A new type of allyl- and prop-2-ynyl-manganese species: generation and reactions with electrophiles

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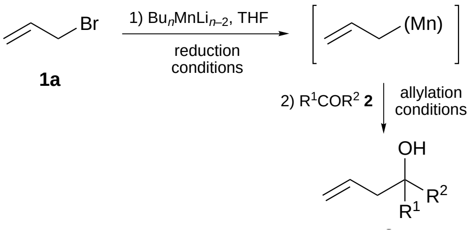
Tetrabutylmanganese ate complex 'Bu_4MnLi_2' reacts with allylic and prop-2-ynylic bromides to generate the corresponding allyl- and prop-2-ynyl-manganese species which further react with electrophiles such as aldehydes, ketones, epoxide and chlorosilanes to afford the corresponding allylated and prop-2-ynylated and/or allenylated products in high yields.

Reactions of many kinds of allyl- and prop-2-ynyl-metals have been reported so far while new types of such reagents will attract much attention.[1] The creation of these new species may provide new methods for selective allylation and prop-2-ynylation. We report here reactions of a new type of allyl- and prop-2-ynyl-manganese reagent generated by the direct reduction of allyl and prop-2-ynyl bromides using manganese ate complex [eqn. (1)]. All of these reagents react with electrophiles efficiently.



1a

(1)

Tributylmanganate 'Bu_3MnLi' reacted with allyl bromide **1a** in THF at −78 °C, and upon addition of benzaldehyde **2a** to the mixture, the allylated product, 1-phenylbut-3-en-1-ol **3a** was obtained in 50% yield. Even if the amount of the manganate was increased to 1.5 equiv. the yield of the product **3a** was at most 66% [eqn. (1), R^1 = Ph, R^2 = H]. In sharp contrast to these facts, tetrabutylmanganate 'Bu_4MnLi_2' showed high reactivity and the allylated product **3a** was produced in 80% yield using an equimolar amount of the reagent.† These results deserve comment. Considering this stepwise procedure, an allylmanganese reagent is possibly generated from allyl bromide by the action of the manganese ate complex as a reductant.[2] Hitherto, two methods for the generation of allylmanganese reagents, by transmetalation[3,4] and direct reduction of allyl halides with low valent manganese (Grignard-type procedure),[5] have been reported.[6]‡ The present reaction is clearly different from these reactions, in view of both the procedure and the reductant used. The substantial difference between the reducing ability of tributylmanganate and that of tetrabutylmanganate is also interesting. Tributylmanganate seems possibly to be in equilibrium between dibutylmanganese and tetrabutylmanganate. Our experiments showed that even reaction with tributylmanganate gave allylated product, but the yield of the product did not exceed 50% based on manganese. These results are likely due to the disproportionation of tributylmanganate, and the present reaction is the first example showing the peculiar reactivity of tetraalkylmanganate, although comparable relative reactivities of tetraalkylmanganates and trialkylmanganates have previously been reported.[7]§ Selected results for the allylation of carbonyl compounds are summarized in Table 1.¶ Aliphatic and aromatic aldehydes as well as ketones are allylated in high yield under mild conditions.

A characteristic feature of the reactivity of the allylmanganese reagent also emerged, as shown in eqns. (2)–(4). From chalcone **2e**, the 1,4-adduct **3e** was obtained as the major product. This is in marked contrast to previously reported reactions using low valent manganese, where only the 1,2-adduct was produced.[5,6]‖ This selectivity may possibly be due to the ate character of the allylmanganese reagent.[8] The allylation even took place with cyclohexene oxide,[9]** while with the keto ester **2g**, the keto moiety was allylated rather than the ester function.[6b]

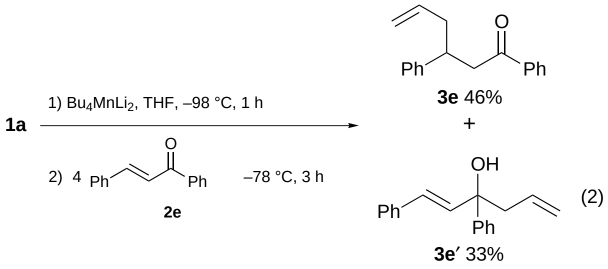
Tetrabutylmanganate also reduced prop-2-ynylic bromides [eqn. (5)]. In this case, allenic and/or prop-2-ynylic products were produced depending on the bulkiness of the electrophiles and the substituent R on the prop-2-ynyl bromides (Table 2). From prop-2-ynyl bromide **1d** (R = H), only the prop-2-ynylic adduct **3o** was obtained in quantitative yield [eqn. (6)].††

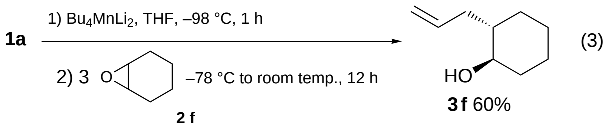
As shown here, tetrabutylmanganate reacts with allyl and prop-2-ynyl bromides to generate allyl- and prop-2-ynyl-

Table 1 Generation of an allylmanganese reagent from allyl bromide **1a** *via* reduction with manganese ate complexes and its reaction with carbonyl compounds **2**[a]

Manganese ate complex (equiv.)	Reduction conditions	Carbonyl compound **2** R^1	R^2		Allylation conditions	Product	Yield (%)[b]
'Bu_3MnLi' (1.0)	−78 °C, 1 h	Ph	H	**2a**	−78 °C to room temp., 4 h	**3a**	50
'Bu_3MnLi' (1.5)	−78 °C, 1 h	Ph	H	**2a**	−78 °C to room temp., 4 h	**3a**	66
'Bu_4MnLi_2' (1.0)	−98 °C, 1 h	Ph	H	**2a**	−78 °C, 0.5 h	**3a**	80
'Bu_4MnLi_2' (1.0)	−98 °C, 1 h	Pr	H	**2b**	−78 °C, 3 h	**3b**	70
'Bu_4MnLi_2' (1.0)	−98 °C, 1 h	Ph	Me	**2c**	−98 °C to room temp., 4 h	**3c**	76
'Bu_4MnLi_2' (1.0)	−98 °C, 1 h	-$(CH_2)_5$-		**2d**	−78 °C, 3 h	**3d**	84

[a] Conditions: allyl bromide **1a** (0.50 mmol) was added to a mixture of manganese ate complex (0.50 mmol) in THF at the temperature shown in the column 'reduction conditions', and the mixture stirred for 1 h. An electrophile was added to the flask, and the resultant mixture was further stirred under the conditions shown in the column 'allylation conditions'. After quenching with saturated NH_4Cl and extraction with Et_2O (30 ml × 3), an organic layer was washed with saturated EDTA and saturated $NaHCO_3$, and the organic layer was dried over $MgSO_4$. After evaporation of solvents, the crude mixture was subjected to chromatography to give the pure product. [b] Isolated yield.





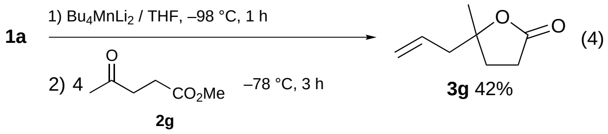


Table 2 Generation and reaction of allenyl- and prop-2-ynyl-manganese species[a]

Prop-2-ynyl bromide	Electrophile	Product	Yield (%)[b] (allenic : prop-2-ynylic)
1b	PhCHO **2a**	**3h**	82 (100 : 0)
1b	EtCHO **2h**	**3i**	75 (100 : 0)
1b	PhCOMe **2c**	**3j**	74 (100 : 0)
1b	Et_2CO **2i**	**3k**	82 (67 : 33)
1c	$PhMe_2SiCl$ **2j**	**3l**	80 (0 : 100)
1c	Me_3SiCl **2k**	**3m**	94 (1 : 99)
1c	Me_2HSiCl **2l**	**3n**	86 (61 : 39)

[a] Conditions: prop-2-ynyl bromide (0.50 mmol) was added to a mixture of 'Bu_4MnLi_2' (0.50 mmol) in THF at −78 °C, and the mixture was stirred for 1 h. An electrophile was added to the flask, at −78 °C and the temperature was allowed to rise to room temp. over > 4 h. After quenching was saturated NH_4Cl and extraction with Et_2O (30 ml × 3), the organic layer was washed with saturated EDTA and saturated $NaHCO_3$, and the organic layer was dried over $MgSO_4$. After evaporation of solvents, the crude mixture was subjected to chromatography to give the pure product. [b] Isolated yield.

manganese reagents where the manganate serves as a reducing agent, not as an alkylating agent. This is a new approach to allylic and prop-2-ynylic manganese reagents which react with aldehydes, ketones, oxirane and chlorosilanes to give the corresponding allylated and prop-2-ynylic and/or allenic products. Further study on the generation and reaction of these reagents is now under investigation.

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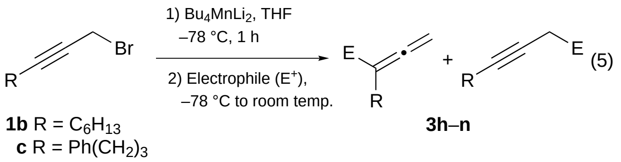

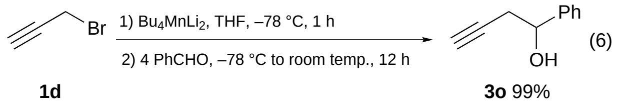

Footnotes and References

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† The formulae 'Bu_3MnLi' and 'Bu_4MnLi_2' and the terms 'tributylmanganate' and 'tetrabutylmanganate' are used tentatively, since the precise structures of the species are not clear at present.

‡ Barbier-type allylations with metallic manganese were also reported (ref. 6).

§ It is known that the reactions of tetraalkylmanganates with acyl chlorides to produce ketones proceed at lower temperature, compared to the reactions of trialkylmanganates, while the yields in these reactions are equally good [ref. 7(*a*)].

¶ A solution of BuLi in hexane (1.6 M; 1.25 ml, 2.0 mmol) was added at −20 °C to a suspension of manganese(II) chloride in THF (63 mg, 0.50 mmol in 5 ml) and the mixture was stirred at −40 to −20 °C for 30 min. Allyl or prop-2-ynyl bromide (0.50 mmol) was added at −98 or −78 °C (at the specified temperature), and the mixture was stirred for 1 h. An electrophile (1.5–2.5 mmol) was added to the mixture, which was further stirred under the conditions shown. After quenching with saturated NH_4Cl and extraction with Et_2O (30 ml × 3), the organic layer was washed with saturated ethylenediaminetetraacetic acid (EDTA) and saturated $NaHCO_3$. The organic layer was dried over $MgSO_4$. After evaporation of solvents, the crude mixture was subjected to chromatography to give the pure product.

‖ The selective 1,4-addition to ethylidenemalonate, which is a good acceptor for the 1,4-addition [*cf.* refs. 3(*c*), 5, 6 and 8], using allylmanganese chloride was also reported [ref. 3(*c*)].

** It was reported that alkylmanganese chloride reacted with oxiranes in the presence of a copper chloride catalyst (ref. 9).

†† This is to the best of our knowledge, the first case of the generation and reaction of prop-2-ynylic manganese reagents.

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