TRIMETHYLCHLOROSILANE - A NEW REAGENT FOR THE KNOEVENAGEL REACTION

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The Knoevenagel reaction is one of the most important methods for obtaining the carbon-carbon bond. This reaction is usually carried out in the presence of bases, often using solvents and rigorous control of the reaction temperature [1-3].

We are the first to report that trimethylchlorosilane (I) may serve as a convenient reagent for carrying out the Knoevenagel reaction of ethyl acetoacetate (I) with aldehydes without the use of solvent and without special precautions. For example, the reaction of (II) with butanal (III), octanal or benzaldehyde in the presence of (I) at ~20°C gives the Knoevenagel reaction products (IVa-c) in 70-75% yield, $CH_3COC (= CHR)CO_2Et$, R = Pr (IVa), C_7H_{13} (IVb), and Ph (IVc).

Trimethylchlorosilane has rather high specificity as a reagent for the Knoevenagel reaction. Under the conditions described above, this silane is not suitable for the Knoevenagel reaction of (II) with acetone, diethyl malonate or of acetone with (III) and may be replaced by acetyl chloride in the reaction of (II) with (III) only with a significant drop in the yield of (IVa) to about 30%.

A sample of 2.5 ml (III) was added gradually with stirring to a mixture of 2.6 ml (II) and 3 ml (I) and maintained for 72 h at ~20°C. The reaction mixture was treated with water and aq. NaHCO₃ and extracted with benzene. The extract was dried over MgSO₄. After solvent removal, the product was distilled in vacuum to yield 2.7 g (75%) (IVa), bp 120-123°C (20 mm), n_D¹⁸ 1.4533. UV spectrum (λ_{max} , ethanol): 220 nm. IR spectrum (KBr, ν , cm⁻¹): 1040, 1142, 1220, 1280, 1380, 1463, 1640, 1673, 1721. The same indices were found for an authentic sample (IVa) [4].

By analogy, the reaction of (II) with octanal and benzaldehyde gave (IVb), bp 147-150°C (12 mm), n_{D}^{17} 1.4632, UV spectrum (λ_{max} , ethanol): 223 nm and (IVc), bp 187-190°C (15 mm), n_{D}^{17} 1.5590, UV spectrum (λ_{max} , ethanol): 225, 285 nm [5, 6].

Thus, we have discovered the capacity of (I) to effect the Knoevenagel reaction of (II) with aldehydes at $\sim 20^{\circ}$ C and provide high yields of the corresponding reaction products.

LITERATURE CITED

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 495-496, February, 1985. Original article submitted October 25, 1984.