Tetrahedron Letters,Vol.29,No.47,pp 6137-6140,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

Allylative Ring Opening of Siloxycyclopropanes by Silver Fluoride and Allylic Chlorides Affording δ,ε-Unsaturated Ketones

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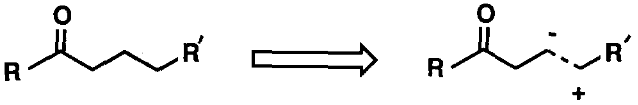
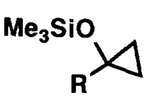
Summary: Unconventional type of allylation reaction at the β-position of ketone carbonyl has been developed based on the β-metallo ketone strategy: treatment of siloxycyclopropanes **1** with allylic chlorides **2** in the presence of silver fluoride results in the effective formation of δ,ε-unsaturated ketones **4**.

The importance of the carbon-carbon bond formation with polarity inversion process at β to ketone carbonyls (eq. 1) has led to considerable interest in developing a variety of (β-acyl)alkyl anion equivalents.[1] For executing such a transformation, the use of β-metal substituted ketones would be the most straightforward although they are not readily accessible.[2] Recently we have found that the methodology comprising the electrophilic ring opening of siloxycyclopropane **1**[3] with metal salts is promising for the generation of β-metal substituted ketones.[4,5] In this communication we describe a simple method for allylation at the β-position of ketone carbonyls based on this siloxycyclopropane approach, in which the β-silver ketone 3 seems to play a key role.


(1)

At the outset, we envisaged that allylic chlorides 2 might well intercept intermediary β-silver ketone 3 in the reaction of **1** with silver tetrafluoroborate ($AgBF_4$).[4b] Unfortunately, the reaction system turned out not suited for this purpose, since $AgBF_4$ reacted with 2 very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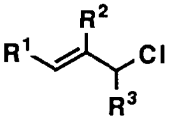
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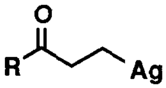
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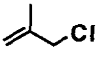
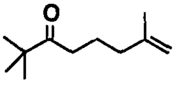
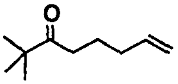
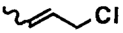
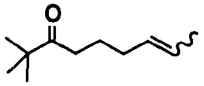
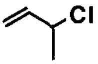
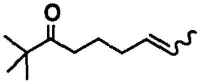
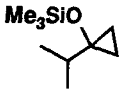
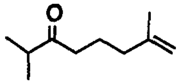
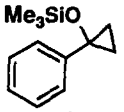
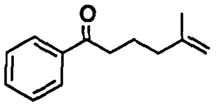
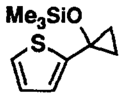
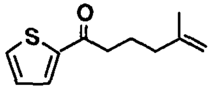
rapidly prior to the reaction with 1. However, the use of silver fluoride (AgF) instead of $AgBF_4$ led our envisagement to meet with success. Thus, the treatment of **1a** with AgF in MeCN/EtOH in the presence of methallyl chloride (2a) (15°C, 4 h) afforded δ,ε-unsaturated

Table 1. Allylative Ring Opening of Siloxycyclopropanes 1 Mediated by AgF.[a]

run	substrate	allylic chloride	solvent	product	yield(%)[b]
1	 **1a**	 **2a**	MeCN-EtOH	 **4a**	75(70)
2			MeCN-MeOH		70
3	**1a**	 **2b**	MeCN-EtOH	 **4b**	71
4			MeCN-MeOH		(53)
5	**1a**	 2c(E/Z=60/40)	MeCN-EtOH	 **4c**	46 (E/Z=76/24)[c]
6	**1a**	 **2d**	MeCN-EtOH	 **4c**	58 (E/Z=73/27)[c]
7	 **1b**	**2a**	MeCN-EtOH	 **4d**	68(53)
8	 **1c**	**2a**	MeOH	 **4e**	65
9	 **1d**	**2a**	MeOH	 **4f**	46

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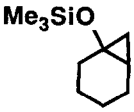
[a] Carried out on 1-3 mmol scale at 15°C for 4 h. [b] GLC (isolated) yield.
[c] Estimated by capillary GLC.

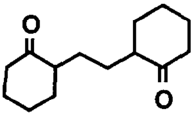
ketone **4a**, a cross-coupling product at β to ketone carbonyl.[6] Results with some representative allylic halides are shown in Table 1. The use of mixed solvents (MeCN/ROH) is indispensable except for the case of methallylation which can be satisfactorily carried out in MeOH only.[7]

The reaction of crotyl chloride (**2c**) with **1a** took place regioselectively at α with respect to the allylic moiety to give **4c** (run 5). To the contrary, the reaction of **1a** with 3-chloro-1-butene (**2d**) gave the same product **4c** selectively (run 6), in which cross-coupling took place at γ position of **2d**. Interestingly, these two crotylation showed nearly identical stereoselectivity (E/Z=3/1).

Our previous result on the reaction of **1** with $AgBF_4$[4b] has shown that **1e** underwent completely siteselective cyclopropane ring cleavage at the peripheral carbon with $AgBF_4$ to give 1,6-diketone **5**. In contrast, methallylation of bicyclic **1e** with AgF proceeded without selectivity in bond cleavage to afford a 46:54 mixture of δ,ε-unsaturated ketones **4g** and **4h** (total yield, 66 %).



1e



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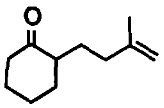
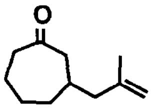
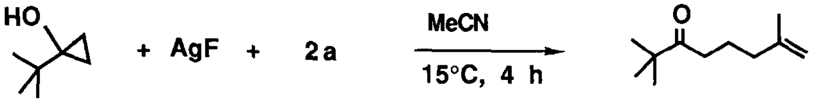


4g



4h

Curiously, for the present allylation to work well, more than two equiv of AgF was required and the use of protic solvents was also indispensable. Accordingly, we suspected the intermediacy of cyclopropanol produced by the reaction of **1** with AgF/ROH. This was supported by the following confirmative results: treatment of **6a** (1 mmol) with AgF (1.5 mmol) and **2a** (1.5 mmol) in acetonitrile afforded **4a** in 60 % yield (eq. 2), whereas the reaction of **1a** under such aprotic conditions gave only a trace amount of **4a**.[8]



(2)

6a **4a** 60 %

A further study of the in situ elaboration of the (β-acyl)-alkylsilver intermediates is currently underway.

Acknowledgement. This work has been supported in part by a Grant-In-Aid from the Ministry of Education, Science and Culture, Japan. We are grateful to Shin-Etsu Chem. Ind. for the gift of Me_3SiCl. We also thank Professor Shinji Murai for informative discussions.

References and Notes

1) For reviews see: a) D. Seebach, Angew. Chem., Int. Ed. Engl., 18, 239 (1979). b) N. H. Werstiuk, Tetrahedron, 35, 205 (1983). c) D. Hoppe, Angew. Chem. Int. Ed. Engl., 23, 932 (1984). d) N. H. Werstiuk in T. A. Hase (Ed.): Umpoled Synthons, Wiley, New York, 1987.

2) For a review of β-metallo ketones, see: I. Ryu and N. Sonoda, J. Synth. Org. Chem. Jpn., 43, 112 (1985).

3) For a review of siloxycyclopropanes, see: S. Murai, I. Ryu, and N. Sonoda, J. Organomet. Chem., 250, 121 (1983).

4) a) I. Ryu, K. Matsumoto, M. Ando, S. Murai, and N. Sonoda, Tetrahedron Lett., 21, 4283 (1980). b) I. Ryu, M. Ando, A. Ogawa, S. Murai, and N. Sonoda, J. Am. Chem. Soc., 105, 7192 (1983). c) I. Ryu, M. Ryang, I. Rhee, H. Omura, S. Murai, and N. Sonoda, Synth. Commun., 14, 1175 (1984). d) I. Ryu, A. Ogawa, N. Sonoda, Nippon Kagaku Kaishi, 442 (1985). e) I. Ryu, S. Murai, N. Sonoda, J. Org. Chem., 51, 2389(1986).

5) β-Metallo esters (ester homoenolates), obtained by the similar ring opening of 1-alkoxy-siloxycyclopropanes with metal salts, have shown useful application in organic synthesis, see: E. Nakamura, S. Aoki, K. Sekiya, H. Oshino, and I. Kuwajima, J. Am. Chem. Soc., 109, 8056 (1987) and references therein. Cf. H. Ochiai, T. Nishihara, Y. Tamaru, and Z. Yoshida, J. Org. Chem., 53, 1343 (1988).

6) A typical experimental procedure is as follows. To a stirred suspension of AgF (5 mmol) in acetonitrile/ethanol (2 mL/0.6 mL) was added dropwise at 15°C a mixed solution of 1a (2 mmol) and allyl chloride 2a (5 mmol) dissolved in acetonitrile (1 mL). After stirring for 4 h at 15°C, the black precipitates were filtered off and the colorless filtrate was extracted into 4-portions of pentane. The combined pentane solution was concentrated and the resultant crude oil was subjected to vacuum distillation to give 2,2-dimethyl-7-methyl-oct-7-en-3-one (4a): (120°C /30 torr(Kugelrohr)) (70 %): IR (neat): 1703, 1650 cm^{-1}; ^1H NMR (100 MHz, CCl_4): δ 1.10 (s, 9H), 1.50-1.82 (m, 5H, including a sharp peak at 1.69), 1.94 (t, J=7 Hz, 2H), 2.36 (t, J=7 Hz, 2H), 4.64 (brs, 2H); MS: m/e 168 (M^+), 111, 97, 85, 83, 69, 57, 55, 41, 29; exact MS: calcd for $C_{11}H_{20}O$ 168.1514, found 168.1491. All products **4a-4h** showed satisfactory spectral and analytical data.

7) In alcoholic solvents, relatively reactive crotyl and 3-butenyl chlorides readily reacted with AgF to give unreactive fluorides.

8) Although the formation of 3 from cyclopropanol and AgF, and the subsequent coupling with allylic halides 2 may be the most plausible pathway leading to 4, there are some alternatives: especially, the role of metallic silver toward 2, as well as the intermediacy of cyclopropoxysilver should be further examined.

(Received in Japan 1 September 1988)