Tetrahedron Letters,Vol.30,No.46,pp 6341-6344,1989
Printed in Great Britain

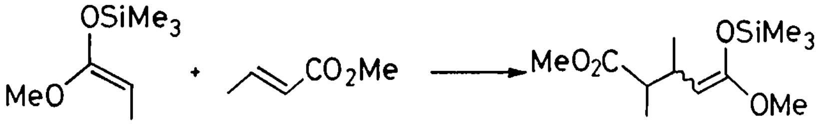
0040-4039/89 $3.00 + .00
Pergamon Press plc

NOVEL CATALYTIC ACTION OF CLAY MONTMORILLONITE ON THE ADDITION REACTIONS OF SILYL KETENE ACETALS TO α,β-ACETYLENIC ESTERS

Makoto Onaka,* Taku Mimura, Ryosuke Ohno, and Yusuke Izumi*
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Chikusa, Nagoya 464, Japan

Summary: Clay montmorillonite shows novel catalytic behavior to the addition of silyl ketene acetals to ynoates as a heterogeneous solid acid, and this activity has been compared with that obtained with trimethylsilyl triflate.

In the previous publications of this series we have demonstrated the utility of clay montmorillonite in carbon-carbon bond-forming reactions such as aldol[1] and Michael[2] additions of enolsilanes to carbonyl compounds. In particular, the addition reactions of silyl ketene acetals (SKA) to α,β-ethylenic esters have been found to proceed smoothly on the clay to afford Michael adducts, which can be isolated as labile silyl ketene acetals after filtration of the clay.[2]



In this communication we wish to report further application of the clay catalyst to the reactions of α,β-acetylenic esters (ynoates) with SKA,[3] which contrasts strikingly with the reactions promoted by a homogeneous acid catalyst, trimethylsilyl triflate (TMSOTf), as well as the addition reactions of lithium enolates with ynoates.

Table 1 summarizes the results of the reactions of the silicon and the lithium enolates of methyl propionate (**1**) with ynoates (**2a-c**). Except for the reaction of **2c**, ferric ion-exchanged montmorillonite (Fe-Mont)[4] catalyzed exclusive 1,2-additions of SKA to **2a** and **2b** to give **3** in high yields, whereas TMSOTf failed to effect the addition. In the case of unsubstituted ynoate **2c**, Fe-Mont mainly induced 1,4-addition to produce (E)-vinylsilane **5c**;[5] this may have resulted from a transient intermediate **5'** through silicon transfer from the enolate oxygen to the α carbon atom. Changing the solvent from dichloromethane to toluene improved the selectivity for 1,4-addition, although the reaction rate slowed down (run 8). The lithium enolate of **1** in HMPA-THF was reactive toward **2**, but a complex mixture of products was obtained except in the reaction with **2a**.

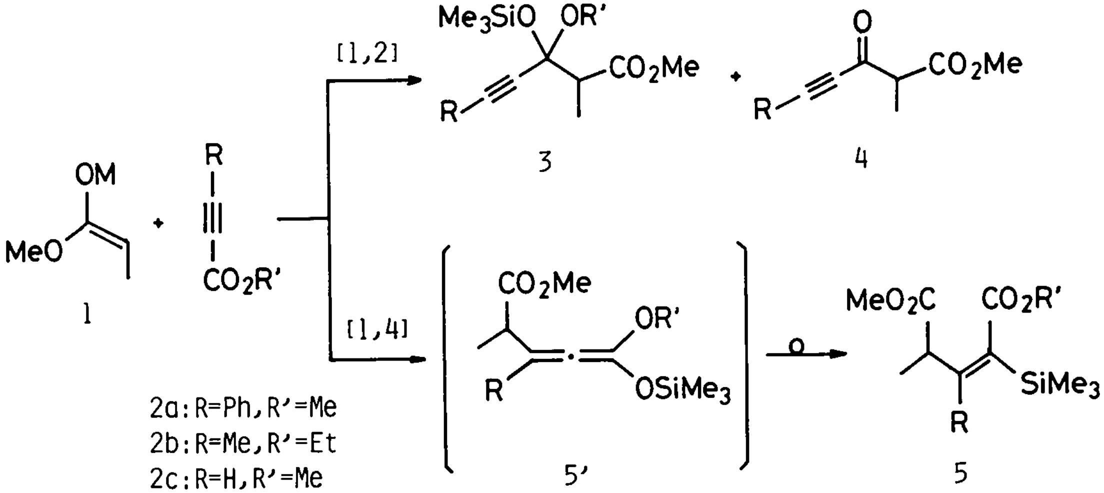


Table 1. Addition of ester enolates **1** to ynoates **2**.

Run	M in enolate	Acceptor	Catalyst	Conditions	Products (% yield)
1	$SiMe_3$	**2a**	Fe-Mont	CH_2Cl_2/-78°C/1.5 h	**3a** (86)
2	$SiMe_3$	**2a**	TMSOTf	CH_2Cl_2/RT/1 d	NR[a]
3	Li	**2a**	---	HMPA-THF/-78°C/2 h	**4a** (58)
4	$SiMe_3$	**2b**	Fe-Mont	CH_2Cl_2/-78°C/1 h	**3b** (89)
5	$SiMe_3$	**2b**	TMSOTf	CH_2Cl_2/RT/1 d	NR[a]
6	Li	**2b**	---	HMPA-THF/-78°C/1 h	CM[b]
7	$SiMe_3$	**2c**	Fe-Mont	CH_2Cl_2/-78°C/5 h	**3c** (10), **5c** (61)
8	$SiMe_3$	**2c**	Fe-Mont	$PhCH_3$/0°C/5 h	**3c** (3), **5c** (77)
9	$SiMe_3$	**2c**	TMSOTf	CH_2Cl_2/RT/1 d	NR[a]
10	Li	**2c**	---	HMPA-THF/-78°C/1 h	CM[b]

[a] No reaction occurred. [b] A complex mixture of products was obtained.

Table 2 shows the results of the addition of silicon and lithium enolates of methyl acetate to **2**. Under the Fe-Mont catalysis, the t-butyldimethylsilyl ketene acetal of **6** is far less reactive than the trimethylsilyl ketene acetal of **1**, requiring higher reaction temperature; moreover, it caused exclusive 1,2-additions to **2a** and **2b** in modest yields, but was inactive to **2c**. In run 11 the product **9a** may have been produced via rapid elimination of a hydroxysilane from an intermediate **7a**.

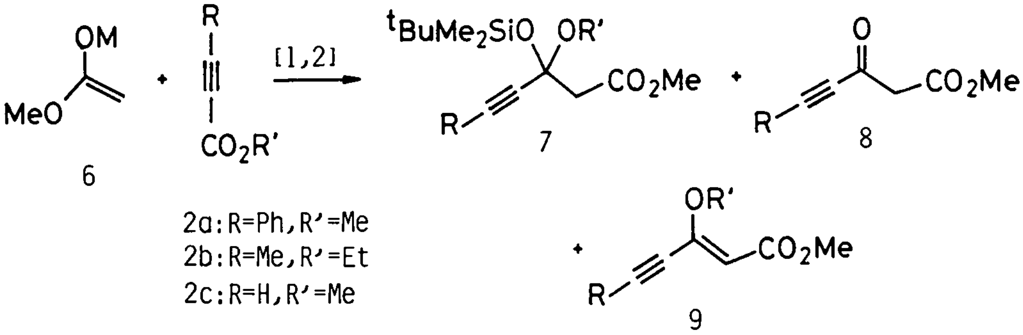


Table 2. Addition of ester enolates **6** to ynoates **2**.

Run	M in enolate	Acceptor	Catalyst	Conditions	Products (% yield)
11	Si^tBuMe_2	**2a**	Fe-Mont	CH_2Cl_2/RT/1 d	**8a** (18), **9a** (44)
12	Si^tBuMe_2	**2a**	TMSOTf	CH_2Cl_2/RT/1 d	**8a** (17)
13	Li	**2a**	---	HMPA-THF/-78°C/2 h	**8a** (17)
14	Si^tBuMe_2	**2b**	Fe-Mont	CH_2Cl_2/RT/1.5 h	**7b** (78)
15	Si^tBuMe_2	**2b**	TMSOTf	CH_2Cl_2/RT/1 d	**8b** (19)
16	Li	**2b**	---	HMPA-THF/-78°C/2 h	CM[a]
17	Si^tBuMe_2	**2c**	Fe-Mont	CH_2Cl_2/RT/1 d	**7c** (4)
18	Si^tBuMe_2	**2c**	TMSOTf	CH_2Cl_2/RT/2 d	**7c** (3)
19	Li	**2c**	---	HMPA-THF/-78°C/2 h	CM[a]

[a] A complex mixture of products was obtained.

Satisfactory yields of the expected products could not be obtained from the TMSOTf-catalyzed reactions and the lithium-enolate additions.

Even with the use of Fe-Mont, 1-methoxy-2-methyl-1-trimethylsiloxypropene and 1-trimethylsiloxycyclohexene (silyl enol ether) did not react with the ynoates examined.

In the reactions of SKA with ynoates, the remarkable difference between Fe-Mont and TMSOTf in catalytic activities could be seen. Fe-Mont seems to be much more strongly acidic[6] than TMSOTf, and thereby can activate a carbonyl group of ynoate to cause 1,2 or 1,4-addition of SKA to the ynoate.

Experimental procedures.

1) Use of Fe-Mont: To suspended Fe-Mont (0.2 g), predried at 120°C/0.5 Torr for 3 h, in CH_2Cl_2 (2 ml) was added under N_2 a solution of **2** (1 mmol) in CH_2Cl_2 (1 ml) and SKA (1.1 mmol) in CH_2Cl_2 (1 ml) successively at the temperature indicated in the Tables; the resulting mixture was then stirred until **2** was consumed. Fe-Mont was filtered through a Celite pad and washed with ether. The combined organic phase was dried over Na_2SO_4, concentrated, and then distillated with Kugelrohr to obtain the products. If necessary, the products were further purified on SiO_2.

2) Use of TMSOTf: A solution of SKA (1.1 mmol) in CH_2Cl_2 (2 ml) was added under N_2 to a mixture of TMSOTf (0.1 mmol) and **2** (1 mmol) in CH_2Cl_2 (3 ml), and the solution was stirred under the conditions shown in the Tables. After neutralization with aq. $NaHCO_3$, the organic products were extracted with ether. The extract was washed with brine and dried over Na_2SO_4, followed by distillation. If necessary, the products were further purified on SiO_2.

3) Use of lithium enolates: To a THF (1 ml) solution of LDA (1.5 mmol) were added under N_2 successively HMPA (1 ml) and a THF solution (2 ml) of methyl propionate (or methyl acetate)(1.5 mmol) at -78°C. After stirring for 0.5 h, **2** (1 mmol) in THF (2 ml) was added at -78°C. The reaction was quenched with aq. NH_4Cl, followed by the same purification procedure as in the case of TMSOTf.

References and Notes

1. M. Kawai, M. Onaka, and Y. Izumi, Bull. Chem. Soc. Jpn., **61**, 1237 (1988); M. Onaka, R. Ohno, M. Kawai, and Y. Izumi, ibid., **60**, 2689 (1987).
2. M. Kawai, M. Onaka, and Y. Izumi, Bull. Chem. Soc. Jpn., **61**, 2157 (1988).
3. The reaction of ethyl propiolate with silyl enol ethers by the use of a stoichiometric amount of $TiCl_4$ was reported to give [2+2] cycloaddition adducts (cyclobutenes): R. D. Clark and K. G. Untch, J. Org. Chem., **44**, 248 (1979). Conjugate addition of organocopper reagents to ynoates is well-known: G. H. Posner, "Organic Reactions," John Wiley & Sons, New York (1972), Vol. 19, p. 1.
4. Fe-Mont was prepared from commercially available sodium ion-exchanged montmorillonite and $Fe(NO_3)_3$. Ion exchange procedures, see Ref. 1.
5. **5c** consisted of a single product as examined by capillary GC analysis (OV-1, 25 m), and (E)-configuration was confirmed with NOE experiments of ^1H NMR.
6. The Fe-Mont catalyst employed has maximum acid strength of $H_0 \leq -8.2$, which was determined by the use of Hammett indicators.

(Received in Japan 29 May 1989)