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Lead-Promoted Allylation of Carbonyl Compounds with Allyl Bromide

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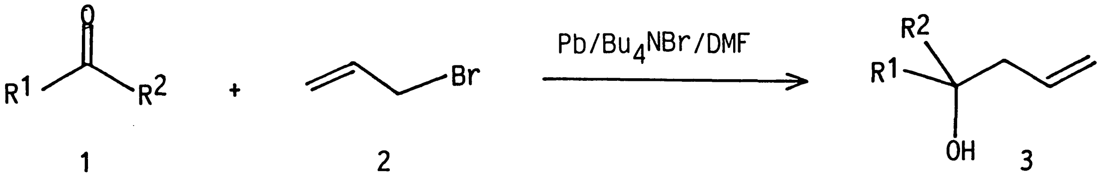
A lead-promoted allylation of carbonyl compounds with allyl bromide in a $Pb/Bu_4NBr/Me_3SiCl/DMF$ system has been performed in good yields with high chemoselectivities: $RCHO > R^1R^2CO > R^1CH(OH)CO_2R^2 \gg R^1CO_2R^2$, lactone, $(RCO)_2O$, and RCOCl.

Allylation of carbonyl compounds with allyl metal reagents has received continuing interest as a promising tool for making carbon-carbon linkage in organic synthesis, and a variety of metals has been utilized for this purpose.[1)] Meanwhile, lead-promoted allylation of carbonyl compounds has not hitherto disclosed; indeed elaboration of allyl substituted leads, even in situ, have scarcely been realized.[2)]

Recently, we have reported an efficient lead-promoted "Barbier-type" reaction of propargyl bromide with aldehydes in a $lead/Bu_4NBr/Me_3SiCl/DMF$ system, suggesting that the unique combination of lead and Bu_4NBr is quite effective for the generation of the intermediary active lead species.[3)] In consequence of the extention work, we now found that the allylation of carbonyl compounds 1 with allyl bromide (2) was successfully performed with the combination of lead and Bu_4NBr in DMF.



1 2 3

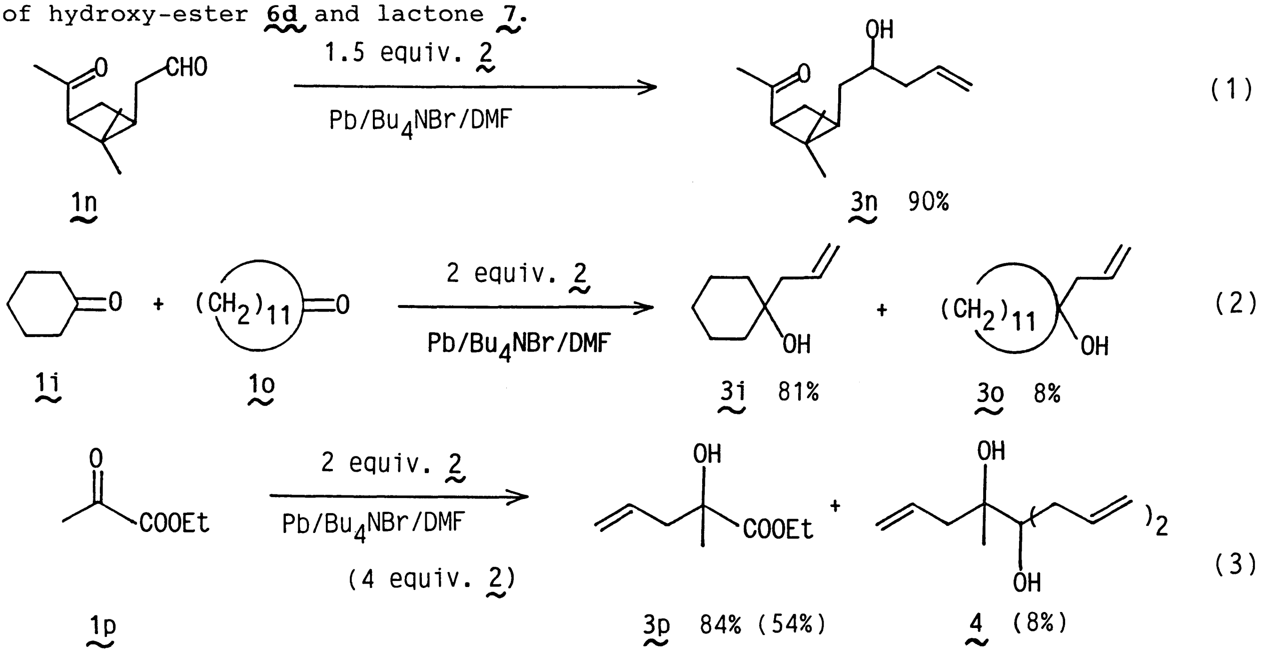
Scheme 1.

A typical experimental procedure (Table 1, entry 2) is as follows. Into a stirred mixture of benzaldehyde (1a, 1 mmol), 2 (2 mmol), Bu_4NBr (1 mmol), and Me_3SiCl (0.2 ml) in DMF (5 ml) was immersed lead plate (> 99.9%; 1.5 x 2 cm^2, 0.5 mm thick) and the stirring was continued at ambient temperature until most of 1a was consumed (2 h). After taking out the lead plate (loosing 1.12 mmol of Pb), usual workup of the mixture afforded the corresponding alcohol 3a (97 %). The reaction was similarly performed (99% yield) without addition of Me_3SiCl when the lead plate was treated with aqueous 10% HCl and air-dried immediately before use.[4)] On the other hand, the effect of Bu_4NBr was remarkable; thus in the absence of Bu_4NBr, only 36% yield of the allylation product 3a was obtained; other salts, e.g., Bu_4NCl, Bu_4NClO_4, KBr, and NaBr, were not effective at all (yields of **3a**: 24-32%).

Though the stoichiometric bromide **2** (1 mol/mol of **1**) was sufficient for the reaction (entry 1), the use of excess bromide **2** was much more effective (entry 2). This would be ascribable to the homocoupling of bromide **2**.[5] The observed stoichiometry (**1a**/**2**/Pb = ca. 1/1/1) suggests that the reaction involves an active divalent organolead (II) reagent rather than tetravalent one (IV) in contrast to the tin-version.[6]

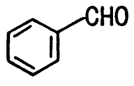
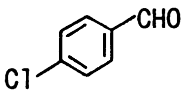
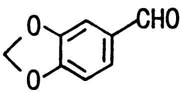
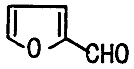
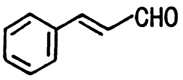
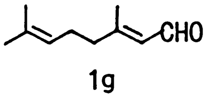
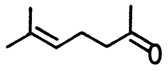
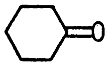
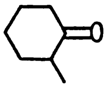
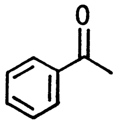
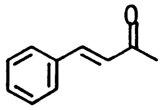
The lead-promoted allylation reaction can be successfully applied to a wide variety of carbonyl compounds. Allylation of aldehydes **1a**-**g** and ketones **1h**-**m** proceeds smoothly (Table 1) with excess bromide **2** (2-4 equiv.). 1,2-Addition took place exclusively with α,β-unsaturated carbonyl compounds **1** (entries 7, 8, and 15). In general, however, other carbonyl functions, e.g., ester, lactone, acyl halide, and acid anhydride, are unreactive toward the in situ generated active lead reagents.[7]

A remarkable feature of the reaction is the high chemoselectivity; thus aldehydes are much more reactive than ketones so that allyl unit can be selectively introduced at the aldehyde carbon of keto-aldehyde **1n** (Scheme 2, Eq. 1). Furthermore, the active lead reagent could discriminate cyclohexanone (**1i**) from cyclododecanone (**1o**) (Eq. 2). Upon treatment with 2 equiv. of bromide **2**, keto-ester **1p** was converted to α-hydroxy-ester **3p** in 84% yield (Eq. 3). Notably, further allylation of ester carbonyl took place, yielding **4** (8%), when **1p** was treated with 4 equiv. of bromide **2**. This unusual result would be due to the effect of the α-hydroxyl group of the intermediary **3p**. In fact, the reaction of α-hydroxy-ester **5a** with 4 equiv. of bromide **2** afforded **6a** while neither the corresponding silyl ether **5b** and non-α-substituted ester **5c** did not give any appreciable amount of allylation products **6b** and **6c** (Scheme 3). Similarly, regioselective allylation of dimethyl malate (**5d**) were performed to give a mixture of hydroxy-ester **6d** and lactone **7**.

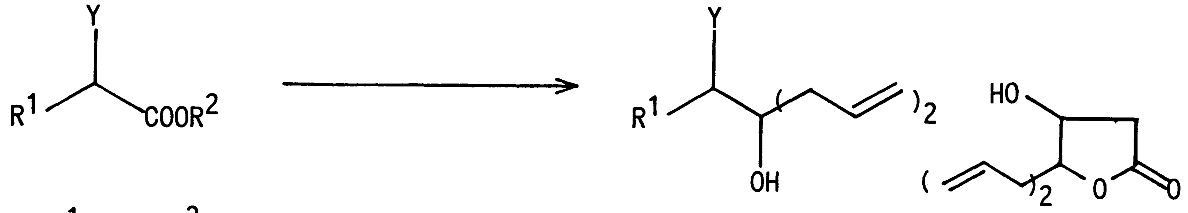


Scheme 2.

Table 1. Reaction of Allyl Bromide with Carbonyl Compounds in a $Pb/Bu_4NBr/Me_3SiCl/DMF$ System[a]

Entry	**1**	**2** (equiv.)	Time[b] h	Yield[c] %
1	 **1a**	1.1	2	89 (73)
2	**1a**	2	2	97
3	 **1b**	2	5	97
4	 **1c**	2	2	99
5	 **1d**	4	5	85
6	 **1e**	2	2	98 (70)
7	 **1f**	2	5	95[e]
8	 **1g**	2	2	90[e] (68)
9	 **1h**	2	5	41[d]
10	**1h**	4	5	68
11	 **1i**	2	5	86 (76)
12	**1i**	4	5	90
13	 **1j**	4	5	88 (45)
14	 **1k**	4	10	98 (50)
15	 **1m**	2	2	84[e]

a) Carried out at ambient temperature. b) Unless otherwise noted, the reaction was continued until most of the starting carbonyl compounds **1** were consumed. c) Isolated yields after column chromatography (SiO_2, hexane/AcOEt: 5/1); numbers in parentheses showing the reported yields obtained in a Sn/**2** (1.5 equiv.)/ether-aqueous HBr (1:1) system.[1e] d) **1h** (35%) was recovered. e) 1,2-Adduct.



5a: R^1= Ph; R^2= Me; Y = OH — 6a 54%
5b: R^1= Ph; R^2= Me; Y = $OSiMe_3$ — 6b 0%
5c: R^1= $(CH_2)_7CH{=}CH_2$; R^2= Et; Y = H — 6c 0%
5d: R^1= CH_2COOMe; R^2= Me; Y = OH — 6d 37% 7 11%

Scheme 3.

As demonstrated above, the lead-promoted allylation reactions were comparable with the tin-version[1e] or rather slightly more effective (ex. entries 1, 6, 8, 11, 13, and 14). Further application of the lead-promoted allylation will be reported in due course.

References

1) For example: a) T. Mukaiyama and T. Harada, Chem. Lett., 1981, 1527; b) J. Souppe, J. L. Namy, and H. B. Kagan, Tetrahedron Lett., 23, 3497 (1982); c) J.-L. Luche and J.-C. Damiano, J. Am. Chem. Soc., 102, 7926 (1980); d) Y. Yamamoto and K. Maruyama, Heterocycles, 18, 357 (1982); e) J. Nokami, J. Otera, T. Sudo, and R. Okawara, Organometallics, 2, 191 (1983); f) T. Hiyama, M.-Sawahata, and M. Obayashi, Chem. Lett., 1983, 1237; g) T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka and M. Yokoyama, J. Org. Chem., 49, 3904 (1984); h) K. Uneyama, N. Kamaki, A. Moriya, and S. Torii, ibid., 50, 5396 (1985); i) M. Wada and K. Akiba, Tetrahedron Lett., 26, 4211 (1985); j) C. Petrier, J. Einhorn, and J. L. Luche, ibid., 26, 1449 (1985); and references cited therein.

2) P. G. Harrison, "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon Press (1982), Vol. 2, p. 629; V. G. K. Das and C. K. Chu, "The Chemistry of the Metal-Carbon Bond," ed by F. R. Hartrey and S. Patai, John Wiley & Sons Ltd. (1985), Vol. 3, p. 1.

3) H. Tanaka, T. Hamatani, S. Yamashita, and S. Torii, Chem. Lett., in contribution.

4) It is likely that addition of Me_3SiCl is effective for the activation of Pb plate surface.

5) Details of the homocoupling of allyl bromide (2) and its analogues will be reported in due course.

6) The tetravalent tin, $(CH_2{=}CHCH_2)_2SnX_2$, has been proposed as an active species in the tin-promoted allylation; see Ref. 1e.

7) Upon similar reacitons with ethyl 11-undecenate, 4-hexyl-4-butanolide, hexanoic anhydride, and benzoyl chloride, no appreciable amounts of the allylation products were obtained.

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