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Conjugate Addition of Organosamarium Reagents to Nitroalkenes†

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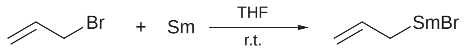
Allylsamarium bromide reacts with nitroalkenes to give conjugate addition compounds in moderate to good yields.

While SmI_2 exhibits excellent behaviour in organic synthesis[1] comparatively little has been reported on the application of samarium metal in organic synthesis. As early as 1971 Evans and coworkers had prepared phenylsamarium iodide from iodobenzene and samarium metal[2] but they found that samarium is not so active as ytterbium. In 1986 Fukuzawa *et al.* prepared organosamarium intermediates similar to Grignard reagents,[3] while Curran *et al.* established the samarium Grignard reaction in 1992.[4] In exploring the application of samarium in organic synthesis, we found that allylsamarium bromide is easy to prepare and the results of its reactions with some substrates were good. Our group have explored the reaction of allylsamarium bromide with some substrates, such as *N*-(2-aminoalkyl)benzotriazoles,[5] imines,[6] nitriles,[7] diorgano diselenides,[9] disulfides,[9] isocyanates and isothiocyanates,[10] *etc.* to give homoallylamines, allylselenides, allylsulfides, butenamides and thiobutenamides, *etc.*

Here, we report that allylsamarium bromide reacts with mononitroalkenes to give 4,5-unsaturated nitro compounds:



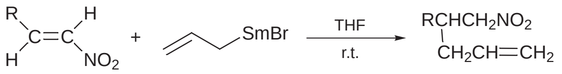


Table 1 Products and yields of reaction of allylsamarium bromide with mononitroalkenes

Entry	R	*T*/°C	*t*/h	Yield (%)
1	Ph	15	1.5	89
2	*m*-BrC_6H_4	15	1.5	90
3	*p*-$MeOC_6H_4$	15	2	81
4	*p*-ClC_6H_4	15	2	88
5	2,4-$Cl_2C_6H_3$	15	2	85
6	*p*-$NO_2C_6H_4$	15	2	48
7	α-C_4H_3O(Furyl)	15	2	83
8	Me_2CHCH_2	15	3	55

The nitro group is particularly versatile in synthesis since it may be transformed into a legion of diverse functionalities.[11] Initial reports[12] of attempted 1,4-addition reactions between monosubstituted nitroalkenes and Grignard reagents were not encouraging, the reaction being characterized by polymerization of the nitroalkene and competing 1,2-addition reactions leading to very poor yields. There were some positive reports, however, on 1,4-addition reaction initiated by organometallics such as Grignard reagents,[13] alkyllithium derivatives[14] and triorganoalanes[15] to mononitroalkenes. We attempted the reaction of allylsamarium bromide with mononitroalkenes and found it occurred fully *via* 1,4-addition to afford 4,5-unsaturated nitroalkenes in moderate to good yields.

Experimental

^1H NMR spectra were recorded in $CDCl_3$ on a JEOL PMX 60si spectrometer using TMS as internal standard. Neat IR spectra were obtained on a PE 683 spectrometer. MS were obtained on a 5989x-I instrument. Microanalyses were performed on a Carlo Erba 1108 instrument. Allylsamarium bromide was prepared from samarium and allyl bromide in dried THF. All the solvents used were predried according to standard procedures. The reaction was performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General Procedure.—Samarium powder (0.33 g, 2.2 mmol) was placed in a three-necked round bottom flask with a magnetic stirring bar. The flask was flushed with nitrogen several times. Tetrahydrofuran (20 mL, anhydrous) and then allyl bromide (0.36 g, 3 mmol) were added. After the mixture was stirred for 3 h at room temperature and the solution became deep-purple, the substrate (2 mmol) was added. The resulting solution was stirred for 2 h and then the reaction was quenched with a few drops of water. After addition of a few drops of dilute hydrochloric acid the mixture was extracted with diethyl ether (2 × 30 mL), washed with saturated aqueous NaCl solution (15 mL) and dried over $MgSO_4$. After filtration and removal of the solvents, the crude product was purified by column chromatography (silica gel) using cyclohexane– ethyl acetate as eluent.

1: $C_{11}H_{13}NO_2$; *m/z* 191 (M^+); δ_H 2.38 (t, 2 H, $J = 6.8$ Hz), 3.42 (qnt, 1 H, $J = 7.0$ Hz), 4.41 (d, 2 H, $J = 8$ Hz), 4.78–5.07 (m, 2 H), 5.27–5.93 (m, 1 H), 7.14 (s, 5 H); IR (ν/cm^{-1}), 3100, 3060, 2940, 1618, 1565, 1389, 920, 765, 700 (Found: C, 69.01; H, 6.88; N, 7.23. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85; N, 7.32%).

2: $C_{11}H_{12}BrNO_2$; *m/z* 270 (M^+); δ_H 2.35 (t, 2 H, $J = 6.6$ Hz), 3.43 (qnt, 1 H, $J = 7.0$ Hz), 4.46 (d, 2 H, $J = 7.6$ Hz), 4.79–5.08 (m, 2 H), 5.28–5.96 (m, 1 H), 7.00–7.65 (m, 4 H); IR (ν/cm^{-1}), 3120, 3090, 2940, 1655, 1565, 1388, 1350, 1260, 965, 924, 785 (Found: C, 48.82; H, 4.43; N, 5.25. $C_{11}H_{12}BrNO_2$ requires C, 48.91; H, 4.48; N, 5.18%).

3: $C_{11}H_{15}NO_3$; *m/z* 221 (M^+); δ_H 2.30 (t, 2 H, $J = 6.3$ Hz), 3.35 (qnt, 1 H, $J = 7.0$ Hz), 3.61 (s, 1 H), 4.34 (d, 2 H, $J = 7.6$ Hz), 4.73–5.02 (m, 2 H), 5.23–5.92 (m, 1 H), 6.82 (q, 4 H, $J = 8.6$ Hz); IR (ν/cm^{-1}), 3100, 3020, 2945, 2860, 1655, 1560, 1390, 1308, 922, 830 (Found: C, 64.99; H, 6.89; N, 6.50. $C_{11}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%).

4: $C_{11}H_{12}ClNO_2$; *m/z* 226 (M^+); δ_H 2.30 (t, 2 H, $J = 6.4$ Hz), 3.41 (qnt, 1 H, $J = 7.2$ Hz), 4.40 (d, 2 H, $J = 8.0$ Hz), 4.76–5.03 (m, 2 H), 5.23–5.88 (m, 1 H), 7.13 (q, 4 H, $J = 7$ Hz); IR (ν/cm^{-1}), 3100, 3056, 2940, 1650, 1560, 1386, 1350, 1095, 1018, 920, 785 (Found: C, 58.62; H, 5.40; N, 6.33. $C_{11}H_{12}ClNO_2$ requires C, 58.54; H, 5.36; N, 6.21%).

5: $C_{11}H_{13}Cl_2NO_2$; *m/z* 260 (M^+); δ_H 2.42 (t, 2 H, $J = 6.8$ Hz), 4.00 (qut, 1 H, $J = 7.0$ Hz), 4.53 (d, 2 H, $J = 7.0$ Hz), 4.83–5.12 (m, 2 H), 5.32–5.98 (m, 1 H), 7.13–7.45 (m, 3 H); IR (ν/cm^{-1}), 3130, 2940, 1645, 1565, 1390, 1108, 924, 865, 785 (Found: C, 50.62; H, 4.34; N, 5.32. $C_{11}H_{11}Cl_2NO_2$ requires C, 50.79; H, 4.26; N, 5.38%).

6: $C_{11}H_{12}N_2O_4$; *m/z* 236 (M^+); δ_H 2.40 (t, 2 H, $J = 6.4$ Hz), 3.58 (qnt, 1 H, $J = 7.2$ Hz), 4.48 (d, 2 H, $J = 6.2$ Hz), 4.80–5.08 (m, 2 H), 5.25–5.92 (m, 1 H), 7.27 (d, 2 H, $J = 8.8$ Hz), 8.13 (d, 2 H, $J = 8.8$ Hz); IR (ν/cm^{-1}), 3130, 3050, 2940, 2870, 1655, 1565, 1385, 1115, 925 (Found: C, 55.72; H, 5.06; N, 11.73. $C_{11}H_{12}N_2O_4$ requires C, 55.93; H, 5.12; N, 11.86%).

7: $C_9H_{11}NO_3$; *m/z* 181 (M^+); δ_H 2.40 (t, 2 H, $J = 6.4$ Hz), 3.55 (qnt, 1 H, $J = 7.0$ Hz), 4.42 (d, 2 H, $J = 7.4$ Hz), 4.78–5.07 (m, 2 H), 5.28–5.84 (m, 1 H), 5.90 (d, 1 H, $J = 3.5$ Hz), 6.13 (dd, 1 H, $J = 3.5$, 1.5 Hz), 7.20 (d, 1 H, $J = 1.5$ Hz); IR (ν/cm^{-1}), 3100, 3000, 2942, 1658, 1560, 1388, 1154, 1015, 920, 745 (Found: C, 59.62; H, 6.20; N, 7.71. $C_9H_{11}NO_3$ requires C, 59.66; H, 6.12; N, 7.79%).

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

8: $C_9H_{17}NO_2$; m/z 171 (M^+); δ_H 0.87 (d, 6 H, $J = 6.0$ Hz), 1.17–1.80 (m, 3 H), 1.90–2.53 (m, 3 H), 4.18 (d, 2 H, $J = 6.0$ Hz), 4.85–5.15 (m, 2 H), 5.40–6.05 (m, 1 H); IR (ν/cm^{-1}), 3100, 2980, 2960, 2890, 1655, 1560, 1390, 996, 920. (Found: C, 63.30; H, 10.12; N, 8.09. $C_9H_{17}NO_2$ requires C, 63.13; H, 10.01; N, 8.18%).

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