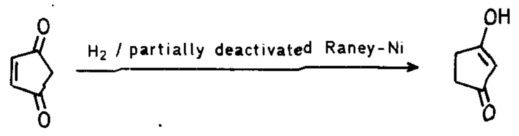
A Convenient Procedure for Preparation of 1,3-Cyclopentanedione

J. Šraga, P. Hrnčiar

Department of Organic Chemistry, Komensky University, Mlynská Dolina, 81600 Bratislava, Czechoslovakia

Previous studies have resulted in three synthetic pathways to the useful 1,3-cyclopentanedione: acid cleavage of 2-acetyl-1,3-cyclopentanedione[1], cyclization of ethyl 4-oxopentanoate[2], and reduction of 4-cyclopentene-1,3-dione by zinc dust[3] or activated zinc filings[4] in glacial acetic acid. We wish to report a procedure which eliminates the difficulties concountered with crystallization of the oily material obtained by all the above mentioned methods, which avoids the tedious removal of the large amounts of solvents, and which gives a higher yield.

Preparation of 1,3-cyclopentanedione by catalytic hydrogenation of the corresponding unsaturated dione has already been investigated and unsatisfactory yields of 1,3-cyclopentanedione using platinum oxide and palladium on charcoal as catalysts have been reported[3,4,5]. We have found that partially deactivated Raney nickel is an excellent catalyst for this application. Partial deactivation of the neutral W-2 catalyst is achieved by washing it with a 0.1% methanol solution of acetic acid as described in Lit.[6]. As high as 120% consumption of the hydrogen is observed and, consequently, less pure product is obtained when the hydrogenation is carried out with the neutral catalyst. Absolute methanol, ethanol, and 95% ethanol may be used solvent in this reaction without any influence on the yield. Both ethyl acetate and tetrahydrofuran are less suitable solvents.



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1,3-Cyclopentanedione:

A solution of 4-cyclopentene-1,3-dione[7] (**1**; 24 g, 0.25 mol) in methanol (350 ml) is hydrogenated at room temperature and at atmospheric pressure with partially deactivated Raney nickel catalyst[6] (3 g) for 4.5–5 h, during which time 0.250–0.263 mol of the hydrogen is absorbed. The catalyst is filtered off, washed with methanol (50 ml) and solvent is removed under reduced pressure and at temperature below 40°. The solid residue is finely powdered, washed three times with ether (3 × 75 ml), and dried in vacuo. The crude dione (23–24 g; m.p. 144–140°) is of 94% purity checked by gas chromatography (80 × 0.2 cm column, Gas Chrom Q with 3% neopentyl succinate and 1% phosphorous acid, 130°). The further purification of the dione may be achieved either by recrystallization from dry acetonitrile (15 ml per gram) with addition of activated carbon or by sublimation at 130°/0.01 torr; yield: 18.5–20 g (75–81%); m.p. 149–151°.

U.V. (ethanol): $\lambda_{max} = 255$ ($\varepsilon = 21000$).

^{1}H-N.M.R. (CD_3COCD_3): $\delta = 2.45$ (s, 4H, $-CH_2-$), 5.13 ppm (s, 1H, $-CH=$).

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Erratum

T. H. Chan, A. Baldassarre, D. Massuda, *Synthesis* **1976**, 801–803.
The last sentence starting on p. 802 should be:
The stereochemistry of **6f** has been assigned to be (Z) by comparison of its ^{1}H-N.M.R. spectrum with those of similar compounds of known stereochemistry[11].