Synthesis of 3-Silylacrylates by Co₂(CO)₈-catalysed Reaction of Methyl Acrylate with Hydrosilanes

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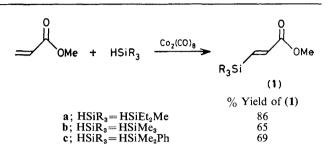
The reaction of an excess of methyl acrylate with hydrosilanes using $Co_2(CO)_8$ as a catalyst gives methyl (*E*)-3-silylacrylates in high yields.

Although it is well known that $\text{Co}_2(\text{CO})_8$ is an effective catalyst for the hydrosilylation of alkenes to produce alkylsilanes, similar reactions of acrylates have not been reported so far.¹ We report here the $\text{Co}_2(\text{CO})_8$ -catalysed reaction of methyl acrylate with hydrosilanes. The reaction of an excess of methyl acrylate with hydrosilanes using $\text{Co}_2(\text{CO})_8$ as a catalyst almost selectively gave the methyl (E)-3-silylacrylates (1) in high yields instead of the corresponding alkylsilanes.

Typically, a solution of methyl acrylate (50 mmol), $HSiEt_{2}$ -Me (10 mmol), and $Co_2(CO)_8$ (0.4 mmol) in benzene (10 ml) was stirred at 25 °C for 3 h. G.l.c. analysis showed that the reaction mixture contained (1a) in 86% yield, along with only a small amount of the alkylsilane.[†] Attempts to apply the reaction to methyl methacrylate and methyl crotonate have so far failed. HSiMe₃ and HSiMe₂Ph similarly reacted smoothly to give (1b) and (1c) in 65 and 69% yields, respectively.

Recently, several metal complexes have been shown to catalyse the reaction of alkenes with hydrosilanes to produce vinylsilanes.² However, the catalysed reaction of acrylates with hydrosilanes usually gives the corresponding alkylsilanes.³

The present reaction offers a synthetically useful method for the preparation of (E)-3-silylacrylates (1) which have been



prepared previously by a low-yielding reaction sequence starting from prop-2-yn-1-ol.⁴

Received, 4th July 1983; Com. 899

References

- G. K. Magomedov, K. A. Andrianov, O. V. Shkolnik, B. A. Izmailov, and V. N. Kalinin, *J. Organomet. Chem.*, 1978, 149, 29; J. F. Harrod and A. J. Chalk, in 'Organic Syntheses via Metal Carbonyls,' eds. I. Wender and P. Pino, Wiley-Interscience, New York, 1977, Vol. 2, p. 673.
- Y. Seki, K. Takeshita, K. Kawamoto, S. Murai, and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 928; R. G. Austin, R. S. Paonessa, P. J. Giordano, and M. S. Wrighton, *Adv. Chem. Ser.*, 1978, **168**, 189; M. A. Schroeder and M. S. Wrighton, *J. Organomet. Chem.*, 1977, **128**, 345; A. Millan, E. Towns, and P. M. Maitlis, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 673.
- 3 I. Ojima and M. Kumagai, J. Organomet. Chem., 1976, 111, 43.
- 4 M. J. Carter, I. Fleming, and A. Percival, J. Chem. Soc., Perkin Trans. 1, 1981, 2415; R. F. Cunico and H. M. Lee, J. Am. Chem. Soc., 1977, 99, 7613.

[†] The vinylsilane (1a) was identified by its i.r. (v_{max} 1730 and 1600 cm⁻¹), ¹H n.m.r. [(CCl₄) δ 6.15 (d, J 19 Hz, 1H) and 7.11 (d, J 19 Hz, 1H)], and mass spectra (M^+ -Et, m/z 157), and gave satisfactory elemental analyses. Satisfactory i.r., ¹H n.m.r., and mass spectra, and elemental analyses were also obtained for (1b) and (1c).