

## ORGANOMANGANESE (II) REAGENTS XXII<sup>1</sup>. COPPER-CATALYZED CONJUGATE ADDITION OF ORGANOMANGANESE REAGENTS TO $\alpha$ , $\beta$ -ETHYLENIC ESTERS.

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**Abstract :** Copper-catalyzed conjugate addition of organomanganese reagents to  $\alpha$ ,  $\beta$  ethylenic esters easily takes place in THF at 0°C, in the presence of 3% CuCl and Me<sub>3</sub>SiCl. Good to moderate yields are obtained from organomanganese reagents prepared from organolithium or organomagnesium compounds.

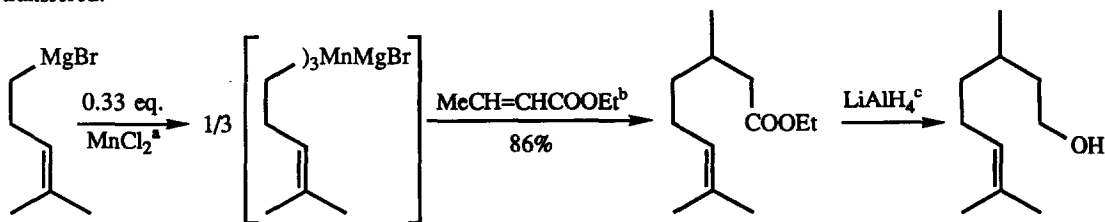
Recently, we have shown that the conjugate addition of organomagnesium reagents to  $\alpha$ ,  $\beta$ -ethylenic esters easily takes place in THF at 0°C in the presence of both cuprous chloride (3%) and Me<sub>3</sub>SiCl (1.2 eq.)<sup>2</sup>. Now, we report that the copper-catalyzed conjugate addition of organomanganese reagents to  $\alpha$ ,  $\beta$ -ethylenic esters can be performed under the same conditions<sup>3</sup>.

The 1,4-addition of n-, s-, and t-alkylmanganese reagents to the  $\beta$ -monosubstituted  $\alpha$ ,  $\beta$ -ethylenic esters led to excellent yields (entries 2 to 6 and 9 to 11). However, when the 1,4-transfer becomes more difficult, e. g. with the less reactive methyl and phenylmanganese chlorides, only moderate yields have been obtained (entries 1 and 7).

A similar influence has also been observed with the more hindered  $\beta$ ,  $\beta$ -bisubstituted  $\alpha$ ,  $\beta$ -ethylenic esters (entry 12). This result is very surprising, since we have previously shown that the copper-catalyzed conjugate addition of organomanganese reagents to  $\alpha$ ,  $\beta$ -ethylenic ketones is generally more efficient than the copper-catalyzed conjugate addition of organomagnesium reagents, especially when the enone bears two substituents in the  $\beta$ -position<sup>4</sup>.

With allylic organomanganese chlorides, which are very reactive (they are almost the only organomanganese chlorides which react with esters), the presence of CuCl does not affect the course of the reaction which always leads to the 1,2-addition product in almost quantitative yields (98%, entry 8).

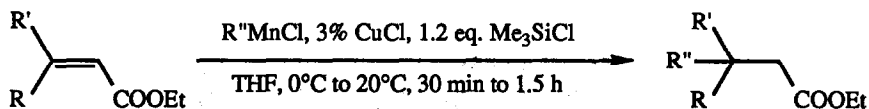
As demonstrated by the short synthesis of citronellol depicted below, the copper catalyzed conjugate addition of organomanganates to enoates can also be achieved successfully. The three R groups bonded to manganese are transferred.



a) 0.6 eq. LiCl; THF, 0°C, 20 min.

b) 3% CuCl, 1.2 eq. Me<sub>3</sub>SiCl, 0°C to 20°C, 1 h. c) THF, 0°C to 20°C, 4 h.

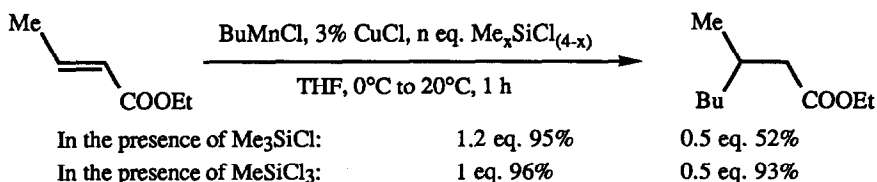
Overall yield: 83%



Entry	R	R'	R''	Metal (R-Metal)	Yield of Isolated Product (%) <sup>a</sup>
1	H	Me	Me	Mg	49 <sup>b</sup>
2	H	Me	Bu	Li	93
3	H	Me	Bu	Mg	97
4	H	Me	iPr	Mg	96
5	H	Me	tBu	Mg	75
6	H	Me	Ph	Li	55
7	H	Me	Ph	Mg	40
8	H	Pr	CH <sub>2</sub> =CHCH <sub>2</sub>	Mg	0 <sup>c</sup>
9	H	Pr	Bu	Mg	91
10	H	iPr	Bu	Mg	89
11	H	Ph	Bu	Mg	90
12	Me	Me	Bu	Mg	44 <sup>d</sup>

a) All products have been isolated by distillation. The main side reaction was the Michael addition of the enolate resulting from the 1,4-addition reaction to the starting enoate. b) 33% of recovered enoate. c) Allylmanganese chloride reacts with Me<sub>3</sub>SiCl. In the absence of Me<sub>3</sub>SiCl (only 3% CuCl), it gave 98% of the 1,2-addition product (based on CH<sub>2</sub>=CHCH<sub>2</sub>MnCl). d) 30% of recovered enoate.

In the previous communication, we have reported that MeSiCl<sub>3</sub> is as efficient as Me<sub>3</sub>SiCl and more economical to perform the copper-catalyzed addition of organomagnesium compounds to enoates<sup>2</sup>. The results presented above show that MeSiCl<sub>3</sub> (0.5 eq.) can also be used with the organomanganese reagents<sup>5</sup>.



It should be noted that the procedure described herein allows to use organomanganese reagents prepared from organomagnesium as well as organolithium compounds. From a preparative point of view, this is interesting since the organolithium compounds do not add in 1,4-manner to enoates, even in the presence of copper salts.

#### References and Notes.

- Part XXI: G. Cahiez and M. Alami, *J. Organomet. Chem.*, in press.
- See the preceding communication in this issue.
- The enoate is added to the mixture RMnCl-Me<sub>3</sub>SiCl-3% CuCl. For the preparation of RMnCl see G. Cahiez and M. Alami, *Tetrahedron* 1989, **45**, 4163. In the absence of Me<sub>3</sub>SiCl the enolate resulting from the 1,4-addition adds immediately to the starting enoate to give the corresponding keto-ester (Claisen reaction).
- G. Cahiez and M. Alami, *Tetrahedron Lett.* 1989, **30**, 3541.

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