

Synthesis of Alkoxysilanes Bearing β -Diketone Group through Hydrosilylation

Yuan YAO, Wei HUANG, Ying HUANG, Yun Zhao YU*

The Center of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100080

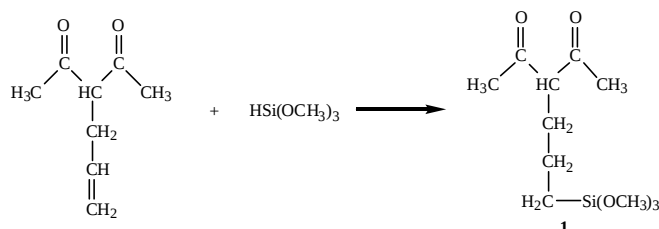
Abstract: Alkoxysilane bearing diketone group was synthesized by hydrosilylation of 3-allyl acetylacetone. It was indicated by the ^1H NMR spectrum that the C=O group does not interfere with the synthesis.

Keywords: Hydrosilylation, alkoxysilane, β -diketone.

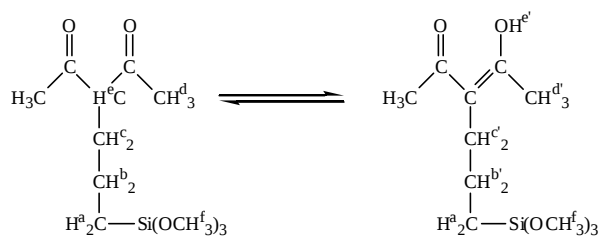
Alkoxysilanes bearing a diketone group are of great interest for the strong chelating ability of the diketone moiety to various metal ions. They can be used in the sol-gel synthesis of materials, which are interesting for catalysts, adsorbents for metal ions and optical materials. They can be used as adhesion promoter as well. The silanes were synthesized by Urbaniak and Schubert's method¹ through condensation of sodium or potassium acetylacetonate with (3-chloropropyl) trialkoxysilanes. Because of the tautomerism of acetylacetone, the products were always a mixture of C-alkylation (22-78%) and O-alkylation (78 - 22%) of acetylacetone. An alternative method for the synthesis of alkoxysilanes with β -diketone group was hydrosilylation of 3-allyl acetylacetone. Some metal 3-allylacetylacetonate were hydrosilylated by this method successfully^{2,3}. However, direct hydrosilylation of 3-allylacetylacetonate was considered to be unfavorable because the reaction of hydrosilanes with the C=O group was doubtful^{1,2}. In the present work, we have reinvestigated the hydrosilylation of 3-allyl acetylacetone, and found that this reaction proceeds in the normal way without interference by the C=O group.

The following is an example. 20.78 g (0.148 mole) 3-allyl acetylacetone (b.p. 91-92°C/2.1 kPa) with 120 ppm of Pt catalyst were added in a 250 mL flask, and then the flask was flashed with high purity nitrogen for 5 minutes. The reactor was heated to 70°C with a water bath. 36.35 g (0.298 mole) hydrotrimethoxysilane (b.p. 82-84°C) was added dropwise. Then the temperature was elevated to 90°C, and kept at this temperature for 30 min to complete the reaction. The excess hydrotrimethoxysilane was removed by distillation in *vacuo*. The hydrosilylation product (34.59 g, 0.132 mole) was analyzed without further purification.

* E-mail: yuyzh@public2.east.net.cn



The ^1H -NMR spectrum was recorded on a DMX 300M spectrometer using CDCl_3 as solvent. The position and integration of signals in the spectrum fit the formula of the hydrosilylation product **1** very well with consideration of the tautomerism:



^1H -NMR, δ ppm, CDCl_3 . δ = 0.63-0.95 (m, 2H, H^f); 1.36-1.42 (m, 2H, H^b); 1.84 (m, H^c) and 2.20 (m, 2H, H^a); 2.14 (s, H^d) and 2.17 (s, 6H, $\text{H}^{d'}$); 3.62 (t, H^e) and 16.71 (s, 1H, $\text{H}^{e'}$); 3.56 (s, 9H, H^f). According to the result of NMR analysis, we reached to the conclusion that the addition of Si-H to C=O was negligible, and hydrosilylation of 3-allyl acetylacetone provided an efficient method for the synthesis of alkoxyasilanes bearing diketone group.

References

1. W. Urbaniak, U. Schubert, *Liebigs Ann. Chem.*, **1991**, 1221.
2. G. Fort, *Brit. Pat. Appl.* 1 473 335 **1977** (CA. 87, 135899s).
3. H. Yoshioka, K. Sato, M. Yamaya, A. Itagaki, *Eur. Pat. Appl.* 268 387 **1987** (CA. 110, 75793j).

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