Heteroatom Chemistry
Volume 2, Number 2, 1991

Reaction of Allyl Bromide with Carbonyl Compounds Mediated By Tributylbismuthine [1]

Yao-Zeng Huang* and Yi Liao

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Received 5 December 1990.

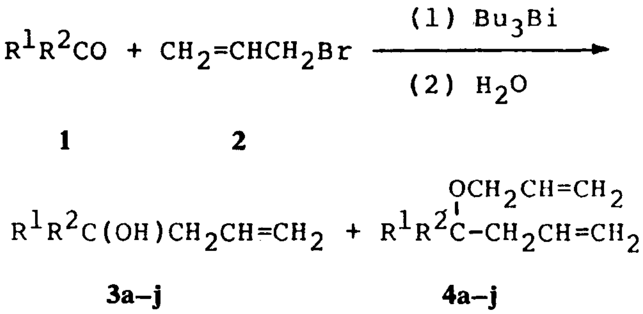
ABSTRACT

In the presence of tributylbismuthine, allyl bromide was found to react with either aldehydes or ketones to give the corresponding homoallylic alcohols and their allylic ethers in good total yields.

INTRODUCTION

Wada et al. reported that either metallic Bi [2] or $BiCl_3$–metal (metal = Zn, Fe, or Al) [3] can mediate a Barbier-type reaction, while we reported a first example of using tributylstibine, an organometallic compound, instead of metal to achieve the same reaction [4]. However, all of these methods were limited to aldehydes affording homoallylic alcohols exclusively. We wish to report here that, by means of tributylbismuthine, ketones as well as aldehydes reacted with allyl bromide to form homoallylic alcohols **3a–j** along with their allylic ethers **4a–j**. The two products were easily separated.

Various aldehydes reacted smoothly with allyl bromide to form **3** and **4**. The proportion of the two products depended upon the amount of allyl bromide used. When an equimolar amount of allyl bromide was allowed to react with an aldehyde, a homoallylic alcohol **3** was obtained predominantly; with two or more equivalents of allyl bromide, **4** was obtained as the major product. On the other hand, in reactions with ketones, even two or more equivalents of allyl bromide gave **3** as the major product and **4** as the minor one. The results are summarized in Table 1.



$$R^1R^2CO + CH_2{=}CHCH_2Br \xrightarrow[(2)\ H_2O]{(1)\ Bu_3Bi}$$

1 **2**

$$R^1R^2C(OH)CH_2CH{=}CH_2 + R^1R^2\overset{\displaystyle OCH_2CH{=}CH_2}{\overset{|}{C}}{-}CH_2CH{=}CH_2$$

3a–j **4a–j**

EXPERIMENTAL

Typical Procedure

Into a mixture of allyl bromide (4.8 mmol) and tributylbismuthine (2.2 mmol) was added the carbonyl compound (2 mmol) under nitrogen. The reaction mixture was stirred at 60–80°C for 4–24 h and monitored by NMR or TLC. After disappearance of the starting material, the mixture was treated with 5% aqueous sodium carbonate solution and extracted with chloroform or ether. The organic solution was dried with magnesium sulfate and evaporated. The two products were isolated and purified by flash column chromatography (silica gel, 9:1 petroleum ether, bp 60–90°C/ethyl acetate). Satisfactory NMR, IR, and MS spectra and micoanalyses were obtained for all the products. The reaction was carried out without solvent or in a solvent such as tetrahydrofuran or hexane.

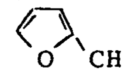
---

*To whom correspondence should be addressed.

Dedicated to Professor Dr. Rolf Appel on the occasion of his 70th birthday.

1042-7163/91/$3.50 + .25

TABLE 1 Syntheses of Homoallylic Alcohols and Their Allylic Ethers

Entry	Carbonyl Compound	Molar Ratio (1/2)	Conditions T(°C)/t(h)	Yield(%)^a	
				3	4
a	C_6H_5CHO	1/1.1	60/5	75	10
		1/2.4	80/5	38	57
		1/9	60/5	34	60
b	p-ClC_6H_4CHO	1/2.4	80/8	35	61
c	p-$NO_2C_6H_4CHO$	1/2.4	60/6	47	51
d		1/2.4	80/7	40	49
		1/9	60/5	42	52
e	$CH_3(CH_2)_7CHO$	1/2.4	60/4	28	62
f	$C_6H_5CH{=}CHCHO$	1/9	60/8	38^b	54^b
g	p-$NO_2C_6H_4COCH_3$	1/9	60/24	57	32
h	$C_6H_5COCH_3$	1/3	60/20	48	24
i	$\overline{CH_2(CH_2)_3C}{=}O$	1/9	60/24	60	24
j	$\overline{CH_2(CH_2)_4C}{=}O$	1/9	60/24	58	21

^{a} Isolated yield.
^{b} No Z isomer was detected on NMR.

1-Phenylbut-3-enyl Allyl Ether (**4a**). Liquid. NMR (CCl_4, TMS,) δ 2.36 (dd, 2H, $J_1 = J_2 = 6.0$ Hz), 3.74 (d, 2H, $J_3 = 5.5$ Hz), 4.18 (t, 1H, $J_1 = 6.0$ Hz), 4.70–5.46 (m, 4H), 5.50–6.04 (m, 2H), 7.25 (s, 5H). IR (neat, cm^{-1}): 1640, 1060, 990, 915. MS (m/z, rel. int. %) 188 (M^+, 0.3), 187 ($M^+ - 1$, 2.1), 147 (47.1), 131 (84), 105 (100). Anal. Calcd. for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.79; H, 8.91.

1-(4-Chlorophenyl)-but-3-enyl Allyl Ether (**4b**). Liquid. bp 84°C/1 mmHg. NMR δ 2.39 (dd, 2H, $J_1 = J_2 = 6.0$ Hz), 3.78 (d, 2H, $J_3 = 5.0$ Hz), 4.24 (t, 1H, $J_1 = 6.0$ Hz), 4.79–5.46 (m, 4H), 5.50–6.24 (m, 2H), 7.30 (s, 4H). IR: 1640, 1080, 990, 910. MS: 222 (M^+, 1.3), 221 (8.2), 181 (51), 165 (100). Anal. Calcd. for $C_{13}H_{15}ClO$: C, 70.12; H, 6.79; Cl, 15.92. Found: C, 69.99; H, 7.04; Cl, 15.99.

1-(4-Nitrophenyl)but-3-enyl Allyl Ether (**4c**). Liquid. bp 120 °C/1 mmHg. NMR δ 2.43 (dd, 2H, $J_1 = J_2 = 6.0$ Hz), 3.80 (d, 2H, $J_3 = 5.0$ Hz), 4.36 (t, 1H, $J_1 = 6.0$ Hz), 4.80–6.30 (m, 6H), 7.42 (d, 2H, $J_4 = 9.0$ Hz), 8.15 (d, 2H, $J_4 = 9.0$ Hz). IR: 3010, 2850, 1640, 1520, 1340, 990, 915, 850. MS: 234 ($M^+ + 1$, 5.2), 233 (1.4), 192 (34), 176 (13). Anal. Calcd. for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.92; H, 6.73; N, 5.79.

1-(2-Furfuryl)but-3-enyl Allyl Ether (**4d**). Oil. NMR δ 2.50 (dd, 2H, $J_1 = 7.0$ Hz, $J_2 = 6.0$ Hz), 3.80 (d, 2H, $J_3 = 5.0$ Hz), 4.27 (t, 1H, $J_1 = 7.0$ Hz), 4.80–5.40 (m, 4H), 5.40–6.10 (m, 2H), 6.25 (m, 2H), 7.37 (s, 1H). IR: 2900, 1635, 995, 915. MS: 179 ($M^+ + 1$, 15.6), 178 (3.5), 137 (63), 121 (45). Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.80; H, 7.50.

4-(Dodec-1-enyl) Allyl Ether (**4e**). bp 82°C/1 mmHg. NMR δ 0.90 (t, 3H, $J = 4.5$ Hz), 1.30 (brs, 14H), 2.21 (dd, 2H, $J_1 = 6.5$ Hz, $J_2 = 6.0$ Hz), 3.30 (m, 1H), 3.93 (d, 2H, $J_3 = 5.0$ Hz), 4.76–5.40 (m, 4H), 5.50–6.14 (m, 2H). IR: 2830, 1628, 980, 900. MS: 255 ($M^+ + 1$, 28.6), 183 (100). Anal. Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 79.82; H, 12.87.

3-(1-Phenylhex-1,5-E-dienyl) Allyl Ether (**4f**). Oil. NMR δ 2.35 (dd, 2H, $J_1 = J_2 = 6.0$ Hz), 3.85 (d, 2H, $J = 6.0$ Hz), 3.91 (m, 1H), 4.80–5.40 (m, 4H), 5.50–6.20 (m, 2H), 5.98 (dd, 1H, $J_3 = 6.0$ Hz, $J_4 = 16.0$ Hz), 6.46 (d, 1H, $J_4 = 16.0$ Hz), 7.25 (s, 5H). MS: 214 (M^+, 2.4), 173 (13), 156 (33), 131 (37), 115 (33), 105 (100), 91 (80). IR: 1630, 990, 905. Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 83.68; H, 8.60.

2-(4-Nitrophenyl)-4-pentenyl Allyl Ether (**4g**). Oil. NMR δ 1.46 (s, 3H), 2.38 (d, 2H, $J = 7.0$ Hz), 3.60 (m, 2H), 4.50–6.20 (m, 6H), 7.43 (m, 2H, $J = 8$ Hz), 8.10 (d, 2H, $J = 8$ Hz). IR: 1630, 980, 900. MS: 247 (M^+, 55), 206 (100), 201 (15), 190 (77), 150 (12), 144 (44). Anal. Calcd. for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.60. Found: C, 67.71; H, 7.41; N, 5.33.

2-Phenyl-4-pentenyl Allyl Ether (**4h**). Oil, NMR δ 1.40 (s; 3H), 2.33 (d, 2H, $J = 6.2$ Hz), 3.50 (m, 2H), 4.40–6.10 (m, 6H), 7.40 (m, 5H). IR: 1660, 990, 900. MS: 202 (M^+, 0.3), 201 ($M^+ - 1$, 1.3), 161 (1.24), 145 (100), 121 (70), 105 (37), 77 (16). Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.80; H, 9.12.

1-Allylcyclopentyl Allyl Ether (**4i**). Oil. NMR δ 1.44 (m, 8H), 2.18 (d, 2H, $J_1 = 6.0$ Hz), 3.85 (d, 2H, $J_2 = 5.0$ Hz), 4.70–5.28 (m, 4H), 5.33–6.30 (m, 2H).

IR: 2880, 1630, 1000, 900. MS: 166 (M$^+$, 2.5), 125 (17), 109 (17), 55 (100). Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.09; H, 10.70.

1-Allylcyclohexyl Allyl Ether (**4j**). Oil. NMR δ 1.40 (m, 10H), 2.17 (d, 2H, J_1 = 6.2 Hz), 3.82 (d, 2H, J_2 = 5.0 Hz), 4.70–5.23 (m, 4H), 5.30–6.30 (m, 2H). IR: 2900, 1635, 990, 900. MS: 180 (M$^+$, 1.6), 179 (9.4), 139 (97), 123 (100). Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.57; H, 11.28.

1-Phenylbut-3-en-1-ol (**3a**). Oil (lit. [5] 228–229°C) NMR δ 2.32 (dd, 2H, $J_1 = J_2$ = 6.2 Hz), 2.94 (brs, 1H), 4.47 (t, 1H, J_1 = 6.2 Hz), 4.74–5.15 (m, 2H), 5.32–6.02 (m, 1H), 7.19 (s, 5H). IR (neat, cm^{-1}): 3350 (vs), 1640, 1040, 990, 920, 760, 700.

1-(4-Chlorophenyl)but-3-en-1-ol (**3b**). Oil. NMR δ 2.30 (dd, 2H, $J_1 = J_2$ = 7.0 Hz), 2.50 (s, 1H), 4.44 (t, 1H, J_2 = 7.0 Hz), 4.72–5.19 (m, 2H), 5.30–6.07 (m, 1H), 7.15 (s, 4H). IR (neat, cm^{-1}): 3320 (vs), 1640 (m), 1040 (s), 1010 (s), 915 (s). Anal. Calcd. for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07; Cl, 19.41. Found: C, 65.54; H, 5.93; Cl, 19.80.

1-(4-Nitrophenyl)but-3-en-1-ol (**3c**). Liquid (lit. [6] 128°C/0.001 mmHg) NMR δ 2.42 (dd, 2H, $J_1 = J_2$ = 6.0 Hz), 2.80 (brs, 1H, OH), 4.76 (t, 1H, J_1 = 6.0 Hz), 4.80–5.30 (m, 2H), 5.40–6.20 (m, 1H), 7.45 (d, 2H, J = 9.0 Hz), 8.03 (d, 2H, J = 9.0 Hz). IR (neat, cm^{-1}): 3360 (vs), 1640 (m), 1600 (s), 1510 (s), 1320 (s), 1010 (s), 915 (s), 850 (s).

1-(2-Furfuryl)but-3-en-1-ol (**3d**). Liquid. 98°C/20 mmHg (lit. [7] 87–93°/3 mmHg) NMR δ 2.50 (dd, 2H, $J_1 = J_2$ = 6.0 Hz), 2.55 (s, 1H), 4.56 (t, 1H, J = 6.0 Hz), 4.81–5.24 (m, 2H), 5.38–5.98 (m, 1H), 6.14 (m, 2H), 7.24 (s, 1H). IR (neat, cm^{-1}): 3320 (vs), 1662 (m), 1640 (m), 1045 (m), 1020 (s), 918 (s).

Dodec-1-en-4-ol (**3e**). Oil. NMR δ 0.88 (t, 3H, J = 4.5 Hz), 1.30 (brs, 14H), 1.96 (s, 1H), 2.17 (m, 2H), 3.50 (m, 1H), 4.81–5.22 (m, 2H), 5.40–6.03 (m, 1H). IR (neat, cm^{-1}): 3350 (s), 1640 (m), 1020 (m), 1000 (m), 920 (m). MS: 184 (M$^+$, 0.14), 167 (1), 143 (9), 69 (100). Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 77.87; H, 12.95.

1-Phenylhexa-1,5-E-dien-3-ol (**3f**). Liquid. 105°C/1 mmHg (lit. [8] 110–111°C/1 mmHg) NMR δ 2.21 (dd, 2H, $J_1 = J_2$ = 6.0 Hz), 2.80 (s, 1H, OH), 4.10 (dt, 1H, $J_2 = J_3$ = 6.0 Hz), 4.73–5.15 (m, 2H), 5.35–6.00 (m, 1H), 5.95 (dd, 1H, J_3 = 6.0 Hz, J_4 = 16.0 Hz), 6.40 (d, 1H, J_4 = 16.0 Hz), 7.10 (s, 5H). IR (neat, cm^{-1}): 3350 (s), 1640 (m).

2-(4-Nitrophenyl)pent-4-en-2-ol (**3g**). Oil. NMR δ 1.55 (s, 3H), 2.14 (s, OH), 2.56 (d, 2H, J = 6.0 Hz), 4.70–6.20 (m, 3H), 7.61 (d, 2H, J = 9.0 Hz), 8.18 (d, 2H, J = 9.0 Hz). IR (neat, cm^{-1}): 3450 (s), 1640 (m), 1340 (s), 1260 (s).

2-Phenylpent-4-en-2-ol (**3h**). Oil (lit. [9] bp 104–104.6°C/24 mmHg) NMR δ 1.45 (s, 3H), 2.60 (s, 1H, OH), 2.43 (d, 2H, J = 6.0 Hz), 4.70–5.30 (m, 2H), 5.35–6.10 (m, 1H), 7.40 (m, 5H). IR (neat, cm^{-1}): 3400 (s), 1635 (s).

1-Allylcyclopentanol (**3i**). Liquid. 60°C/10 mmHg (lit. [10] bp 63°C/10 mmHg) NMR δ 1.59 (brs, 8H), 2.27 (d, 2H, J = 6.2 Hz), 2.00 (s, 1H, OH), 4.76–5.40 (m, 2H), 5.46–6.36 (m, 1H). IR (neat, cm^{-1}): 3400 (s), 2800 (s), 1630 (m), 1060 (m), 1000 (vs).

1-Allylcyclohexanol (**3j**). Liquid. 72°C/10 mmHg (lit. [11] bp 188–192°C) NMR δ 1.46 (brs, 10H), 2.12 (d, 2H, 6.2 Hz), 2.30 (s, 1H, OH), 4.70–5.30 (m, 2H), 5.36–6.30 (m, 1H). IR (neat, cm^{-1}): 3400 (s), 2880 (s), 1630 (m), 1440 (m), 980 (m), 900 (s).

ACKNOWLEDGMENT

We thank the National Natural Science Foundation of China and Academia Sinica for financial support.

REFERENCES AND NOTES

[1] This paper is the 94th report on the studies of the synthetic application of elementoorganic compounds of the fifteenth and sixteenth groups.
[2] M. Wada, K-y. Akiba, *Tetrahedron Lett.*, *26*, 1985, 4211.
[3] M. Wada, H. Ohki, K-y. Akiba, *Tetrahedron Lett.*, *27*, 1986, 4771; M. Wada, H. Ohki, K-y. Akiba, *J. Chem. Soc., Chem. Commun.*, 1987, 708.
[4] Y. Z. Huang, C. Chen, Y. C. Shen, *Tetrahedron Lett.*, *29*, 1988, 1395.
[5] A. F. L. Holding, W. A. Ross, *J. Chem. Soc.*, 1954, 145.
[6] K. Konig, W. P. Neumann, *Tetrahedron Lett.*, *6*, 1967, 495.
[7] A. M. Shur, B. V. Matyushinskii, *Chem. Abstr. 49*, 1955, *11618h*.
[8] P. B. Venuto, A. R. Day, *J. Org. Chem.*, *29*, 1964, 2735.
[9] W. Jaworshy, *Ber. Deut. Chem. Gesells.*, *42*, 1909, 437.
[10] G. Crane, C. E. Boord, A. L. Henne, *J. Am. Chem. Soc.*, *67*, 1945, 1237.
[11] Saizew, *J. Russ. Phy. Chem. Gesellschaft*, *41*, 1909, 105 (Beilstein H6, 50).