

BARBIER-TYPE REACTION WITH TRIALKYLSTIBINE ¹

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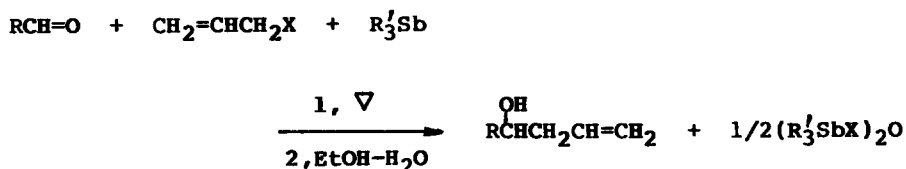
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Summary. In the presence of trialkylstibine, various aldehydes react readily with allyl halides to form homoallylic alcohols in excellent yield.

Allylation of carbonyl compounds to homoallylic alcohols is an important synthetic operation. Many metals have been used to promote this Barbier-type reaction with allyl halides.^{2,3} However, no report appeared in the literature by using organometallics. In continuation of our studies on organo-antimony compounds in synthetic application,⁴ we would like to report here the first example of the Barbier-type reaction by means of organometallics.

On heating equivalent amounts of aldehyde, allyl bromide and trialkylstibine at about 80°C, homoallylic alcohol was obtained after hydrolysis, along with bis-(bromo-trialkyl-antimony)-oxide⁵ as shown in **Scheme 1**.

Scheme 1





Triethylstibine⁶ and tri-n-butylstibine⁷ have similar property to promote the reaction. The reactivity of allyl iodide is almost the same as the bromide, while that of allyl chloride is somewhat lower. A variety of aldehydes undergo the reaction readily; the following table shows the reaction conditions and results. Ketones such as cyclohexanone and acetophenone did not work at all under the similar conditions. Thus, this reaction is chemoselective.

The reaction could be performed without solvent, or in solvent such as tetrahydrofuran under refluxing.

Typical procedure: Aldehyde (2.0 mmoles), allyl halide (2.5 mmoles) and trialkylstibine (2.2 mmoles) were stirred and heated under nitrogen. After the aldehyde disappeared, the reaction mixture was treated with ethanol (2 ml) for 0.5 hour. The homoallylic alcohol was separated by column chromatography (1:1 alumina-silica gel), eluted with ethyl acetate/petroleum ether (15:85). All products were identified by comparison with authentic sample or by MS, IR, ¹H NMR and microanalysis.

Table. Allylation of Aldehydes with Allyl Halides
Promoted by Trialkylstibine

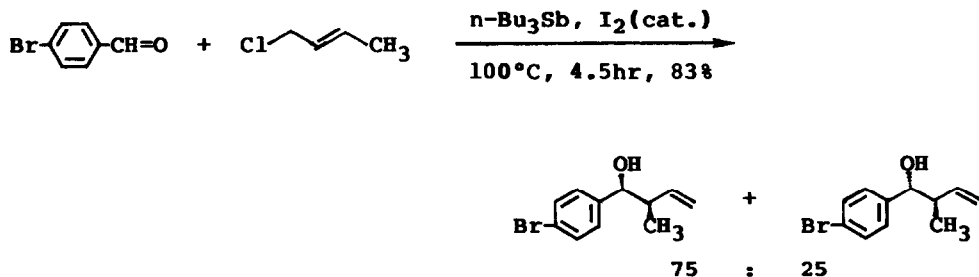
Entry	X	R	R'	Reaction Temp(°C)	Conditions Time(hr)	Yield (%) [*]
1	Br	n-C ₈ H ₁₇ -	C ₂ H ₅ -	90	19	87
2	Br	n-C ₇ H ₁₅ 	C ₂ H ₅ -	85	6	91
3	Br	C ₆ H ₅ 	C ₂ H ₅ -	80	16	95
4	Br	2-furfuryl-	C ₂ H ₅ -	80	16	92
5	Br	p-ClC ₆ H ₄ -	C ₂ H ₅ -	80	7.5	96
6	Br	p-ClC ₆ H ₄ -	n-C ₄ H ₉ -	100	5.5	95 ^{**}
7	Br	p-BrC ₆ H ₄ -	n-C ₄ H ₉ -	85	6	95
8	Br	C ₆ H ₅ -	n-C ₄ H ₉ -	80	16	93
9	I	C ₆ H ₅ -	n-C ₄ H ₉ -	80	8	95 ^{**}
10	Cl	C ₆ H ₅ -	n-C ₄ H ₉ -	100	5	60 ^{**}

* Isolated yield by column chromatography unless double starred;

** Estimated by ¹H NMR analysis.

Crotyl chloride reacted with p-bromobenzaldehyde mediated by tri-n-butylstibine,⁸ but catalytic amount of iodine was needed to promote the reaction. The result is depicted in **Scheme 2**.

Scheme 2

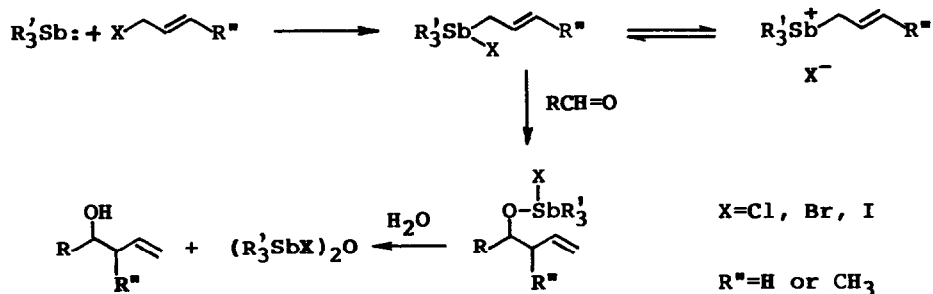


5-(4-Bromophenyl)-2-penten-5-ol, the isomer resulted from the addition of terminal carbon in crotyl to carbonyl compound, was not found.

Detailed studies showed that allyl bromide reacted with triethylstibine at room temperature, forming pentavalent organoantimony salt,⁹ allyl-triethylstibonium bromide.¹⁰ This salt reacts with benzaldehyde at 80°C, forming a

moisture sensitive oil, bromo-alkoxy-triethylstiborane according to ^1H NMR. So the reaction mechanism is postulated as **Scheme 3**.

Scheme 3



We proposed trialkylstibine attacked the halogen atom of allyl halide at first,¹¹ the allyl anion that formed combined with halostibonium to give penta-valent organoantimony compound, which reacted with aldehyde. The allyl anion might undergo nucleophilic attack on carbonyl directly in the presence of substrate, forming halogeno-alkoxy-trialkylstiborane. The homoallylic alcohol was obtained after hydrolysis.

It is interesting to note that the organometallics instead of metals could be served as mediator in Barbier-type reaction.

Acknowledgement. Thanks are due to the Science Fund of Academia Sinica for financial support.

References and Notes

1. This paper is the 58th report on the studies of the application of elemento-organic compounds of the fifteenth and sixteenth groups in organic synthesis.
2. T.Hiyama, K.Kimura and H.Nozaki, *Tetrahedron Lett.*, **1981**, 1037; T.Hiyama, M.Sawahata and M.Obayashi, *Chem.Lett.*, **1983**, 1237; C.Petrier, J.Einkorn and J.L.Luche, *Tetrahedron Lett.*, **26**, 1449(1985); M.Wada and K.Akiba, *Tetrahedron Lett.*, **26**, 4211(1985); H.Tanaka, S.Yamashita, T.Hamatami, Y.Ikemoto and S.Torii, *Chem.Lett.*, **1986**, 1611; J.Soupe, J.L.Namy and H.B.Kagan, *Tetrahedron Lett.*, **1982**, 3497, and references cited therein.
3. After our experiments have run to completion, we see Butsugan's report using antimony metal: Y.Butsugan, H.Ito and S.Arakt, *Tetrahedron Lett.*, **28**, 3707(1987).
4. Y.Z.Huang, Y.C.Shen and C.Chen, *Tetrahedron Lett.*, **26**, 517(1985); *ibid.*, **27**, 2903(1986).
5. Bis-(bromo-tri-n-butyl-antimony)-oxide: white crystal, m.p. 61-63°C (from

- ethyl acetate-petroleum ether). $^1\text{H NMR}(\text{TMS}/\text{CCL}_4)$: 1.01(t, $J=5.0\text{Hz}$, 9H), 1.22-1.68(m, 6H), 1.68-2.06(m, 6H), 2.06-2.51(m, 6H); IR(KCl): 780(s), 750(s), 520(w); MS(EI) $m/e(\text{rel. intensity})$: 373(Bu_3SbBr , 100); Satisfactory microanalyses obtained: ± 0.13 .
6. C.H.Bamford, D.L.Levi and D.M.Newitt, *J.Chem.Soc.*, **1946**, 468.
7. J.Seifter, *J.Amer.Chem.Soc.*, **61**, 530, (1939).
8. 3-Methyl-4-(4-bromophenyl)-1-buten-4-ol: colorless oil. $^1\text{H NMR}(\text{TMS}/\text{CCl}_4)$: erythro-form: 0.92(d, $J=7.0\text{Hz}$, 3H), 2.19(brs, 1H), 2.35(m, 1H), 4.37(m, 1H, collapsed to doublet, $J=5.5\text{Hz}$, with added D_2O), 4.70-5.20(m, 2H), 5.60(m, 1H), 7.06(d, $J=10.0\text{Hz}$, 2H), 7.39(d, $J=10.0\text{Hz}$, 2H); threo-form: 0.83(d, $J=7.0\text{Hz}$, 3H), 2.13(brs, 1H), 2.35(m, 1H), 4.20(m, 1H, collapsed to doublet, $J=7.0\text{Hz}$, when D_2O added), 4.70-5.20(m, 2H), 5.60(m, 1H), 7.06(d, $J=10.0\text{Hz}$, 2H), 7.39(d, $J=10.0\text{Hz}$, 2H); IR(neat): 3400(s), 1640(m), 1010(s), 920(m); MS(EI) $m/e(\text{rel. intensity})$: 240(M^+ , 0.1), 223(14), 187(84), 157(19), 77(100); Satisfactory microanalyses obtained: ± 0.22 . The diastereoisomer ratio was determined by $^1\text{H NMR}$. [ref. M.Wada, H.Ohki and K.Akiba, *Tetrahedron Lett.*, **27**, 4771(1986)].
9. Some similar examples see: G.Wittig and H.Laib, *Ann.*, **580**, 57(1953); K.Issleib and B.Hamann, *Z.anorg.Chem.*, **339**, 289(1965); K.Issleib and R.Lindner, *Ann.*, **707**, 120(1967).
10. White solid, m.p.73-76°C (from benzene), sensitive to moisture. $^1\text{H NMR}(\text{TMS}/\text{CCl}_4)$: 1.50(t, $J=7.0\text{Hz}$, 9H), 2.62(q, $J=7.0\text{Hz}$, 6H), 3.32(d, $J=7.2\text{Hz}$, 2H), 4.94-5.00(m, 2H), 6.05(m, 1H); IR(KCl): 1622(m), 705(s); MS(EI) $m/e(\text{rel. intensity})$: 299(M^+-Et , 5), 289($\text{M}^+-\text{C}_3\text{H}_5$, 25), 249(M^+-Br , 100); Satisfactory microanalyses obtained: ± 0.20 .
11. For the halophilic reaction of tertiary-phosphine, see: H.Hoffman and H.J.Diehr, *Angew.Chem.Int.Ed.Engl.*, **3**, 737(1964).

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