

ORGANOMANGANESE (II) REAGENTS XVIII¹
COPPER-CATALYZED 1,4- ADDITION OF ORGANOMANGANESE
CHLORIDE COMPOUNDS TO CONJUGATED ETHYLENIC ALDEHYDES.

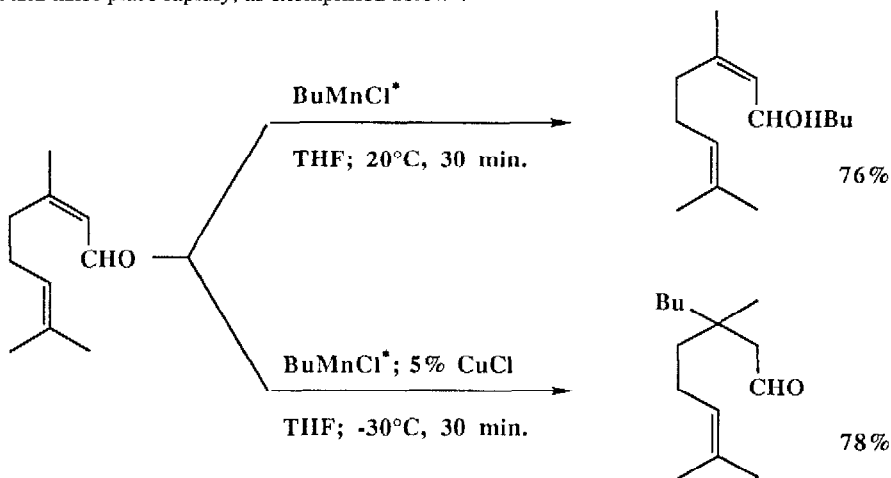
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Abstract : Organomanganese chlorides react with β -mono or β,β -bisubstituted α,β -ethylenic aldehydes in the presence of a catalytic amount of copper chloride to give good yields of 1,4-addition products in THF at -30°C .

Lately, we have found that the copper-catalyzed conjugate addition of organomanganese reagents to α,β -ethylenic ketones proceeds in excellent yields². The wide scope of this reaction and its interest for preparative purposes prompted us to extend our study to other α,β -unsaturated carbonyl derivatives. We now report some results concerning the α,β -ethylenic aldehydes.

As evidenced in Table I, alkyl, aryl and alkenyl manganese chlorides react in THF at -30°C with β -mono or β,β -bisubstituted α,β -ethylenic aldehydes, in the presence of 5% copper chloride, to give the 1,4-addition products in good yields³. It is worthy of note that, in these conditions, the 1,2-addition of the organomanganese reagents to the carbonyl group only occurs in a slight extent whereas in the absence of copper chloride the 1,2-addition is predominant and takes place rapidly, as exemplified below⁴:



* Prepared from BuMgCl

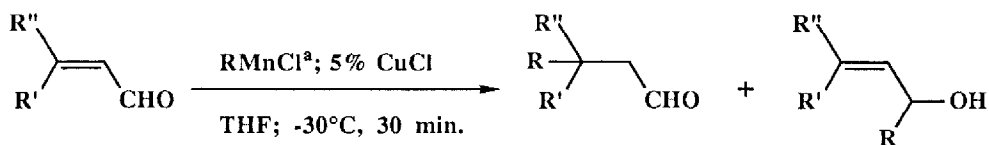
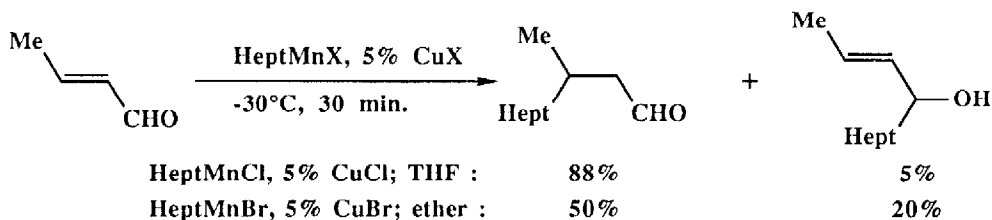


Table I. Copper-Catalyzed Conjugate Addition of Organomanganese Chlorides to β -Mono or β,β -Bisubstituted α,β Ethylenic Aldehydes^b.

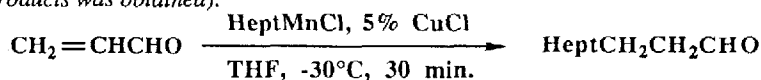
Entry	R	R'	R''	MX ^a	Yield (%) ^c of 1,4-Addition Product	Yield (%) ^c of 1,2-Addition Product
1	Me	H	Hept	LiCl	88	5
2	"	"	"	MgCl ₂	72	10
3	"	"	Ph	Li	60	5
4	"	"	Ph	MgCl ₂	50	5
5	Pr	H	Bu	Li	65	5
6	"	"	"	MgCl ₂	72	7
7	Hept	H	Me	MgCl ₂	80	5
8	Me	Me	Hept	MgCl ₂	80	7
9	"	"	"	LiCl	67	15
10	"	"	Me	MgCl ₂	83	3
11	"	"	Ph	MgCl ₂	76	6
12	"	"	Bu	MgCl ₂	78	5
13	"	"	MeCH=CH	MgBr ₂	49	20
14	Me ₂ C=CCH ₂ CH ₂	Me	Bu	MgCl ₂	78	5
15	"	"	Bu	LiCl	65	15

a) RMnCl being prepared from RMgCl or RLi and MnCl₂, it is always accompanied by lithium or magnesium salts (MX) issuing from the metal-metal exchange reaction. b) For a general procedure see ref. 3. c) Yield of isolated product.

Generally, the organomanganese chlorides prepared from organomagnesium compounds gave better yields of 1,4 addition product than those accruing from organolithium compounds (entries 5 and 6, 8 and 9, 14 and 15). The conjugate addition reaction can be also performed in ether. However, the yields are lower than in THF and the proportion of 1,2 addition products is higher :



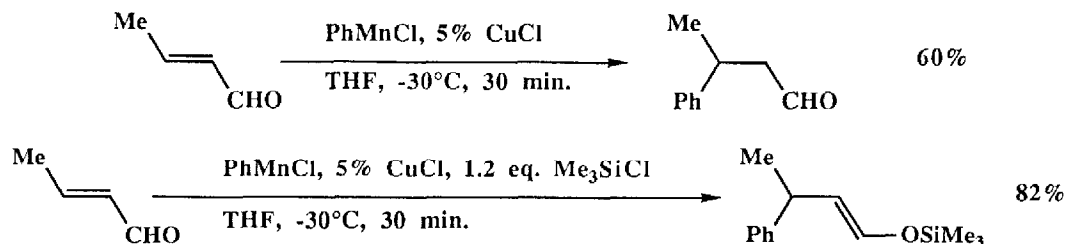
It is known that the conjugate addition of lithium organocuprates to α,β -ethylenic aldehydes gives better yields of 1,4 addition products in the presence of trimethylchlorosilane which traps the intermediate enolate and therefore prevents its reactions with the starting enal⁵ (e.g. aldolisation or Michael addition). In our case, such an effect was generally not observed. Thus, the copper-catalyzed addition of heptylmanganese chloride to acrolein led to a low yield of decanal, even in the presence of trimethylchlorosilane, owing to the high reactivity of this enal (*a large amount of heavy products was obtained*).



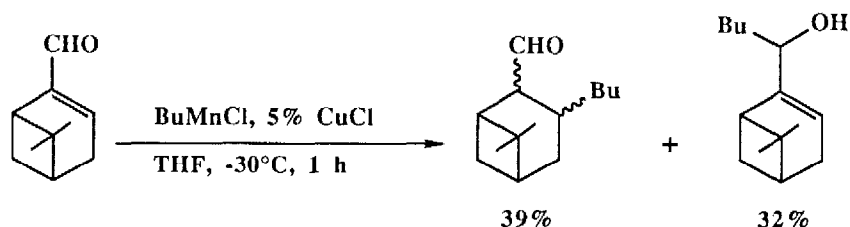
No Me_3SiCl : 40%

1.2 eq. Me_3SiCl : 43%

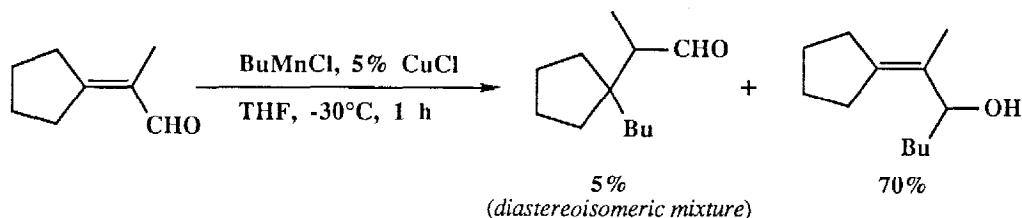
Nevertheless, in some special cases, the yield of 1,4 addition product was improved when trimethylchlorosilane was added to the reaction mixture before the α,β -ethylenic aldehyde. This is illustrated by the following examples:



All our attempts to perform the reaction of an organomanganese chloride with an α,β -bisubstituted α,β -ethylenic aldehyde resulted in unsatisfactory yields of the desired 1,4-addition product since the 1,2-addition process is very competitive⁶.

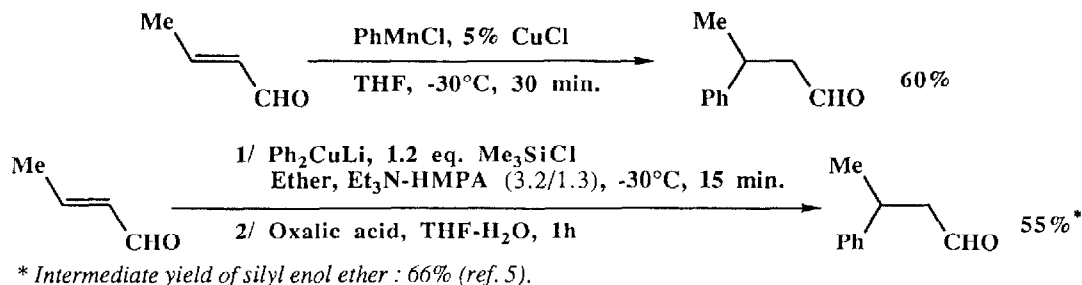


This is especially true for the α,β,β -trisubstituted α,β -ethylenic aldehydes.

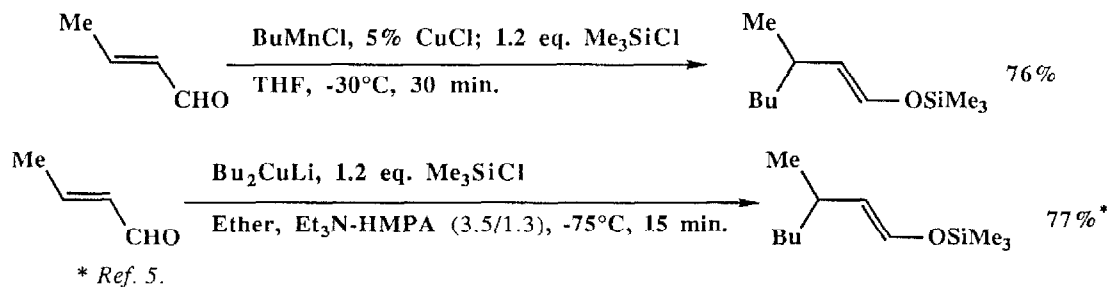


In conclusion, the copper-catalyzed conjugate addition of organomanganese chlorides to β -mono or β,β -bisubstituted α,β -ethylenic aldehydes gives good yields of 1,4-addition products. The results are similar to those obtained via

lithium organocuprates in the presence of trimethylchlorosilane⁵. However our method is more simple to carry out since it allows to obtain the aldehyde in one step instead of the two steps required with an organocuprate (*the 1,4 addition-silylation and the desilylation steps cannot be performed according to a one-pot procedure*). Furthermore the use of trimethylchlorosilane and HMPA, a very hazardous material, is avoided.



The copper-catalyzed conjugate addition of organomanganese chlorides can also be used to prepare the silyl enol ether according to a one-pot procedure.



It is worthy of note that the presence of HMPA is always useless. On the other hand, with butylmanganese chloride, the reaction was performed at only -30°C (with Bu_2CuLi : -75°C).

Finally, let us recall that the yields reported in the case of organocuprates are based on the transfer of only one of the two R groups involved in the reaction. Moreover, organomanganese reagents are cheaper than organocuprate².

References and Notes.

- For part XVII see G. Cahiez and M. Alami, *Tetrahedron*, 1989, **45**, 4163.
- G. Cahiez and M. Alami, *Tetrahedron Lett.*, 1989, **30**, 3541.
- General Procedure:** To 50 mmoles of RMnCl in solution in THF (80 ml) were added, at -30°C in 15 min., 50 mmoles of α,β -ethylenic aldehyde. After 30 min., the reaction mixture was hydrolyzed with 80 ml of 1N HCl. After usual work-up, the product was isolated by distillation.
- For the 1,2 addition of RMnCl to aldehydes see: G. Cahiez and B. Figadère, *Tetrahedron Lett.*, 1986, **26**, 4445.
- C. Chuit, J.P. Foulon and J. Normant, *Tetrahedron*, 1980, **36**, 2305. The 1,4-addition of $\text{Me}_5\text{Cu}_3\text{Li}_2$ to α,β -ethylenic aldehydes has also been reported: D.L.J. Clive, V. Farina and P.L. Beaulieu, *J. Org. Chem.*, 1982, **47**, 2572. For a closely related preparation of silyl enol ethers from α,β -ethylenic aldehydes see also: Y. Horiguchi, S. Matsuzawa, E. Nakamura and I. Kuwajima, *Tetrahedron Lett.*, 1986, **27**, 4025.
- With methacrolein the 1,4 addition product is only accompanied by polymeric products.

