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Novel Synthetic Method for 2-Methyl-2-cyclopentenone from Diallyl Adipate by Two-Pot Reactions

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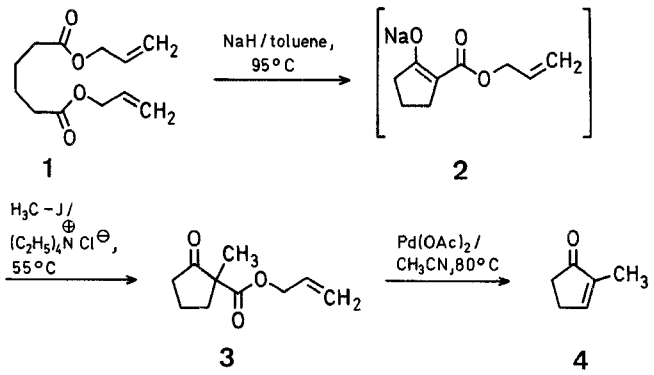
2-Methyl-2-cyclopentenone (**4**) is an important starting material for the synthesis of many cyclopentanoid natural products, and nearly 20 methods have been proposed for its synthesis[1]. However, these methods cannot be said to be satisfactory, particularly for large scale preparations. They give rather low overall yields, need many steps, or use expensive starting materials. We now present a convenient preparation of **4** by two-pot reactions using cheaply available starting material. The key reaction is the palladium-catalyzed decarboxylation-dehydrogenation reaction of allyl β-ketocarboxylates, which we have discovered. We have reported a facile synthesis of α,β-unsaturated ketones from allyl β-ketocarboxylates using palladium/1,2-bis[diphenylphosphino]ethane as a catalyst in acetonitrile[2]. Recently we found that the reaction proceeds more efficiently using a phosphine-free palladium catalyst[3].

As shown in the following scheme, the Dieckmann condensation of diallyl adipate (**1**), followed by methylation gives allyl 1-methyl-2-cyclopentanonecarboxylate (**3**) in 87% overall yield. Then **3** is subjected to the palladium-catalyzed decarboxylation-dehydrogenation to give **4** isolated in 75% yield (92% yield by G.L.C. analysis).



In summary, the single and easy procedure, the mild reaction conditions, the simple work up, the high yield (79%), and the high purity of the product make the present synthesis a convenient synthetic method for 2-methyl-2-cyclopentenone (**4**) on a large scale.

Diallyl adipate (**1**) is commercially available from Tokyo Kasei Kogyo Co., Ltd. or prepared in an almost quantitative yield by acid-catalyzed esterification of adipic acid with allyl alcohol in benzene by removing water with a Dean-Stark trap[4].

Allyl 1-Methyl-2-cyclopentanonecarboxylate (3):

To a suspension of sodium hydride (60% in mineral oil; 2.1 g, 88.5 mmol; prewashed with dry *n*-hexane) in dry toluene (40 ml) is added allyl alcohol (1.7 ml) over a period of 10 min. After evolution of hydrogen ceases, a solution of diallyl adipate (**1**; 20 g, 88.5 mmol) in dry toluene (20 ml) is added dropwise with constant stirring at room temperature. After the addition is complete, the mixture is stirred for 10 min at room temperature and then at 95°C for an additional 1 h. Dry toluene is added through a condenser from time to time in order to keep the reaction mixture fluid enough for efficient stirring. Between 40 ml and 60 ml of dry toluene is added in this manner. Upon completion, the water condenser is replaced by a Claisen adapter, oil bath is heated to 130°C, and the stirring is continued until allyl alcohol no longer distills (complete removal of allyl alcohol is necessary to avoid the retro-Dieckmann condensation after methylation in the following step). After the reaction mixture has cooled to room temperature, the same amount of the dry toluene as the distillate, methyl iodide (13.7 ml, 0.117 mol), and tetraethylammonium chloride (2.9 g, 17.7 mmol) are added successively to the mixture. The resulting mixture is stirred at 55°C for 4 h. The reaction mixture is cooled in an ice bath and unreacted sodium hydride is destroyed with methanol. Ice-cold 3 normal hydrochloric acid (200 ml) is slowly added with constant stirring, and the mixture is extracted with dichloromethane (4 × 50 ml). The combined organic extracts are washed with sodium hydrogen carbonate solution (30 ml) and brine (3 × 30 ml), followed by drying with magnesium sulfate. The solvents are evaporated and the residual oil is distilled under reduced pressure to give **3**; yield: 13.8 g, (87%); b.p. 71°C/0.8 torr.

$C_{10}H_{14}O_3$	calc.	C 65.92	H 7.74
(182.2)	found	66.11	7.79

I.R. (neat): ν = 3100, 2955, 2930, 1760, 1735, 1650, 1165 cm^{-1}.

^{1}H-N.M.R. (CCl_4) δ = 1.2 (s, 3H); 1.5–2.5 (m, 6H); 4.3–4.5 (d, J = 6Hz, 2H); 4.9–5.3 (m, 2H); 5.4–6.0 ppm (m, 1H).

2-Methyl-2-cyclopentenone (4):

A solution of the allyl ester **3** (10 g, 55 mmol) in dry acetonitrile (10 ml; distilled from calcium hydride) is added dropwise to a boiling pale-yellow solution of palladium acetate (123 mg, 0.54 mmol) in dry acetonitrile (30 ml) over a period of 30 min. The resulting mixture is refluxed for an additional 5 min whereupon most of the catalyst deposits at the bottom as a mirror. The mixture is cooled and then passed through a short florisil column followed by washing with dichloromethane (30 ml). The combined filtrate and washing are distilled at atmospheric pressure to remove most of the solvents. The remaining crude product is distilled under reduced pressure to give **4**; yield: 4.1 g, (79%); b.p. 74°C/44 torr; G.L.C. analysis (conditions: silicone DC 550 packed column, 3 m × 3 mm, 150°C) shows ≧ 95% purity, containing 2-methylcyclopentanone < 5% as a by-product.

I.R. (neat): ν = 2910, 1690, 1630, 1430, 1320, 1060 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 1.76 (m, 3H); 2.59–2.15 (m, 4H); 7.16 ppm (m, 1H).

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[1] A good summary of the preparative methods reported before 1980 has been given: R.L. Funk, K.P.C. Vollhardt, *Synthesis* **1980**, 118. Recent reports: B.W. Disanayaka, A.C. Weedon, *Synthesis* **1983**, 952.
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[4] cf. V.M. Micovic, *Org. Synth. Coll. Vol.* II, 264 (1943).