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METALLIC BISMUTH MEDIATED ALLYLATION OF ALDEHYDES TO HOMOALLYLIC ALCOHOLS

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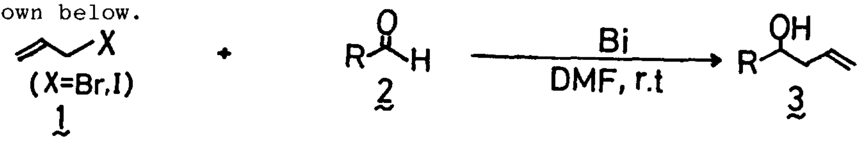
Abstract: In the presence of metallic bismuth, allyl halides were found to react with aldehydes under mild conditions to give the corresponding homoallylic alcohols in good yields.

Among group VB elements, bismuth metal is cheaper and less toxic than arsenic or antimony and can be expected to play some role in organic synthesis according to its enhanced metallic character. To our knowledge, however, its synthetic utility is hitherto unknown. We now wish to communicate the first example of the Grignard-type allylation of aldehydes (**2**) just using metallic bismuth[1] and allyl halides (**1**, X=Br,I) to afford the corresponding homoallylic alcohols (**3**)[2] in good yields. The overall scheme is shown below.



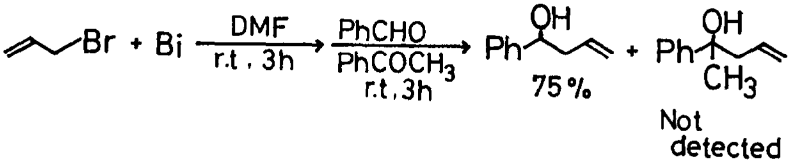
The reaction was carried out by the following two procedures. 1) Method A, metallic bismuth was stirred with an allyl halide in DMF at room temperature for 2~4 h and then the mixture was reacted with an aldehyde for 2~3 h ; 2) Method B, metallic bismuth was stirred with a mixture of an allyl halide and an aldehyde in DMF at room temperature for 12 h (Barbier-type reaction). Allyl chloride did not give the expected adduct (**3**) at all, different from its bromide and iodide. Some typical results are described in Table 1. When an α,β-unsaturated aldehyde was used, 1,2-addition product was obtained selectively. Both aromatic and aliphatic aldehydes reacted smoothly to afford the corresponding homoallylic alcohols in good yields, however, acetophenone gave the desired product only in low yield under the same conditions ($<$5% yield by ^{1}H NMR). Based on this reactivity difference, we

Table 1 Bismuth Mediated Synthesis of Homoallylic Alcohols[a]

Allyl halide	Aldehyde	Method	Yield of **3**(%)[b]
$CH_2=CHCH_2Br$	C_6H_5CHO	A	94
$CH_2=CHCH_2Br$	C_6H_5CHO	B	98
$CH_2=CHCH_2I$	C_6H_5CHO	B	98
$CH_2=CHCH_2Br$	$p\text{-}MeOC_6H_4CHO$	A	98
$CH_2=CHCH_2Br$	$C_6H_5CH_2CH_2CHO$	A	97
$CH_2=CHCH_2Br$	$C_6H_5CH_2CH_2CHO$	B	53
$CH_2=CHCH_2Br$	$CH_3(CH_2)_7CHO$	A	80[c] (85)[d]
$CH_2=CHCH_2Br$	$CH_3(CH_2)_7CHO$	B	58[c]
$CH_2=CHCH_2Br$	$(CH_3)_2CHCHO$	A	70[e] (88)[d]
$CH_2=CHCH_2Br$	$C_6H_5CH=\underset{\substack{\vert \\ C_6H_{13}}}{C}CHO$	A	70

a) All the products gave satisfactory IR and ^{1}H NMR spectra. The molar ratio of an allyl halide :bismuth:an aldehyde=1.2: 1.2:1.0
b) Isolated yields by thin-layer chromatography (hexane:ethyl acetate=9:1), based on aldehydes, are given unless otherwise stated. c) Isolated yield by kugelrohr distillation. d) Estimated by ^{1}H NMR. e) Isolated yield by flash column chromatography (hexane:ethyl acetate=9:1).

could discriminate benzaldehyde from acetophenone as shown in the next equation. Thus, this reaction is chemoselective.



Although the reaction mechanism is not yet clear at the present stage, we assume that some allylbismuth reagent is formed through the oxidative addition of an allyl halide to metallic bismuth. The mechanistic detail and related work are now in progress.

References and Notes

1. In our early investigation, commercially available bismuth shot (99.999%, Wako Pure Chemical Industries, Ltd.) was scraped with a rasp for use in the present reaction. Bismuth powder (100 mesh, 99.999%, Aldrich Chemical Co.) is also effective and more convenient for the reaction.
2. Allylations of carbonyl compounds using Mn, Zn, Sn, and Ce have been reported. a)T. Hiyama, M. Sawahata, and M. Obayashi, Chem.Lett., 1237 (1983). b)P. Christian and J. L. Luche, J. Org. Chem., **50**, 910 (1985). c)T. Mukaiyama and T. Harada, Chem. Lett., 1527 (1981). d)J. Nokami, J. Otera, T. Sudo, and R. Okawara, Organometallics., **2**, 191 (1983). e)K. Uneyama. H. Matsuda, and S. Torii, Tetrahedron Lett., **25**, 6017 (1984). f)T. Imamoto, T. Kusumoto, Y. Tawarayama, Y. Sugiura, T. Mita, Y. Hatanaka and M. Yokoyama, J. Org. Chem., **49**, 3904 (1984).

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