

SmI₂ Promoted Coupling Reaction of Isocyanates to Oxamides

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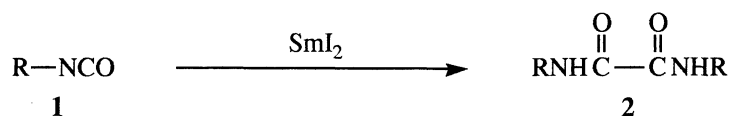
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Oxamides were obtained in moderate to good yields by the reaction of isocyanates with the SmI₂/HMPA/THF system under mild conditions. The system also caused desulfurization of isothiocyanates to give isocyanides in good yields.

Lanthanoid reagents such as SmI₂, Yb and trichlorolanthanoids are getting to be more and more useful for organic synthesis utilizing their unique characteristics such as strong reducing power and oxophilicity.¹⁾

In continuing studies on exploring lanthanoid reagents, we found that SmI₂ reacts with heterocumulenes such as isocyanates and isothiocyanates to give oxamides and isocyanides, respectively. We report here novel methods for dimerization of isocyanates into oxamides, and desulfurization of isothiocyanates to the corresponding isocyanides using the SmI₂/HMPA/THF system under an N₂ atmosphere at room temperature.

Thus, the SmI₂/HMPA/THF system causes the coupling reaction of isocyanates (**1**) to give oxamides (**2**) in moderate to good yields.



Oxamides (**2**) were obtained in moderate to good yields by the treatment of isocyanates (**1**) with an equimolar amount of SmI₂ in HMPA/THF. The results are summarized in Table 1. As can be seen from the table, the aryl isocyanates react with SmI₂ more rapidly than alkyl isocyanates (runs 1-5) and give higher yields. In the case of 1-naphthyl isocyanate (run 5), the reaction was carried out at -78 °C for 2 h and then the mixture was slowly heated up to -20 °C and stirred for additional 2 h, to give N,N'-di(1-naphthyl)oxamide (**2e**) in 72% yield. Higher temperature gave 1-naphthylamine as a main product together with **2e**.

A typical procedure is as follows: Phenyl isocyanate (**1a**) (1 mmol, 119

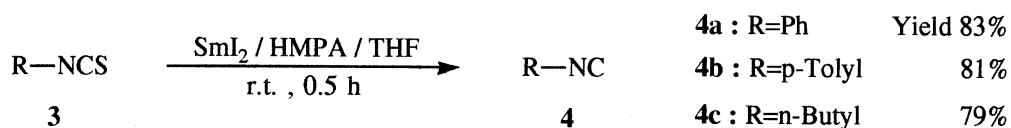
Table 1. Synthesis of oxamides (**2**) from isocyanates (**1**)

Run	R-NCO	Reaction		Yield of 2 /%	
		temp/°C	time/h		^{a)}
1	1a Phenyl	r.t.	2.0	2a	62
2	1b p-Tolyl	r.t.	2.5	2b	82
3	1c 2,6-Dimethyl-phenyl	r.t.	4.0	2c	71
4	1d p-Chlorophenyl	r.t.	7.0	2d	61
5	1e 1-Naphthyl	-78 — -20	4.0	2e	72
6	1f Cyclohexyl	r.t.	12.0	2f ^{b)}	44 ^{c)}
7	1f Cyclohexyl	65	8.0	2f ^{b)}	52 ^{c)}
8	1g n-Propyl	65	12.0	2g ^{b)}	31 ^{c)}

a) Isolated yield based on RNCO. b) A small amount of the corresponding ureas (RNHCONHR) was also obtained. c) GC yield.

mg), SmI₂ (1.2 mmol, THF 0.1 M solution 12 ml) and HMPA (0.5 ml) were stirred for 2 h at room temperature under N₂. The color changed from blue to yellow. After the reaction mixture was concentrated in vacuo until ca. half of the solvent was removed, the reaction was quenched with HCl (2 M HCl 1 ml) and water (80 ml). The precipitated white solid was collected, dried and recrystallized from THF/hexane (1:2) to give colorless crystals (**2a**) (0.3 mmol, 62%).

Furthermore, the SmI₂/HMPA/THF system has been found to cause the desulfurization of isothiocyanates (**3**) to give isocyanides (**4**) in good yields.



These reactions seem to proceed via electron transfer from Sm(II) to the heterocumulenes.

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References

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