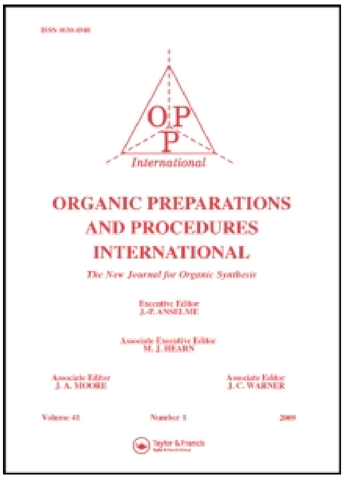

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# AN IMPROVED PROCEDURE FOR THE PREPARATION OF 3-METHYL-2-CYCLOPENTEN-1-ONE

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# AN IMPROVED PROCEDURE FOR THE PREPARATION OF 3-METHYL-2-CYCLOPENTEN-1-ONE

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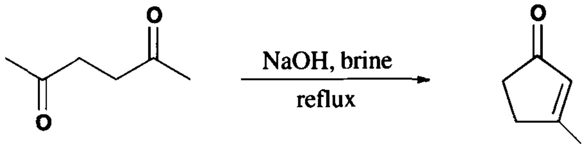
3-Methyl-2-cyclopenten-1-one (**2**) is a useful intermediate in the synthesis of many natural products, including the trichothecenes,[1,2] cortisone[3] and precapnelladiene.[4] Enone **2** has been synthesized by several methods, including ring opening of furans followed by base-catalyzed aldol condensation,[5] lactone rearrangement,[6] Rh(II)-catalyzed carbon-hydrogen insertion,[7] as well as base-catalyzed aldol condensation of 2,5-hexanedione (**1**).[2,8] The aldol condensation, first reported by Robinson,[3] is plagued by low yields accompanied by contamination of the product with substantial quantities of unchanged starting material, which necessitates additional purification steps. Thus, total yields of distillable materials are typically about 40%, of which one-fifth is dione **1**.[8] We report herein a modification in Robinson's aldol condensation procedure that delivers a higher yield of **2** and results in a significant reduction in the quantity of **1** appearing in the desired product.

The improvement was accomplished by using a reaction mixture that is more dilute and nearly saturated with NaCl and by slower addition of **1** to the hot aqueous base. Yields of 60–70% of crude **1** containing from 0–4% of diketone **1** are obtained reproducibly upon distilling the crude reaction mixture.



**1** **2**

## EXPERIMENTAL SECTION

The $^1H$ and $^{13}C$ NMR spectra were recorded on samples in $CDCl_3$, using a GE QE-300 spectrometer operating at 300 and 75 MHz, respectively. Infrared spectra (IR) were recorded on thin films, using a Nicolet 510P FT-IR instrument.

**3-Methyl-2-cyclopenten-1-one.**- Sodium hydroxide (5.0 g, 0.125 mol), water (250 mL), and saturated sodium chloride solution (500 mL) were combined in a 1-L three-neck round-bottom flask, equipped with a reflux condenser, addition funnel, heat source, and either mechanical or magnetic stirring. The mixture was heated to vigorous reflux, and a solution of 2,5-hexanedione (**1**, 28.5 g, 0.25 mol) in 60 mL of water was added dropwise over 1 hr. The reaction mixture was maintained at reflux for an additional 45 min, at which time it was biphasic, having a deep orange lower phase and a black upper phase. The hot mixture was rapidly poured into about 1.5 L of crushed ice contained in a 4-L beaker. The resulting biphasic solution was saturated with NaCl, and the black-colored contaminants were removed by vacuum filtration through a bed of Celite®. The resulting light orange solution was extracted with $CH_2Cl_2$ (3 x 200 mL), the combined organic layers were dried ($Na_2SO_4$), and the solvent was removed by rotary evaporation. Distillation of the residual oil afforded 14.5 g (60%) of **2**, bp 68–69°/8 torr, lit.[8] bp 74–76°/16 torr. The spectral data of the product were consistent with those reported previously.[8] $^1$H NMR data ($CDCl_3$): $\delta$ 2.10 (s, 3H), 2.40 (m, 2H), 2.59 (m, 2H), 5.90 (s, 1H); $^{13}$C NMR data: $\delta$ 19.4, 33.0, 35.7, 130.6, 178.8, 210.1; IR data (neat): 1706, 1702, 1633 cm$^{-1}$.

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