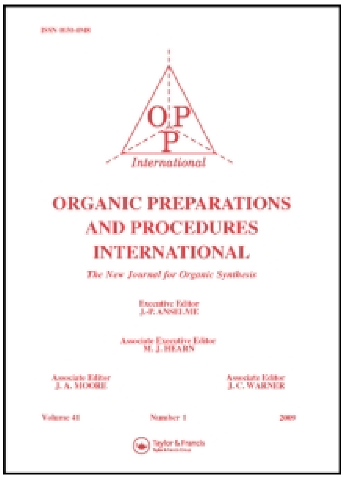

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IMPROVED SYNTHESIS OF 2,4-HEXADIENOIC ACID

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IMPROVED SYNTHESIS OF 2,4-HEXADIENOIC ACID[†]

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2,4-Hexadienoic acid (**1**, sorbic acid) is a useful starting material for the synthesis of 8(E), 10(E)-dodecadienol,[1] which is a sex pheromone component of many insects.[2] Compound **1** is available from natural sources (e. g. from the plant *Sorbus aucuparia*[3]) or can be prepared by the Wittig-Horner reaction[4] or by the Doebner modification[5] of the Knoevenagel from 2(E)-butenal (**2**) and malonic acid (**3**) in the presence of pyridine. Although this latter procedure involving heating a mixture of 2(E)-butenal, malonic acid in pyridine at 80° for 3 hrs (Eq. 1), uses cheaper reagents than Wittig-Horner process, it gave very low yield (28-32%). The low yield stems from the competing self-condensation of 2(E)-butenal which is faster than the condensation of **2** with **3**. This process can be followed by the deepening of the color of the reaction time. The polycondensation products can also react with **3** producing polysorbic acids. We now report our modification of this synthesis which results in a higher yield of 1 (40-70%).

$$\underset{\textbf{2}}{CH_3CH{=}CHCHO} + \underset{\textbf{3}}{CH_2(CO_2H)_2} \xrightarrow[80^\circ,\ 3\ hrs]{pyridine} \underset{\textbf{1}}{CH_3CH{=}CHCH{=}CHCO_2H}$$

In order to decrease the self-condensation, **2** was added dropwise to a stirred solution of **3** in pyridine at 80°. In this case, the color of reaction mixture remained only slightly yellow and the yield was higher. We also attempted to catalyze this reaction with piperidine.[6] However, piperidine catalyzed the self-condensation of **2** better than the condensation of **2** with **3**. In all cases, the reaction mixture contained only polysorbic acids.

EXPERIMENTAL SECTION

2(E)-Butenal (Fluka) was freshly distilled. Pyridine (Fluka) was dried over potassium hydroxide then distilled from potassium hydroxide. Malonic acid (Fluka, purum grade) was recrystallized from methanol before use, mp. 135°. ^{1}H NMR spectra (TMS as internal standard) were taken at 100 MHz and Varian XL-100 spectrometer in a mixture of $CDCl_3$ and DMSO-d_6.

2(E),4(E)-Hexadienoic acid (**1**).- To a vigorously stirred solution of malonic acid (100.0 g, 0.96 mol) in dry pyridine (110 ml, 1.36 mol) was added 2(E)-butenal (80 ml, 0.98 mol) at such a rate (1-1.5 ml/min) at 80° as to maintain a moderate gas evolution; the resulting mixture was then stirred for 2 hrs at 120°. After cooling, it was poured into a mixture of water (200 ml) and ice (50 g). Conc. sulfuric acid (50 ml) was added to the resulting suspension with cooling (at 0°) and stirring. The white precipitate formed was collected, washed with water (50 ml) and air dried at 25° to yield **1** (75.3 g, 70%) as white crystals, mp. 133-134°, lit.[3,5] 134.5°.

^{1}H NMR: δ 8.58 (br. s, 1H, CO_2H), 7.22 (dd+l. r., J_1 = 16Hz, J_2 = 10Hz, 1H, =C-C^3H=), 6.0-6.4 (m, 2H, -C^4H = C^5H-), 5.78 (d, J = 16Hz, 1H, =CH-CO), 1.84 (d+l. r., J = 6Hz, 3H, CH_3C=).

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