# The Synthesis of Butenamides and Thiobutenamide by an Organosamarium Reagent<sup>+</sup>

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An organosamarium reagent reacts with isocyanates (or isothiocyanate) to afford butenamides (or thiobutenamide) in THF.

Not only have intensive studies been carried out on the use of samarium diiodide in organic synthesis,<sup>1,2</sup> but the application of samarium metal has also stimulated great interest.3-5 Curran has reported the samarium Grignard reaction.<sup>6</sup> Our group has studied the reaction of an organosamarium reagent with an imine,7 the synthesis of allyl selenides (or sulfides) using an organosamarium reagent<sup>8,9</sup> and homoallylamines from an organosamarium reagent and nitriles.<sup>10</sup> We have also reported that isocyanates react with isopropyl- or sec-butyl-magnesium bromide catalysed by Cp<sub>2</sub>TiCl<sub>2</sub> to afford amide,<sup>11</sup> and phenylisocyanate reacts with Grignard reagents catalysed by Cp<sub>2</sub>TiCl<sub>2</sub> at room temperature to afford reduction-coupling products.<sup>12</sup> Herein we wish to report that an organosamarium reagent reacts with isocyanates (or isothiocyanate) to afford butenamides (or thiobutenamide) in THF. The products were identified by IR, <sup>1</sup>H NMR and MS spectra. The advantages of this method are its rapid reaction, simple operation and mild and neutral conditions. The results are summarized in Scheme 1.

### Experimental

General Experimental Procedure.—Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use. IR spectra were recorded on a Perkin-Elmer-983 G-7500; <sup>1</sup>H NMR spectra were obtained with a JEOL FX-90Q in CDCl<sub>3</sub> solution using TMS as internal standard ( $\delta$ /ppm). MS spectra were recorded with a Hewlett-Packard 5989 A mass spectrometer.

Samarium (0.33 g, 2.2 mmol), THF (20 ml) and allyl bromide (0.30 g, 2.5 mmol) were added to a three-necked flask with stirring at room temperature under nitrogen. When the mixture became purple, stirring was continued for 1 h until the samarium powder disappeared. Isocyanate (or isothiocyanate) (1 mmol) was then added to the solution, and the mixture was stirred at room temperature for an appropriate time. 10 ml water was added. The reaction mixture was extracted with diethyl ether ( $3 \times 40$  ml), the diethyl ether solution was washed with water ( $3 \times 40$  ml) and dried over MgSO<sub>4</sub>. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (CH<sub>2</sub>Cl<sub>2</sub> and MeOH as eluent).

CH<sub>3</sub>C<sub>6</sub>H<sub>3</sub>(NHCOCH<sub>2</sub>CHCH<sub>2</sub>)<sub>2</sub>: mp 134–136 °C;  $\delta_{\rm H}$  8.10–7.30 (m, 5 H), 6.31–5.89 (m, 2 H), 5.63–5.21 (d, 4 H), 3.62–3.35 (d, 4 H), 2.41–2.33 (s, 3 H);  $\nu_{\rm max}/{\rm cm}^{-1}$  3430, 3040, 1690, 1650, 1610, 1206, 986, 598; MS (EI) *m*/*z* 122 (100.00), 190 (71.05), 121 (48.21), 69 (33.23), 149 (28.77), 258 (27.73), 217 (24.66), 175 (22.73).

C<sub>6</sub>H<sub>5</sub>NHCOCH<sub>2</sub>CHCH<sub>2</sub>: mp 91–92 °C;  $\delta_{\rm H}$  7.96–7.21 (m, 6 H), 6.28–5.80 (m, 1 H), 5.60–5.18 (d, 2 H), 3.60–3.29 (d, 2 H);  $\nu_{\rm max}/$  cm<sup>-1</sup> 3425, 3020, 1684, 1648, 1607, 1202, 983, 600; MS (EI) *m/z* 93 (100), 161 (47.30), 69 (41.67), 77 (26.54), 162 (17.93), 120 (13.48), 70 (9.67), 42 (6.13).

p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHCOCH<sub>2</sub>CHCH<sub>2</sub>: mp 96–97 °C;  $\delta_{\rm H}$  7.92–7.18 (m, 5 H), 6.23–5.78 (m, 1 H), 5.58–5.15 (d, 2 H), 3.59–3.26 (d, 2 H), 2.39–2.29 (s, 3 H);  $\nu_{\rm max}/{\rm cm}^{-1}$  3418, 3015, 1679, 1643, 1601, 1200, 980, 595; MS ?(EI) m/z 107 (100.00), 175 (43.26), 69 (36.35), 91 (32.21), 176 (21.02), 134 (17.34), 92 (11.62), 70 (8.95).



#### Scheme 1

 $p\text{-NO}_2\text{C}_6\text{H}_4\text{NHCOCH}_2\text{CHCH}_2$ : mp 108–110 °C;  $\delta_{\rm H}$  8.05–7.24 (m, 5 H), 6.30–5.84 (m, 1 H), 5.62–5.21 (d, 2 H), 3.62–3.33 (d, 2 H);  $\nu_{\rm max}/\text{cm}^{-1}$  3433, 3045, 1696, 1611, 1208, 993, 607; MS (EI) m/z 138 (100.00), 122 (47.35), 206 (41.23), 69 (35.70), 93 (21.63), 207 (18.94), 123 (14.82), 139 (10.20).

C<sub>10</sub>H<sub>7</sub>NHCOCH<sub>2</sub>CHCH<sub>2</sub>: mp 119–120 °C;  $\delta_{\rm H}$  8.26–7.40 (m, 8 H), 6.35–5.83 (m, 1 H), 5.53–5.14 (d, 2 H), 3.52–3.26 (d, 2 H);  $\nu_{\rm max}/{\rm cm}^{-1}$  3420, 3072, 1698, 1652, 1606, 1198, 996, 610; MS (EI) *m*/*z* 143 (100.00), 211 (42.66), 115 (39.05), 144 (17.97), 116 (10.39), 212 (8.97), 114 (7.48), 127 (6.64).

 $\begin{array}{l} \text{C}_{6}\text{H}_{5}\text{NHCSCH}_{2}\text{CHCH}_{2}\text{CHCH}_{2}\text{coil}; \ \delta_{\mathrm{H}}\ 7.91\text{--}7.18 \ (\mathrm{m, 6}\ \mathrm{H}),\ 6.23\text{--}5.74 \\ (\mathrm{m, 1}\ \mathrm{H}),\ 5.60\text{--}5.22 \ (\mathrm{d, 2}\ \mathrm{H}),\ 3.52\text{--}3.27 \ (\mathrm{d, 2}\ \mathrm{H});\ \nu_{\mathrm{max}}/\mathrm{cm}^{-1}\ 3415, \\ 3028,\ 1648,\ 1600,\ 1495,\ 1200,\ 992,\ 603;\ \mathrm{MS}\ (\mathrm{EI})\ m/z\ 177\ (100.00), \\ 176\ (72.14),\ 144\ (61.97),\ 85\ (40.48),\ 178\ (39.64),\ 77\ (26.54),\ 93\ (19.80),\ 136\ (15.34). \end{array}$ 

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# J. CHEM. RESEARCH (S), 1998 257

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