., in press.
2) J. Tsuji and S. Imamura, Bull. Chem. Soc. Jpn., 40, 197 (1967).
3) We have already reported that β,γ-unsaturated esters underwent regioselective oxidative acetoxylation with $PdCl_2/C_5H_{11}ONO/KOAc$ catalyst system in acetic acid to give γ-acetoxy-α,β-unsaturated esters. See; J. Tsuji, K. Sakai, H. Nagashima, and I. Shimizu, Tetrahedron Lett., 22, 131 (1981).
4) For review; T. L. Ho, Syn. Commun., 4, 265 (1974).

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