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SYNTHESIS OF β-MERCURI KETONES BY THE REACTION OF SILOXYCYCLOPROPANES WITH MERCURIC ACETATE AND THEIR CONVERSION TO α-METHYLENE KETONES AND γ-KETOESTERS[1]

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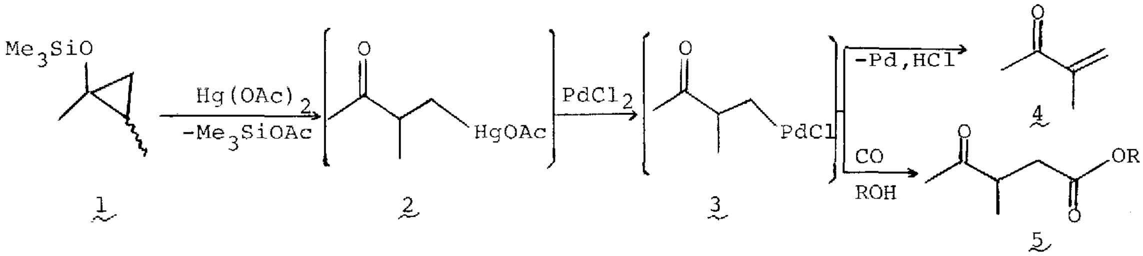
Summary: Siloxycyclopropanes were quantitatively converted to β-acetoxymercuri ketones by the reaction with mercuric acetate. Successive treatment with palladium chloride or palladium chloride/carbon monoxide gave α-methylene ketones or γ-ketoesters, respectively, in good yields.

α-Methylene ketones are an important structural unit often found in a variety of sesquiterpens or antibiotics and developing a convenient method for the preparation of them is a matter of highly desired.[2] γ-Ketoesters are also useful intermediates for further elaboration to cyclopentenones and furans. For the synthesis of α-methylene ketones and γ-ketoesters, the use of β-metal ketones as the intermediates seems to be very attractive. β-Metal ketones could afford enones or γ-dicarbonyl compounds in principle by the way of familiar β-hydride elimination or carbon monoxide insertion,[3] respectively. The basic problem which must be overcome in this plan lies in the fact no satisfactory access to β-metal ketones has been known except for a few restricted cases.[4]

In this communication we wish to report a convenient synthesis of β-mercuri ketones (2) by the reaction of mercuric acetate with siloxycyclopropanes (1), readily available from enol silyl ethers and zinc carbenoid reagents,[5,6] and their conversion to α-methylene ketones (4) or γ-ketoesters (5) by the way of subsequent transmetalation into β-pallado ketones (3) using palladium chloride.[7]



In methanol, siloxycyclopropanes (1) readily reacted with mercuric acetate to give β-acetoxymercuri ketones (2) generally in excellent yields (r. t., 0.5 h). We attempted one-pot-conversion of siloxycyclopropanes to α-methylene ketones by successive addition of palladium chloride to the solution containing β-mercuri ketones, which turned out to be successful. For example, 1-siloxy-1-phenyl-2-methylcyclopropane (1b) (1 mmol) was treated with mercuric acetate (1 mmol) in methanol (5 ml) at 20° for 0.5 h. Then to the mixture were added palladium chloride (1 mmol), lithium chloride (2 mmol), and lithium carbonate (2 mmol) and stirring was continued for 10 h at 38°. Gas chromatographic analysis showed almost quantitative formation (98 %) of α-methylene propiophenone (4b). Results are shown in the Table 1. This synthesis turned out to work well for catalytic process, namely the reaction using 0.1 mmol of 1b in the presence of 2 mmol of cupric chloride as oxidant gave 87 % of 4b (see run 4 and also runs 6,9 in Table 1). On the reaction with 1-phenyl-1-siloxycyclopropane (1a), which has no substituent at C_2 position, overoxidation giving 3,3-dimethoxy-1-phenyl-propane-1-one (33 %) and demercurated propiophenone (27 %) predominated.[8] Desired phenyl vinyl ketone 4a could be obtained in 80 % by merely changing the solvent from methanol to acetonitrile at the second stage (see run 2).

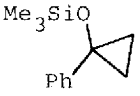
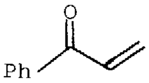
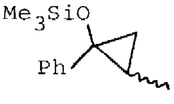
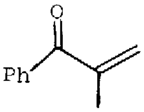
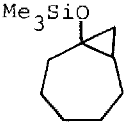
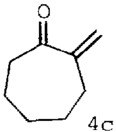
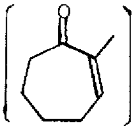
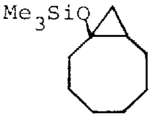
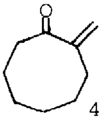
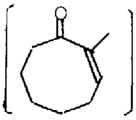
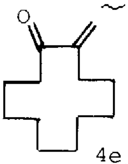
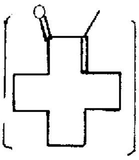
In bicyclic systems (1c and 1d), isomerization of the products (4c and 4e) took place to some extent. This undesirable side reaction could be fairly restrained by the addition of triethylamine as a scavenger of 'HPdCl' which was most likely to cause the isomerization (see run 7 and run 11).

It should be noted that the ring cleavage took place highly selectively at least substituted cyclopropane carbon in the case of 1b-1e, which was essential to realize the present α-methylene ketone synthesis.[9]

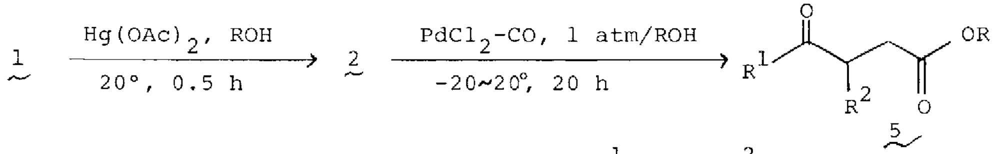
From β-mercuri ketones prepared in situ in alcohol γ-ketoesters (5) could be also prepared, when β-mercuric ketones were treated with palladium chloride under a flow of carbon monoxide.[10]

The present two types of transformations from siloxycyclopropanes show that β-pallado ketones can be generated by transmetalation via β-mercuri ketones.[11] We are continuing our efforts to explore useful synthetic reactions via β-metal ketones.

Table 1. Synthesis of α-Methylene Ketones (4) from Siloxycyclopropanes (1).

run	substrate (1)	reagent[a)]	product (4)	yield (%)[b)]
1	 1a	$Hg(OAc)_2$-$PdCl_2$	 4a	trace[c)]
2		$Hg(OAc)_2$-$PdCl_2$[d)]		80
3	 1b	$Hg(OAc)_2$-$PdCl_2$	 4b	98
4		$Hg(OAc)_2$-$PdCl_2$-$CuCl_2$[e)]		87
5	 1c	$Hg(OAc)_2$-$PdCl_2$	 4c []	80(18)
6		$Hg(OAc)_2$-$PdCl_2$-$CuCl_2$[e)]		68(20)
7		$Hg(OAc)_2$-$PdCl_2$-NEt_3[f)]		80(0)
8	 1d	$Hg(OAc)_2$-$PdCl_2$	 4d []	97(0)
9		$Hg(OAc)_2$-$PdCl_2$-$CuCl_2$[e)]		94(0)
10	 1e	$Hg(OAc)_2$-$PdCl_2$	 4e []	61(38)[g)]
11		$Hg(OAc)_2$-$PdCl_2$-NEt_3[f)]		80(17)[g)]

a) All reactions were carried out on a 1 mmol scale as described in the text. Every case LiCl (2 mmol) and Li_2CO_3 (2 mmol) were also added.
b) GLC yields. The yields of by-products are given in the parentheses.
c) Instead 3,3-dimethoxypropiophenone (33 %) and propiophenone (28 %) were isolated
d) After mercuration, MeOH was evaporated and CH_3CN (5 ml) was introduced.
e) For 1 mmol of siloxycyclopropane, 0.1 mmol of $PdCl_2$ and 2 mmol of $CuCl_2$ were added.
f) To the mixture 1 ml of triethylamine was added before the addition of $PdCl_2$.
g) E and Z mixture.



5

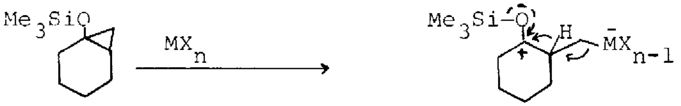
R^1=t-Bu, R^2=H, R=Me 52 %

R^1=Ph, R^2=Me, R=Me 48 %

R^1=R^2=$\leftarrow CH_2 \rightarrow_4$, R=Et 46 %

References and Notes

1) Synthesis via Silyl Alkenyl Ethers, Part XV. Part XIV: I.Ryu, S.Murai, Y. Hatayama, and N. Sonoda, Tetrahedron Lett., 3455 (1978).
2) Recent works: J-L. Glas, Tetrahedron Lett., 2111 (1978); T. Shono, I. Nishiguchi, T. Komamura, and S. Sasaki, J. Am. Chem. Soc., 101, 984 (1979); I. Paterson and I. Fleming, Tetrahedron Lett., 995 (1979).
3) R. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974.
4) β-Lithio ketone from β-bromo ketone and lithium: D. P. G. Hamon, and R. W. Sinclar, J. C. S. Chem. Comm., 890 (1968); β-Mercuri ketones have been prepared from mercuric acetate and cyclopropanols in acetic acid, which are not suitable for synthetic purpose with respect to availability and stability: A. DeBoey and C. H. DePuy, J. Am. Chem. Soc., 92, 4008 (1970); C. H. DePuy and J. U. Lanen, J. Org. Chem., 39, 3360 (1974).
5) S. Murai, T. Aya, and N. Sonoda, J. Org. Chem., 38, 4354 (1973); I. Ryu, S. Murai, and N. Sonoda, Tetrahedron Lett., 4611 (1977).
6) This approach to β-metal ketones is based on the observation of zinc iodide promoted isomerization of siloxycyclopropanes to 2-methylene siloxycycloalkanes. The ionic intermediate shown below should give β-metal ketones if appropriate desilylation (broken arrow) overwhelms the observed 1,2-shift of hydrogen for isomerization (solid arrow).



See, S. Murai, T. Aya, T. Renge, I. Ryu, and N. Sonoda, J. Org. Chem., 39, 858 (1974); I. Ryu, S. Murai, S. Otani, and N. Sonoda, Tetrahedron Lett., 1995 (1977).
7) Synthesis by transmetalation of organomercurials with palladium salts: R. F Heck, J. Am. Chem. Soc., 90, 5518 (1968); R. C. Larlock, J. Org. Chem., 40, 3237 (1975); J. K. Stille and P. K. Wong, J. Org. Chem., 40, 335 (1975).
8) The formation of 3,3-dimethoxypropiophenone might be due to oxypalladation of initially formed phenyl vinyl ketone followed by β-elimination and subsequent addition of methanol.
9) This manner of ring cleavage coincided with that by bromine[a] and was contrasted with that by ferric chloride induced chlorination.[b]
a) S. Murai, Y. Seki, and N. Sonoda, J. C. S. Chem. Comm., 1032 (1976).
b) Y. Ito, S. Fujii, and T. Saegusa, J. Org. Chem., 41, 2037 (1976).
10) In this case, to a stirred suspension of $PdCl_2$ (5 mmol) in alcohol (5 ml) β-mercuri ketones prepared in situ in the corresponding alcohol (5 mmol, 5 ml) was added.
11) β-Pallado carbonyl intermediates: J. K. Stille and R. Divakaruni, J. Org. Chem., 44, 3474 (1979); M. O. Terpko and R. F. Heck, J. Am. Chem. Soc., 101, 5282 (1979).

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