SHORT PAPER

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Gem-diallylation of acyl azides with allylsamarium bromide under mild conditions†

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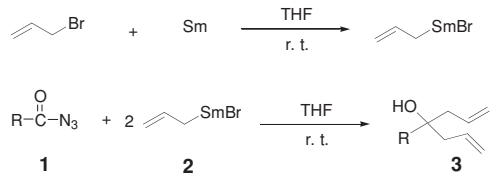
Allylsamarium bromide reacts with acyl azides to give the corresponding *gem*-diallylation products, 4-alkyl-1,6-heptadienes-4-ols (**3**), in good to excellent yields. This novel reaction proceeds readily within a few minutes at room temperature.

Keywords: allylsamarium bromide, acyl azides

The addition of allylic organometallics to carbonyl compounds is an important synthetic method for the construction of carbon–carbon bonds.[1] Various metals such as In, Sm, Mg, Zn, Sn, and so on have been used for this purpose.[2] However, some allylic organometallic reagents have to be prepared under relatively harsh conditions, which limits their application in organic synthesis to some extent.[3] Usually, homoallylic alcohols are obtained utilising this method, but little attention has been paid to the geminal diallylation of carbonyl compounds.

During our previous study, we have found that allylsamarium bromide is an excellent allylation reagent due to its advantageous properties exploited in organic synthesis. In most cases, the reactions mediated by allylsamarium bromide can proceed under mild conditions, and our group has subsequently developed a series of reactions with allylsamarium bromide. For example, we have found that oximes and nitriles can react with allylsamarium bromide to give the corresponding diallylation products respectively.[4] Very recently, our group also reported the reaction of allylsamarium bromide with lactones and acyclic amides.[5] As a part of our ongoing study, we report herein the diallylation of acyl azides mediated by allylsamarium bromide to afford the corresponding diallyl alkyl carbinols in good yields (Scheme 1). To the best of our knowledge, geminal diallylation of acyl azides with allylsamarium bromide has not yet been reported.



Scheme 1

To investigate the scope and generality of the reaction, a number of aromatic acyl azides and aliphatic acyl azides were used in this reaction, and the results are summarised in Table 1.

Noteworthy is the fact that when aliphatic acyl azides were used, this reaction could also be carried out smoothly as well, though a little longer time was needed.

This reaction is also regioselective. When cinnamoyl azide was used as substrate (Entry 9), only the 1,2-addition product was obtained selectively, and no 1,4-addition product was found (Scheme 2).

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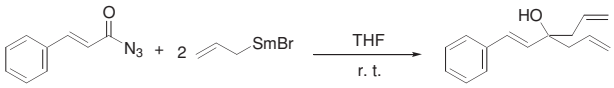
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 The *gem*-diallylation of acyl azides mediated by allylsamarium bromide

Entry	Substrate **1**	**Product**	Time/ min	Yield/%[a]
1	$C_6H_5CON_3$	**3a**	3	75
2	*p*-$CH_3C_6H_4CON_3$	**3b**	3	87
3	*p*-$CH_3OC_6H_4CON_3$	**3c**	3	95
4	*p*-$ClC_6H_4CON_3$	**3d**	3	91
5	*p*-$FC_6H_4CON_3$	**3e**	3	95
6	*m*-$CH_3C_6H_4CON_3$	**3f**	3	88
7	*m*-$ClC_6H_4CON_3$	**3g**	5	90
8	2-Furyl CON_3	**3h**	5	98
9	$C_6H_5CH{=}CHCON_3$	**3i**	5	96
10	$C_6H_5CH_2CON_3$	**3j**	10	82

[a]Isolated yields based on acyl azides.



Scheme 2

We also tried acyl chlorides or bromides as substrates in this reaction. But unfortunately, we only got a complex mixture. In conclusion, we have demonstrated that allylsamarium bromide can react readily with acyl azides to afford the corresponding *gem*-diallylation products, 4-alkyl-1, 6-heptadienes-4-ols (**3**), in good to excellent yields. It is well known that diallyl alkyl carbinols are important intermediates of great synthetic potential, since they can be easily converted to many important building blocks for natural and bioactive products syntheses.[6] Besides, they are good starting materials for the synthesis of hydroxyl lactone.[7] In view of the good regioselectivity, experimental simplicity, excellent yields, mild reaction conditions as well as short reaction time, the present method could have high potential in practical application.

Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker AC-400 instrument as $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) were reported in ppm and coupling constants *J* are given in Hz. IR spectra were taken as thin films with a Bruker Vector-22 infrared spectrometer. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources and were used without further purification.

General procedure for the synthesis of 4-alkyl-1,6-heptadienes-4-ols (**3**): Samarium (0.33 g, 2.2 mmol) and allyl bromide (0.30 g, 2.5

mmol) in THF (20 ml) were added to a three-necked flask with stirring at room temperature under a nitrogen atmosphere. When the mixture became purple, stirring was continued for another 1h. until the samarium powder disappeared. Then acyl azide (1 mmol) was added to the solution, and the mixture was stirred at room temperature for an appropriate time. Finally, the reaction mixture was quenched with 5 ml 1 M HCl, and extracted with diethyl ether (3 × 15 ml). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane-ethyl acetate (4:1) as eluent).

Compound (**3a**): –lit[8] ν_{max}/(cm^{-1}): 3447, 3075, 2978, 1638, 1445, 916, 702. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.21 (s, 1H, OH), 2.50–2.70 (m, 4H), 5.10–5.21 (m, 4H), 5.60–5.71 (m, 2H), 7.21–7.42 (m, 5H, ArH). ($C_{13}H_{16}O$ requires C, 82.94; H, 8.57%. Found: C, 82.7; H, 8.6%). *m*/*z* 171 (M^+-17, 10%), 147 (11%), 105 (100%), 77 (35%), 41 (29%).

Compound (**3b**): ν_{max}/(cm^{-1}): 3448, 3075, 2978, 1639, 1438, 999, 817. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.22 (s, 1H, OH), 2.39 (brs, 3H, CH_3), 2.51–2.74 (m, 4H), 5.10–5.17 (m, 2H), 5.60–5.70 (m, 2H), 7.17–7.35 (m, 4H, ArH). ($C_{14}H_{18}O$ requires C, 83.12; H, 8.97% Found: C, 83.2; H, 8.7%). *m*/*z* 185 (M^+-17, 4%), 161 (17%), 119 (100%), 91 (36%), 41 (33%).

Compound (**3c**): ν_{max}/(cm^{-1}): 3448, 3075, 2978, 1639, 1513, 1036, 916, 717. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.27 (s, 1H, OH), 2.51–2.71 (m, 4H), 3.81–3.99 (brs, 3H, OCH_3), 5.10–5.18 (m, 4H), 5.64–5.70 (m, 2H), 6.90–7.35 (m, 4H, ArH). ($C_{14}H_{18}O_2$ requires C, 77.03; H, 8.31%. Found: C, 76.9; H, 8.5%). *m*/*z* 201 (M^+-17, 1%), 177 (18%) 135 (100%), 77 (15%).

Compound (**3d**): ν_{max}/(cm^{-1}): 3462, 3076, 2979, 1640, 1490, 1093, 1093, 919, 830. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.26 (s, 1H, OH), 2.50–2.70 (m, 4H), 5.10–5.14 (m, 4H), 5.58–5.63 (m, 2H), 7.31–7.37 (m, 4H, ArH). ($C_{13}H_{15}ClO$ requires C, 70.11; H, 6.79%. Found: C, 70.1; H, 6.8%). *m*/*z* 205 (M^+-17, 8%), 181 (12%), 139 (100%), 41 (43%).

Compound (**3e**): ν_{max}/(cm^{-1}): 3456, 3076, 2980, 1640, 1510, 919, 817. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.25 (s, 1H, OH), 2.50–2.71(m, 4H), 5.10–5.15 (m, 4H), 5.57–5.68 (m, 2H), 7.01–7.40 (m, 4H, ArH). ($C_{13}H_{15}FO$ requires C, 75.70; H, 7.33% Found: C, 75.9; H, 7.3%). *m*/*z* 189 (M^+-17, 78%), 123 (100%), 95 (12%).

Compound (**3f**): ν_{max}/(cm^{-1}): 3461, 3077, 2979, 1640, 999, 917. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.25 (s, 1H, OH), 2.35 (brs, 3H, CH_3), 2.50–2.72 (m, 4H), 5.13–5.17 (m, 4H), 5.55–5.65 (m, 2H), 7.22–7.40 (m, 4H, ArH). ($C_{14}H_{18}O$ requires C, 83.12; H, 8.97% Found: C, 83.3; H, 9.1%). *m*/*z* 185 (M^+-17, 2%), 161 (14%), 119 (100%), 91 (33%), 41 (35%).

Compound (**3g**): -lit[8] ν_{max}/(cm^{-1}): 3463, 3076, 2979, 1639, 998, 919, 787. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.27 (s, 1H, OH), 2.50–2.71 (m, 4H), 5.11–5.16 (m, 4H), 5.56–5.65 (m, 2H), 7.22–7.45 (m, 4H, ArH). ($C_{13}H_{15}ClO$ requires C, 70.11; H, 6.79% Found: C, 70.2; H, 6.5%). *m*/*z* 205 (M^+-17, 3%), 181 (15%), 139 (100%), 41 (45%).

Compound (**3h**): ν_{max}/(cm^{-1}): 3445, 3077, 2980, 1640, 1158, 916, 735. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.33 (s, 1H, OH), 2.51–2.73 (m, 4H), 5.11–5.64 (m, 2H), 6.23 (s, 1H), 6.33 (s, 1H), 7.38 (s, 1H). ($C_{11}H_{14}O_2$ requires C, 74.13; H, 7.92% Found: C, 74.0; H, 7.8%). *m*/*z* 161 (M^+-17, 1%), 137 (30%), 95 (100%), 67 (5%), 41 (54%).

Compound (**3i**): –lit[8] ν_{max}/(cm^{-1}): 3442, 3076, 2979, 1639, 998, 919, 787. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm): 2.00 (s, 1H, OH), 2.40–2.50 (m, 4H), 5.17–5.26 (m, 4H), 5.84–5.92 (m, 4H), 6.27–6.30 (d, *J*=16 Hz 1H), 6.62–6.66 (d, *J*=16.4 Hz, 1H), 7.26–7.42 (m, 5H, ArH). ($C_{15}H_{18}O$ requires C, 84.07; H, 8.47%. Found: C, 84.0; H, 8.2%). *m*/*z* 197 (M^+-17, 4%), 131 (100%), 103 (42%), 77 (24%), 41 (44%).

Compound (**3j**): –lit[8] ν_{max}/(cm^{-1}): 3441, 3079, 2078, 1639, 910, 733. ^{1}H NMR (400 MHz , $CDCl_3$) δ_H (ppm):1.63 (s, 1H, OH), 2.20-2.30 (m, 4H), 2.80 (brs, 2H, CH_2), 5.13–.21 (m, 4H), 5.88–6.01 (m, 2H), 7.26–7.44 (m, 4H, ArH). ($C_{14}H_{18}O$ requires C, 83.12; H, 8.97%. Found: C, 82.9; H, 8.8%). *m*/*z* 185 (M^+-17, 3%), 119 (20%), 91 (86%), 77 (21%), 41 (100%).

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References

1 (a) R.W. Hoffman, *Angew. Chem., Int. Ed. Engl*., 1982, **21**, 555; (b) Y. Yamamoto and K. Maruyama, *Heterocycles*, 1982, **18**, 357; (c) Y. Yamamoto, *Acc. Chem. Res*., 1987, **20**, 243; (d) Y. Yamamoto and N. Asao, *Chem. Rev*., 1993, **93**, 2207 and references cited therein.

2 For example: (a) A. Durant, J.L. Delplancke, V. Libert and J. Reisse, *Eur. J. Org. Chem*., 1999, 2845; (b) F. Machrouhi, E. Parlea and J.L. Namy, *Eur. J. Org. Chem*., 1998, 2431; (c) Y.N. Bubnov, M.A. Misharin and A.V. Ingnatenko, *Tetrahedron Lett*., 1997, **38**, 6259; (d) R.L. Snowden, B.L. Muller and K.H. Schulte-Elte, *Tetrahedron Lett*., 1982, **23**, 335.

3 (a) J. Barluenga, J. Florez and M. Yus, *Synthesis,* 1983, **5**, 378; (b) M. Gaudemar, *Bull. Soc. Chim. Fr*., 1962, **5**, 974; (c) B.M. Mikhailov, Y.N. Bubnov, A.V. Tsyban and M.S. Grigoryan, *J. Organometal. Chem*., 1978, **154**, 131.

4 (a) X.S. Fan and Y.M. Zhang, *Tetrahedron Lett*., 2002, **43**, 5475; (b) M.X. Yu, Y.M. Zhang and H.Y. Gou, *Synth. Commun*., 1997, **27**, 1495.

5 (a) Z.F. Li and Y.M. Zhang, *Tetrahedron Lett*., 2001, **42**, 8507; (b) Z.F. Li and Y.M. Zhang, *Tetrahedron,* 2002, **58**, 5301.

6 (a) G. Sabitha, C.S. Reddy, R.S. Babu and J.S. Yadav, *Synlett*., 2001, 1787; (b) D.Y. Kong, H.T. Li, S.Q. Lu and X.H. Lei, *Acta Pharmaceutica Simca,* 1990, **25**, 349.

7 E. Bardshiri, T.J. Simpson, A.I. Scott and K. Shishido, *J. Chem. Soc. Perkin Trans. 1*, 1984, **8**, 1765.

8 X. Gao, J. Zheng, J.Y. Zhou and S.H. Wu, *Acta Chimica Sinica,* 1993, **51**, 1191.