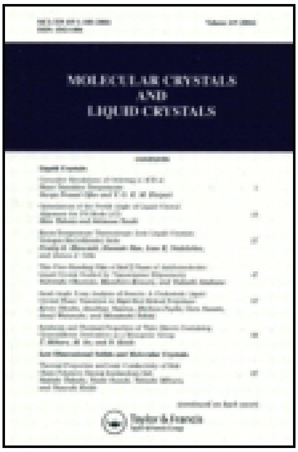

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Organic Reaction Without Solvent. Efficient Synthesis of Thiocarbonylimidazolide

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ORGANIC REACTION WITHOUT SOLVENT. EFFICIENT SYNTHESIS OF THIOCARBONYLIMIDAZOLIDE

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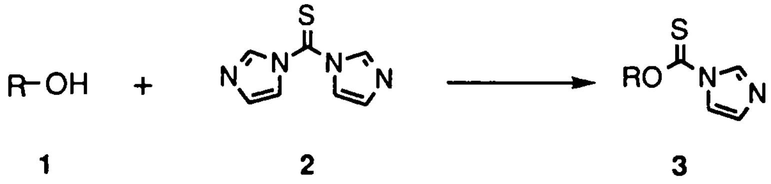
Abstract Thiocarbonylimidazolide has been prepared from thiocarbonyldiimidazole and alcohol simply by grinding in a mortar at ambient temperature.

Reductive removal of hydroxyl group, *i.e.* replacement of hydroxyl group into hydrogen, has been an important synthetic transformation in synthetic organic chemistry.[1] Among various procedures for such purpose, radical dehydroxylation by Barton protocol[2] has been widely utilized especially in natural product syntheses, because many functional groups tolerate radical reaction condition. As substrates for such radical reaction, thiocarbonylimidazolide **3** has been employed often because thiocarbonylimidazolide **3** can be prepared from alcohol **1** and thiocarbonyldiimidazole **2** under neutral reaction condition. However, preparation of thiocarbonylimidazolide **3**, especially from secondary cyclic alcohol, frequently encountered difficulty asking longer reaction time at elevated temperature,[3] large excess of thiocarbonyldiimidazole **2** or even *N,N*-dimethylaminopyridine as an activator under inert atmosphere.[4]

In the course of our synthetic study of some natural products,[5] we met the same problem and found that the problem has been solved by carrying out the reaction without solvent (Scheme 1).

Scheme 1



The reaction was conducted simply by grinding alcohol **1** and thiocarbonyldiimidazole **2** in a mortar at room temperature in ambient atmosphere. The reaction was monitored by TLC and worked up by medium pressure liquid chromatography. Some representative examples are shown in Table 1. Primary and secondary alcohols and phenol afforded the corresponding thiocarbonylimidazolides **3** in satisfactory yields.[6] Not only crystalline alcohol but also oily alcohol provided thiocarbonylimidazolide **3** (entry 10). Tertiary alcohols were recovered unchanged. Grinding both substrates **1** and **2** with a pestle in a mortar was essential to get satisfactory results. Simply stirring powder or irradiation of ultrasound in entry 1 did not accelerate the reaction. The reaction under high pressure did not improve yield even at 8 Kba in entry 9.

In conclusion, we have shown that the thiocarbonylimidazolides **3** were prepared from alcohol **1** and thiocarbonyldiimidazole **2** simply by grinding in a mortar at room temperature in ambient atmosphere.

Acknowledgments We thank Prof. N. Katagiri, Pharmaceutical Institute, Tohoku University, for high pressure experiments.

References

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2. D. H. R. Barton, R. S. H. Motherwell and W. B. Motherwell, *J. Chem. Soc., Perkin Trans. 1*, 2363 (1981).
3. M. Toyota, Y. Nishikawa, T. Seishi and K. Fukumoto, *Tetrahedron*, **50**, 10183 (1994).
4. K. C. Nicolaou, P. G. Nantermet, H. Ueno, R. K. Guy, E. A. Couladouros and E. J. Sorensen, *J. Am. Chem. Soc.*, **117**, 624 (1995).
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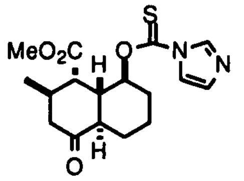
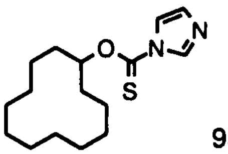
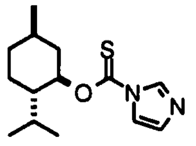
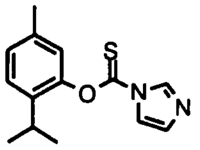
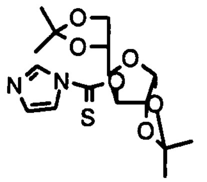
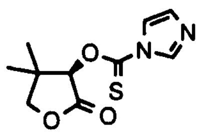
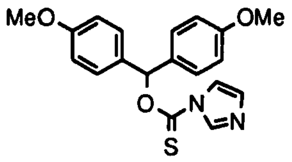
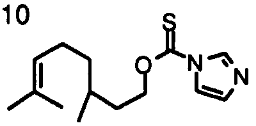
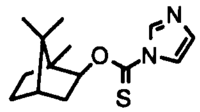
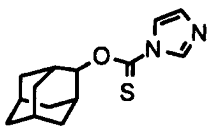
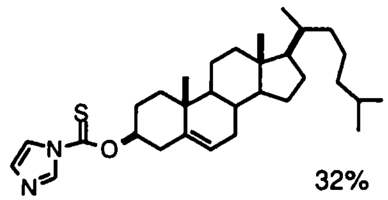
6. All imidazolides **3** in the Table 1 exhibited satisfactory IR, NMR, MS and elemental analyses.

Table 1. Synthesis of thiocarbonylimidazolide **3** without solvent.[a]

Entry		Yield[b]	Entry		Yield[b]
1		81%	7		93%
2		88%	8		99%
3		89%	9		94%
4		85%	10		91%
5		56%	11		15%
6		32%			

[a] All reactions were carried out by grinding alcohol **1** and thiocarbonylimidazole **2** in a mortar with a pestle.

[b] All yields refer isolated pure products.