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Palladium- and Platinum-Catalyzed Reaction of Siloxycyclopropanes with Acid Chlorides. A Homoenolate Route to 1,4-Dicarbonyl Compounds

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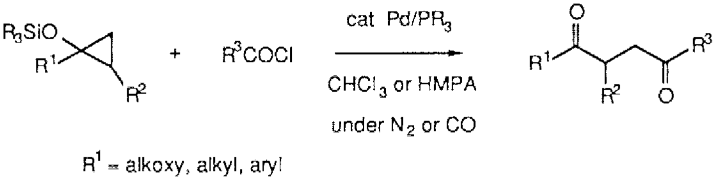
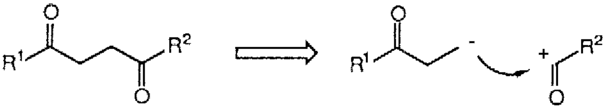
Summary: 1,4-Keto esters and 1,4-diketones have been synthesized by the palladium-catalyzed reaction of siloxycyclopropanes and acid chlorides.

Stoichiometric chemistry of metal homoenolates have been attracting considerable interests of organic and organometallic chemists.[1] Through recent studies on the *catalytic* coupling of siloxycyclopropanes with carbonyl compounds[2] and aryl triflates,[3] we have demonstrated that *catalytic* homoenolate chemistry provides a useful new synthetic method for carbon-carbon bond formation. We now report that palladium- and platinum-catalyzed coupling of siloxycyclopropanes with acid chlorides provides an efficient synthetic route to 1,4-keto esters and 1,4-diketones (eq 1), which involves a novel retrosynthetic dissection depicted in eq 2.[4]



(1)



(2)

Preparation of 1,4-keto esters has been achieved in a very simple manner (Table I). For instance, heating an equimolar mixture of 1-*tert*-butyldimethylsiloxy-1-isopropoxycyclopropane[5] and benzoyl chloride in $CHCl_3$ in the presence of 1-5 mol% of $PdCl_2(PPh_3)_2$ afforded the desired 1,4-keto ester in 97% isolated yield (entry 1). Similarly, the reaction of a trimethylsiloxy counterpart proceeded with equal facility (entry 2). The palladium-catalyzed reaction with aliphatic acid chlorides, however, was found to be less satisfactory: The acylation with 3-phenylpropanoyl chloride gave the desired keto ester in only 45% yield (entry 5). It is yet noteworthy that the intermolecular acylation is much faster than an intramolecular Friedel-Crafts acylation.which may yield indanone.[6] The low yield could however be circumvented by switching the catalyst from palladium to platinum. Thus, the reaction between nearly equimolar amounts of the reactants in the presence of 5-10 mole% of $PtCl_2(PPh_3)_2$ afforded the desired aliphatic keto ester in high yield (entries 6 and 7). For instance, a preparative-scale reaction of 1-ethoxy-1-trimethylsiloxycyclopropane, now commercially available from Aldrich, with propionyl chloride afforded ethyl 4-oxohexanonate in 68% isolated yield.[7] The ring cleavage of a 2-methyl-substituted cyclopropane (R^2 = Me in eq 1) took place exclusively at the less substituted carbon-carbon bond and gave 2-methylesters in high yield (entries 8 and 9).[8]

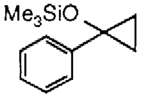
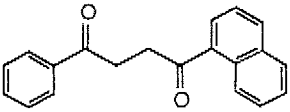
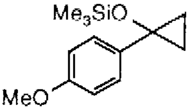
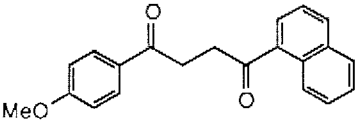
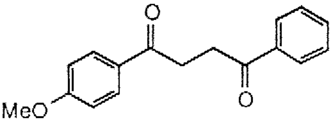
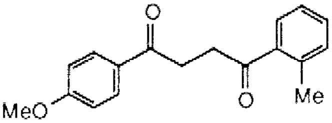
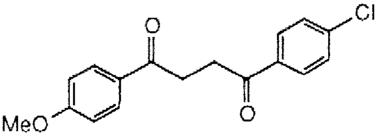
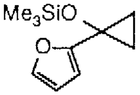
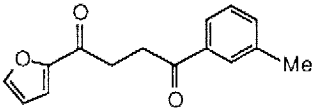
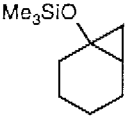
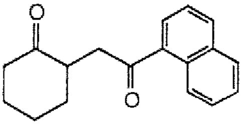
Development of conditions suitable for the preparation of 1,4-diketones by this route met with considerable difficulties. The reaction of siloxycyclopropanes listed in Table II gave virtually no trace of the desired products under the conditions used in Table I. Moderate yields could only be realized in the reaction performed in a polar solvent such as HMPA and *N,N'*-dimethylpropyleneurea. Some indications of decarbonylation of an acylpalladium intermediate[9] prompted us to examine the reaction under CO pressure. To our satisfaction, the reaction of the siloxycyclopropanes with aromatic acid chlorides in HMPA proceeded under 10 atm of carbon monoxide (Table II). We observed that the use of a mixture of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ and triphenyl phosphite generally gives higher yield than a palladium catalyst having triphenylphosphine as a ligand.[10,11]

Table I. 1,4-Keto Esters by Acylation of Ester Homoenolates[a]

entry	siloxycyclopropane			acid chloride	catalyst[b]	%yield[c]
	R^1	R^2	SiR_3			
1	O^iPr	H	Si^tBuMe_2	C_6H_5COCl	A	97
2	O^iPr	H	$SiMe_3$	C_6H_5COCl	A	90
3	OEt	H	Si^tBuMe_2	*p*-ClC_6H_4COCl	A	83
4	OEt	H	$SiMe_3$	*p*-$MeOC_6H_4COCl$	A	86[d]
5	OEt	H	$SiMe_3$	$C_6H_5CH_2CH_2COCl$	A	45[d]
6	O^iPr	H	Si^tBuMe_2	$C_6H_5CH_2CH_2COCl$	C	83
7	OEt	H	$SiMe_3$	CH_3CH_2COCl	C	68
8	OEt	Me	$SiMe_3$	C_6H_5COCl	A	86
9	OEt	Me	$SiMe_3$	*p*-ClC_6H_4COCl	B	93[e]

[a]The reaction was performed with one equiv each of the reactants (unless noted otherwise) at 90-100 °C in the presence of 5 mol% of the catalyst indicated (cf. footnote 7). [b]Catalyst A = $(PhCO)PdCl(PPh_3)_2\cdot(CH_2Cl_2)$, B = $PdCl_2(PPh_3)_2$, C = $PtCl_2(PPh_3)_2$. Catalysts A and B gave essentially the same results. [c]Isolated yield. [d]Slight excess (1.2 equiv) of the cyclopropane was used. [e]Two equivalents of the cyclopropane was used.

Table II. 1,4-Diketones by Acylation of Ketone Homoenolates[a]

entry	siloxycyclopropane	acid chloride	1,4-diketone	% yield[b]
1		1-$C_{10}H_7COCl$		53[b,c]
2				69
3		C_6H_5COCl		75
4		2-MeC_6H_4COCl		77[c]
5		4-ClC_6H_4COCl		55
6		3-MeC_6H_4COCl		52
7		1-$C_{10}H_7COCl$		46

[a] The reaction was performed as described in footnote 10 [5 mol% Pd/2 x $P(PhO)_3$] [b] 1.5 equiv of the cyclopropane was used. [c] $PdCl_2(PPh_3)_2$ was used as a catalyst.

In summary, we have demonstrated that the catalytic homoenolate chemistry provides a straightforward approach to the synthesis of 1,4-dicarbonyl compounds.[12] We are currently investigating the mechanistic details of the present reaction that may involve catalytic activation of the carbon-carbon bond of the cyclopropanes.[13]

Acknowledgment. E.N. thanks the Asahi Glass Foundation for financial support.

References and Notes

1. For pertinent references, see: Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1987,** *109,* 8056.
2. Oshino, H.; Nakamura, E.; Kuwajima, I. *J. Org. Chem.* **1985,** *50,* 2802.
3. Aoki, S.; Fujimura, T.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1988,** *110,* 3296.
4. For some previous syntheses of 1,4-dicarbonyl compounds: (1) (a) McMurry, J. E.; Melton, J. *J. Am. Chem. Soc.* **1971,** *93,* 5309. (b) Stetter, H.; Schreckenberg, M. *Angew. Chem. Int. Ed. Engl.* **1973,** *12,* 81. (c) Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1974,** *96,* 5272. (d) Miyashita, M.; Yanami, T.; Yoshikoshi, A. *J. Am. Chem. Soc.* **1976,** *98,* 4679. (e) Shimada, J.-i.; Hashimoto, K.; Kim. B. H.; Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984,** *106,* 1759. (f) Welch, S. C.; Chayabunjonglerd, S. *J. Am. Chem. Soc.* **1979,** *101,* 6768. (g) Sato, T.; Okazaki, H.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1988,** *110,* 5209.
5. Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986,** *108,* 3745.
6. In the reaction of pivaloyl chloride, decarbonylation of the acid chloride produced a substantial amount of 4-keto pimelate due to incorporation of carbon monoxide formed in situ (cf. Aoki, S.; Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1988,** *29,* 1541.)
7. 1,4-Keto ester synthesis: A solution of 1-ethoxy-1-trimethylsiloxycyclopropane (2.14 g, 11 mmol), benzoyl chloride (0.82 g, 10 mmol), and PtCl$_2$(PPh$_3$)$_2$ (78 mg, 0.1 mmol) in 5 mL of dry CDCl$_3$ in a degassed sealed tube was heated at 90 °C for 24 h and the reaction mixture was distilled to obtain ethyl 4-oxohexanoate (1.08 g, 68% yield).
8. For chiral homoenolate of methyl isobutyrate, see: Nakamura, E.; Sekiya, K.; Kuwajima, I. *Tetrahedron Lett.* **1987,** *28,* 337.
9. The palladium-catalyzed reaction with naphthoyl chloride gave varying amounts of naphthalene.
10. Use of a platinum catalyst did not improve the yield of 1,4-diketones. The 1,4-diketone synthesis with aliphatic and α,β-unsaturated acid chlorides has thus far been unsuccessful.
11. 1,4-Diketone synthesis: A solution of 1-trimethylsiloxy-1-(4-methoxyphenyl)cyclopropane (0.4 mmol), 2-methylbenzoyl chloride (0.2 mmol), $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.005 mmol), and triphenyl phosphite (0.02 mmol) in 0.8 mL of HMPA was heated at 100 °C for 20 h under CO pressure (10 atm) to obtain the desired 1,4-diketone (77%) after flash column chromatography.
12. For previous synthesis of 1,4-dicarbonyl compounds using homoenolate chemistry, see: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1984,** *106,* 3368; *Tetrahedron Lett.* **1986,** *27,* 83; Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. *Angew. Chem. Int. Ed. Engl.* **1987,** *26,* 1157. (h) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z. *Tetrahedron Lett.* **1985,** *26,* 5559.
13. Preliminary mechanistic studies supported such a mechanism. For references on the carbon-carbon bond activation by homogeneous metal complexes, see ref 3.

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