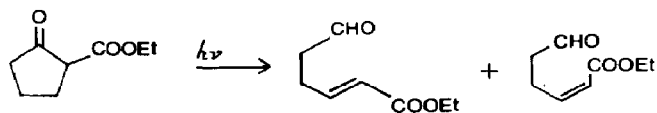


Organic Photochemical Synthesis

Ethyl 6-oxohex-2-enoates



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1. Procedure

A solution of 12 g (0.077 mol) of 2-ethoxycarbonylcyclopentanone (note 1) in dry benzene (110 cm³) is placed in a tubular Pyrex reactor (23 cm long and 6 cm outside diameter) with an internal water-jacketed Vycor immersion well (22 cm long and 5 cm outside diameter). The reactor is equipped with a reflux condenser and with a nitrogen inlet at the bottom. A Philips HPLN 400 W medium pressure mercury arc (note 2) is suspended in the immersion well. The solution is purged with nitrogen and irradiated for 4 h (notes 3 and 4). The benzene is removed by distillation (note 5) under reduced pressure (boiling point, 40 °C at 180 mmHg), and the liquid residue is distilled (short path) to give 7.1 - 7.6 g (59% - 63%) of ethyl 6-oxohex-2-enoate as a mixture (note 6) of *E* and *Z* isomers (boiling point, 108 - 125 °C at 15 mmHg).

2. Notes

(1) 2-Ethoxycarbonylcyclopentanone is commercially available (Aldrich or Merck) but contains some diethyl adipate. It may be purified by the following procedure. 50 g of commercial material in ethanol (60 cm³) are added to a solution of sodium hydroxide (17.2 g) in water (50 cm³). The mixture is stirred for 1 h, after which the sodium salt has completely precipitated. The precipitate is filtered, washed with water (20 cm³) and ether (3 × 50 cm³) and then dried under vacuum. The yield varies between 90% and 97%. This purified sodium salt is added to 1 M hydrochloric acid (350 cm³), and the ketoester is extracted with ether (3 × 100 cm³). The ethereal solution is dried and distilled to give pure ketoester (boiling point, 102 - 104 °C at 11 mmHg).

(2) The external fluorescent envelope (coated with yttrium vanadate activated by europium) is removed from a Philips HPLN 400 W bulb. The 400 W medium pressure mercury arc which is contained inside the bulb can

then be used with PB 400 C200 stabilization ballast. This set makes a very cheap irradiation system.

(3) The checkers used a conventional 450 W medium pressure mercury arc (Applied Photophysics) and a reactor with a quartz probe.

(4) The progress of the reaction can be monitored by gas-liquid chromatography (GLC) using a column made up as 10% SE 30 on Chromosorb W.

(5) Alternatively the solvent may be removed at 20 - 25 °C with a rotary evaporator.

(6) Both GLC and ^1H nuclear magnetic resonance analysis suggest that the mixture is 70% *E* isomer and 30% *Z* isomer. The mixture can be separated with a good (or spinning-band) distillation column. The boiling points are as follows: *Z* isomer, 68 °C at 0.5 mmHg; *E* isomer, 78 °C at 0.5 mmHg.

3. Merits of the preparation

The synthesis is straightforward and can be carried out on a small scale (0.5 g) or with a large amount (20 g) of 2-ethoxycarbonylcyclopentanone. The other method [1] for preparing methyl or ethyl 6-oxohex-2-enoates involves the unsymmetrical chain-lengthening of glutaraldehyde with trimethyl or triethyl phosphonoacetate in dimethylformamide solution containing sodium ethoxide (yield, 40% or less).

A similar procedure can be used to make ethyl 2-methyl-6-oxohex-2-enoates (80% - 86% of an *E-Z* mixture) from 2-ethoxycarbonyl-2-methylcyclopentanone.

- 1 B. G. Kovalev, N. P. Dormidontova and A. A. Shamshurin, *Zh. Org. Khim.*, 5 (1969) 1775; *Chem. Abstracts*, 72 (1970), no. 12001a.

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