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Reactions of silylcarbamates with ketones

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Abstract

The reaction of *N*,*N*-dialkyl-*O*-trimethylsilyl carbamates with different carbonyl compounds gives enamines under mild conditions in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

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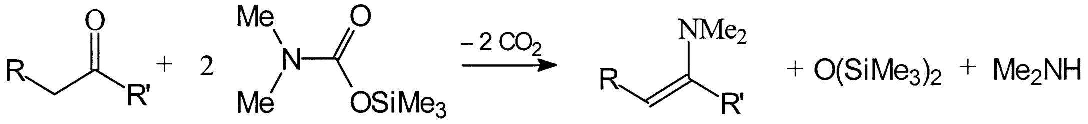
Although a number of methods are available for the synthesis of enamines, difficulties are often encountered if the amine is volatile, e.g. dimethylamine (bp 7°C). The preparation of dimethylamino enamines requires either a long reaction time or expensive reagents.[1–11] As part of our study on silylcarbamates[12,13] we have examined their reactions with several carbonyl compounds.

The reactions of *N*,*N*-dialkyl-*O*-trimethylsilyl carbamates with different carbonyl compounds were carried out without any solvent, generally at room temperature with exclusion of moisture. The optimum molar ratio of silylcarbamates and oxo compound was 2.5:1. The reaction usually gives enamines (see Scheme 1).



Scheme 1.

At least two equivalents of silyl carbamates are needed in the reaction since they take part, not only in the formation of the enamine, but also as dehydrating agents.

In the case of acetylacetone, only one of the two carbonyl groups is converted into an enamine, even with an excess of silylcarbamate. The reaction with ethyl acetoacetate takes place on the oxo group. Data concerning compounds prepared by the above method are summarized

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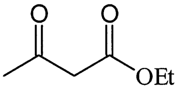
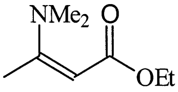
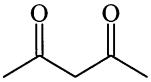
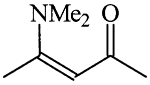
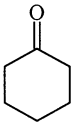
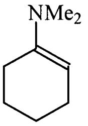
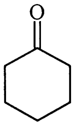
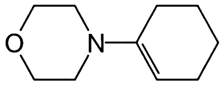
in Table 1. All compounds were identified by IR, ^{1}H and ^{13}C NMR spectroscopy. This reaction proceeded to completeness also with morpholine-*N*-carboxylic acid trimethylsilyl ester (product **4**), but the amine and carbon dioxide, which is evolved in the reactions, gave the ammonium carbamate salt as an undesired byproduct. Using a nonpolar solvent or applying higher temperature (50–60°C), the amount of this salt can be decreased. At the same time the yield of enamine increases.

Table 1
Reaction conditions and yields of the prepared enamines **1**–**4**

	Ketone	Yield %	Product	B. p. (1-2 mmHg)	Reaction time
1		86		82-84	4 h
2		95		68-70	16 h
3		55		30-32	2 h
4	 *	50		76-78	5 h

* reaction of morpholine-*N*-carboxylic acid trimethylsilyl ester with cyclohexanone

We examined some further reactions by GC-MS and IR spectroscopy. The *N*,*N*-dialkyl-*O*-trimethylsilyl carbamates (R = Et, Pr, Bu) reacted with 2-butanone and 2-pentanone by the formation of 2-dialkyl(but-2-en-2-yl)amine and 2-dialkyl(pent-2-en-2-yl)amine. However if R = Me, the reaction gave the self-condensation products of the ketones. In all cases cyclic ketones (cyclopentanone, cyclohexanone) were converted to enamines. The reaction of *N*,*N*-dialkyl-*O*-trimethylsilyl carbamates with acetone and aldehydes always led to self-condensation. Some of the above products were isolated; related data are shown in Table 2.

Table 2
Reaction conditions and yields of the prepared enamines **5**–**10**

	Ketone	$R_2NC(O)OSiMe_3$ R =	Bp °C/mmHg	Yield%	Conditions
5	3-Heptanone	Me	165–170/760	84	Rt, 4 h
6	3-Pentanone	Me	125–130/760	85	Rt, 1 h
7	Cyclopentanone	Pr	213–215/760	80	100°C, 1 h
8	Cyclopentanone	Bu	216–220/760	68	100°C, 1.5 h
9	Cyclopentanone	Morpholino	250–254/760	76	100°C, 2 h
10	Cyclohexanone	Bu	168–171/20	73	100°C, 2 h

The reaction between *N*,*N*-dimethyl-*O*-trimethylsilyl carbamate and propionaldehyde, 4′-hydroxy-acetophenone, acetonylacetone, 1-hydroxy-2-butanone, α-ketoglutaric acid and 1-tetralone did not lead to the desired enamine product. Since the silylamines react with 1-tetralone or cyclohexanone by the formation of silyl enol ethers,[10,11] therefore we also examined the reaction of silyl enol ethers with *N*,*N*-dimethyl-*O*-trimethylsilyl carbamate. No reaction was observed. On the basis of this result we conclude that the formation of enamines does not take place via silyl enol ethers.

In the above-mentioned reactions products are formed under mild conditions. They require only a small excess of reagents. The reactions are fast and the yields are fairly good. These advantages make this reaction attractive, especially for the preparation of enamines from volatile amines.

Acknowledgements

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References

1. Meyer, K. H. *Chem. Ber*. **1921**, *54*, 2265.
2. Mannich, C.; Davidson, H. *Chem. Ber*. **1930**, *69*, 2106.
3. Glickman, S. A.; Cope, A. C. *J. Am. Chem. Soc*. **1945**, *67*, 1017.
4. Gardner, C.; Kerrigan, V.; Rose, J. D.; Weedon, B. C. *J. Chem. Soc*. **1949**, 789.
5. White, W.; Weingarten, H. *J. Org. Chem*. **1967**, *32*, 213.
6. Weingarten, H.; White, W. *J. Org. Chem*. **1966**, *31*, 2874 and 4041.
7. Riviere-Baudet, M.; Satgé, J. *Rec. Trav. Chim*. **1970**, *89*, 1281.
8. Pommier, J. C.; Roubineau, A. *J. Organomet. Chem*. **1973**, *50*, 101.
9. Comi, R.; Franck, R. W.; Reitano, M.; Weinreb, S. M. *Tetrahedron Lett*. **1973**, *33*, 3107.
10. Hellberg, L. H.; Juarez, A. *Tetrahedron Lett*. **1974**, *40*, 3553.
11. Yamamoto, Y.; Maui, C. *J. Org. Chem*. **1998**, *63*, 377.
12. Knausz, D.; Meszticzky, A.; Szakács, L.; Csákvári, B.; Újszászy, K. *J. Organomet. Chem*. **1983**, *265*, 11.
13. Mörtl, M.; Knausz, D.; Kolos, Zs.; Szakács, L.; Csákvári, B. *J. Organomet. Chem*. **1994**, *482*, 183.