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CARBON-CARBON BOND FORMATION WITH METALLIC MANGANESE

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Metallic manganese is found to reduce allylic bromides and achieve the Barbier-type carbonyl addition of allyl unit.

In view of metallic resources for the future,$^{1)}$ manganese should play more important roles for organic synthesis. Whereas oxidation with manganese element is widely used,$^{2)}$ reduction using the same element has been scarcely studied. An exceptional example is disclosed recently which employs the reagent generated from 1:1 mixture of manganese(II) chloride and lithium aluminum hydride. Though effective for the Grignard-type carbonyl addition,$^{3)}$ details of the reagent remained unknown. Furthermore, preparation of this reagent is sometimes troublesome. We have since been studying the synthetic reactions of low valent manganese and found that metallic manganese powder with the particle size of 10 µm is readily applicable to C-C bond formation including the Barbier carbonyl addition.$^{4)}$

A typical experimental procedure is as follows. Manganese powder (10 µm, Alfa, 0.39 g, 7 mmol) suspended in tetrahydrofuran (THF) (20 ml) containing iodine (0.25 g, 1 mmol) was heated to reflux for 2 h under an argon atmosphere. To this mixture was added a THF (10 ml) solution of allyl bromide (0.52 ml, 6 mmol) and benzaldehyde (0.102 ml, 1 mmol), and the mixture was again heated at reflux overnight. Workup and purification by column chromatography gave 1-phenyl-3-buten-1-ol (**1**) (0.121 g, 82% yield). Generally 7 molar equivalents of manganese and 6 molar equivalents of allyl bromide were employed for the reaction with better results.$^{7)}$ Although the reaction can be carried out without the activator (67% yield of I), the activation by iodine gave reproducible yields. Hg metal was also applicable for the activator (63% yield of allyl bromide-undecanal adduct). Allyl diethylphosphate also was used for the allyl-carbonyl addition only in the presence of a Lewis acid coactivator such as diethylaluminum chloride or aluminum(III) chloride (41 or 31% yield of **1**, respectively).

The reaction was applied to other aldehydes and ketones to give the allyl adducts in good yields as shown in Table 1. With α,β-unsaturated aldehydes and ketones, 1,2-addition took place exclusively (runs 6, 7, 12, and 13). This procedure should be particularly useful for large scale synthesis of homoallyl alcohols in the field of perfume industry.$^{8)}$ 2-Phenylpropanal gave erythro/threo$^{9)}$ homoallyl alcohols (3:1) with the preferred

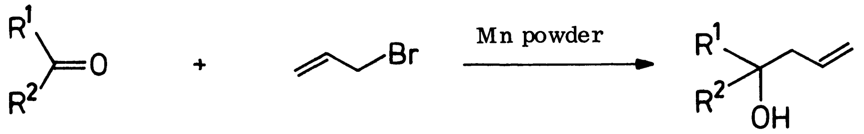
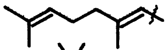
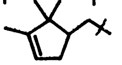
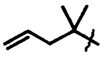
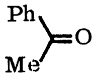
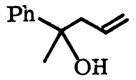
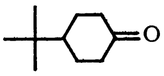
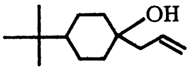
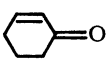
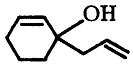
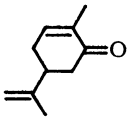
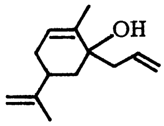


Table 1. Synthesis of Homoallyl Alcohols with Manganese Powder[a)]

Run	R of RCHO	$RCH(OH)CH_2CH=CH_2$ (% yield)
1	C_6H_5	82
2	p-BuO-C_6H_4	97
3	p-Cl-C_6H_4	89
4	$C_6H_5CH(CH_3)$	89[b)]
5	n-$C_{10}H_{21}$	58
6	$C_6H_5CH=CH$	78
7		97
8	 (Ref. 8)	63
9		68

Run	Ketone	Ketone Adduct (% yield)
10		 (76)
11		 (89)[c)]
12		 (93)
13		 (87)

a) All the reactions were carried out with aldehyde (1 mmol), allyl bromide (6 mmol), manganese powder (7 mmol), and iodine (1 mmol) in THF (20 ml) at reflux temperature. b) Erythro : threo (see Ref. 9) = 3 : 1. c) Axial alcohol : equatorial alcohol = 57 : 43.

formation of the Cram product. In contrast to the $MnCl_2$-$LiAlH_4$ reagent system, ca. 1:1 mixture of axial alcohol and equatorial one formed in the addition to 4-t-butylcyclohexanone. Methallyl bromide also can be used for the addition. Thus, the reaction with benzaldehyde gave 3-methyl-1-phenyl-3-buten-1-ol in 78% yield.[10, 11)]

References

1) A. Mizuno, Kagaku No Ryoiki, 36, 110 (1982).

2) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., Menlo Park, California (1972), pp. 257-291.

3) T. Hiyama, M. Obayashi, and A. Nakamura, Organometallics, 1, 1249 (1982).

4) Both σ-$C_3H_5Mn(CO)_5$ (Ref. 5) and π-$C_3H_5Mn(CO)_4$ (Ref. 6) failed to react with benzaldehyde.

5) H. D. Kaesz, R. B. King, and F. G. A. Stone, Z. Naturforsch. B , 15, 682 (1960).

6) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, J. Am. Chem. Soc., 83, 1601 (1961).

7) Use of 3 mmol of manganese and allyl bromide afforded the same product **1** in 81% yield, but for other substrates the yields of the allyl adducts were slightly lower.

8) Polish patent 110254; Chem. Abstr., 96, 122286e (1982).

9) Erythro corresponds to l-product, while threo means u-product: D. Seebach and V. Prelog, Angew. Chem., Int. Ed. Engl., 21, 654 (1982)

10) Allyl bromides having δ-hydrogen(s) such as 1-bromo-3-methyl-2-butene and 1-bromo-2-butene gave the corresponding benzaldehyde adduct in poor yields (13% and 32% respectively). The disappointingly low yields may be ascribed to the decomposition of the intermediate allylmanganese species to 1,3-dienes.

11) In the absence of the carbonyl component, dimerization of allyl bromide was observed (Cf. Ref. 12). 1-Bromo-3-methyl-2-butene gave a 62:26:12 mixture of 2,7-dimethyl-2,6-octadiene, 3,3,6-trimethyl-1,5-heptadiene and 3,3,4,4-tetramethyl-1,5-hexadiene in 52% isolated yield. Cinnamyl bromide dimerized in quantitative yield to give three isomeric coupling products. Benzyl bromide was converted to bibenzyl (89% yield).

12) D. Momose, K. Iguchi, T. Sugiyama, and Y. Yamada, Tetrahedron Lett., 24, 921 (1983) and references cited therein.

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