SYNTHESIS OF CINNAMYLPHOSPHONATES

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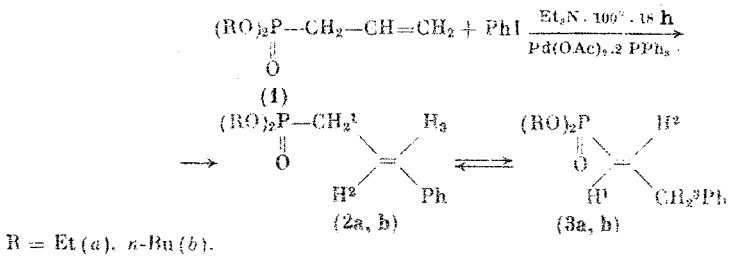
Cinnamylphosphonates may be obtained by the reaction of sodium dialkyl phosphites with cinnamyl chloride. However, the product yields did not exceed 23% [1]. Lu and Zhu [2] later proposed a synthesis for these compounds based on the cross-coupling of dialkyl phosphites with cinnamyl acetate in the presence of bis(trimethylsilyl)acetamide. The reaction proceeds upon heating of the reagents for 70 h using nickel 1,5-cyclooctadiene as the catalyst [2].

We have found that cinnamylphosphonates may be obtained by the Heck reaction of allylphosphonate (1) and iodobenzene in the presence of catalytic amounts of $Pd(OAc)_2$. The yield of phosphonates 2a and 2b was 80%.



R = Et (*a*), *n*-Bu (*b*).

A PMR spectral study showed that phosphonates 2a and 2b are 1:1 mixtures of tautomeric forms 2 and 3. The coupling constants of the vicinal protons are 15-20 Hz, indicating the formation of trans-alkenylphosphonates.

Diethyl γ-Phenylallylphosphonate (2a, 3a) (general procedure). A sample of 2.3 ml (20 mmoles) iodobenzene was added to a mixture of 3.6 ml (20 mmoles) diethyl allylphosphonate, 0.6 ml (30 mmoles) triethylamine, 225 mg (0.2 mmoles) $Pd(OAc)_2$, and 110 mg (0.4 mmoles) PPh_3. The reaction mixture was maintained for 18 h at 100°C in a dry argon atmosphere and then cooled to room temperature. A sample of 8 ml ether was added. The precipitate was filtered off. The filtrate was washed with two 10-ml portions of 1% hydrochloric acid and three 20-ml water portions and dried over Na_2SO_4. Ether was distilled off and the residue was distilled in vacuum to give 2a, 3a in 80% yield, bp 130°C (0.3 mm). ^{31}P NMR spectrum (δ, ppm): 32.0. PMR spectrum at 400 MHz in $CDCl_3$ (δ, ppm, ^3J, Hz, TMS): 2a) -2.3 d.d (H^1), 5.2 m (H^2), 5.6 m (H^3, $^3J_{H^2H^3}$ 20.0), 3a) 4.9 d.d (H^1), 7.4 d (H^2), 3.3 d (H^3, $^3J_{H^1H^2}$ 15.0).

Dibutyl γ-phenylallylphosphonate (2b, 3b) was obtained in 79% yield, bp 135°C (0.1 mm). ^{31}P NMR spectrum (δ, ppm): 31.5. PMR spectrum at 400 MHz in $CDCl_3$ (δ, ppm, ^3J, Hz, TMS): 2b) 2.6 d.d (H^1), 5.4 m (H^2), 5.9 m (H^3, $^3J_{H^2H^3}$ 23.0), 3b) 5.0 d.d (H^1), 7.4 d (H^2), 3.4 d (H^3, $^3J_{H^1H^2}$ 15.0).

LITERATURE CITED

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