J. Chem. Research (S), 1998, 256–257†

The Synthesis of Butenamides and Thiobutenamide by an Organosamarium Reagent†

Mingxin Yu,[a] Yongmin Zhang*[a] and Cangtao Qian[b]

[a]*Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China*
[b]*Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai, 200032, P.R. China*

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,[1,2] but the application of samarium metal has also stimulated great interest.[3–5] Curran has reported the samarium Grignard reaction.[6] 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[8,9] and homoallylamines from an organosamarium reagent and nitriles.[10] We have also reported that isocyanates react with isopropyl- or *sec*-butyl-magnesium bromide catalysed by Cp_2TiCl_2 to afford amide,[11] and phenylisocyanate reacts with Grignard reagents catalysed by Cp_2TiCl_2 at room temperature to afford reduction-coupling products.[12] 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, ^{1}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

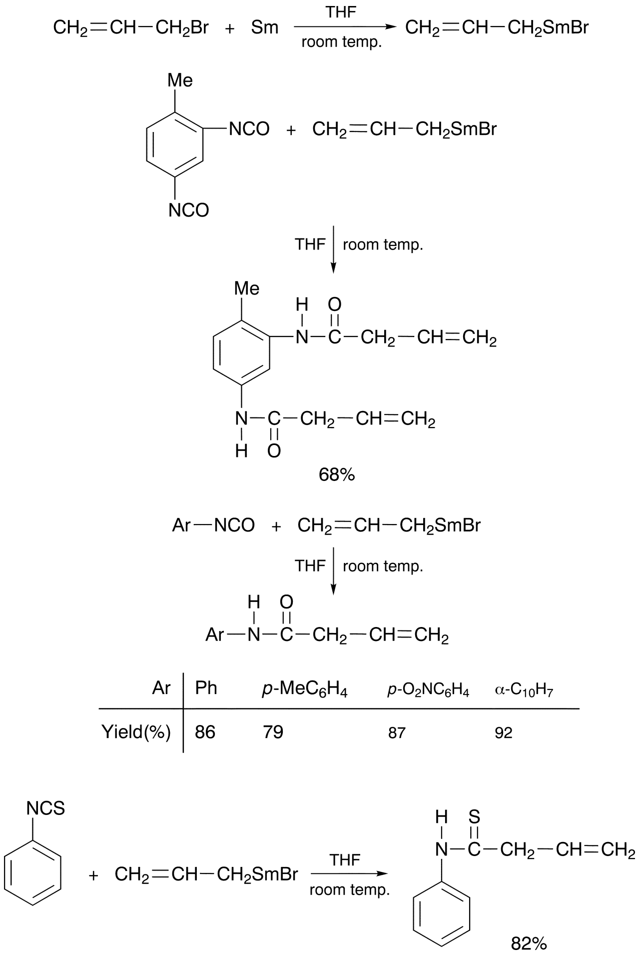
General Experimental Procedure.—Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use. IR spectra were recorded on a Perkin-Elmer-983 G-7500; ^{1}H NMR spectra were obtained with a JEOL FX-90Q in $CDCl_3$ solution using TMS as internal standard (δ/ppm). MS spectra were recorded 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 × 40 ml), the diethyl ether solution was washed with water (3 × 40 ml) and dried over $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (CH_2Cl_2 and MeOH as eluent).

$CH_3C_6H_3(NHCOCH_2CHCH_2)_2$: mp 134–136 °C; δ_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); ν_{max}/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).

$C_6H_5NHCOCH_2CHCH_2$: mp 91–92 °C; δ_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); ν_{max}/cm^{-1} 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-$CH_3C_6H_4NHCOCH_2CHCH_2$: mp 96–97 °C; δ_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); ν_{max}/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).



Ar	Ph	*p*-MeC_6H_4	*p*-$O_2NC_6H_4$	α-$C_{10}H_7$
Yield(%)	86	79	87	92

Scheme 1

p-$NO_2C_6H_4NHCOCH_2CHCH_2$: mp 108–110 °C; δ_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); ν_{max}/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).

$C_{10}H_7NHCOCH_2CHCH_2$: mp 119–120 °C; δ_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); ν_{max}/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).

$C_6H_5NHCSCH_2CHCH_2$: oil; δ_H 7.91–7.18 (m, 6 H), 6.23–5.74 (m, 1 H), 5.60–5.22 (d, 2 H), 3.52–3.27 (d, 2 H); ν_{max}/cm^{-1} 3415, 3028, 1648, 1600, 1495, 1200, 992, 603; MS (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).

We thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science for financial support.

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Received, 26th November 1997; Accepted, 30th December 1997
Paper E/7/08538J

References

1 G. A. Molender, *Chem. Rev.*, 1992, **92**, 29.
2 G. A. Molender and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
3 M. Lautens and Y. Ren, *J. Org. Chem.*, 1996, **61**, 2210.
4 M. Hojo, H. Ihara and A. Hosomi, *J. Am. Chem. Soc.*, 1996, **118**, 3533.
5 T. H. Chuang, J. M. Fang, W. T. Jiang and Y. H. Tsai, *J. Org. Chem.*, 1996, **61**, 1794.
6 D. P. Curran and M. J. Totleben, *J. Am. Chem. Soc.*, 1992, **114**, 6050.
7 J. Q. Wang and Y. M. Zhang, *Synth. Commun.*, 1996, **26**, 2473.
8 M. X. Yu, Y. M. Zhang and W. L. Bao, *Synth. Commun.*, 1997, **27**, 609.
9 M. X. Yu and Y. M. Zhang, *Synth. Commun.*, 1997, **27**, 2743.
10 M. X. Yu, Y. M. Zhang and H. Y. Gou, *Synth. Commun.*, 1997, **27**, 1495.
11 Y. M. Zhang, J. L. Jiang and Y. Q. Chen, *Tetrahedron Lett.*, 1987, **28**, 3815.
12 Y. M. Zhang, J. L. Jiang and Zh. X. Zhang, *Tetrahedron Lett.*, 1988, **29**, 651.