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Short Communications

Cyclopentane-1,3-dione Revisited

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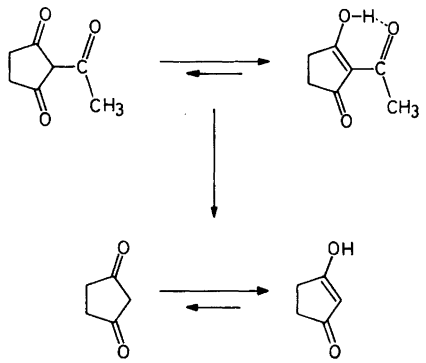
Cyclopentane-1,3-dione is a seemingly simple compound which resisted synthesis for a long time.[1-3] We observed that it was formed by hydrolysis of dilute solutions of 2-acetylcyclopentane-1,3-dione in hot hydrochloric acid and then had to be purified by sublimation.[4,5]

There have been reports, however, that this hydrolysis is difficult to reproduce and may give "varying yields".[6-9] The formation of 4,5-dioxoheptanoic acid (4,6?) has been mentioned.[9] Some alternative methods for preparation of cyclopentane-1,3-dione have been described.[6-10]

Cyclopentane-1,3-dione continues to be an interesting intermediate, *e.g.* Refs. 11–15. Since its preparation had given reasonable results in our hands (see also Refs. 16, 17) I have reinvestigated the hydrolysis of 2-acetylcyclopentane-1,3-dione.

2-Acetylcyclopentane-1,3-dione is almost completely enolic and quite acidic. The hydrolysis is expected to proceed by attack of water on an *O*-protonated keto form and could give either cyclopentane-1,3-dione or 4,6-dioxoheptanoic acid. High acidity could promote condensations. Also cyclopentane-1,3-dione is enolic, acidic and reactive.



Thus concentrations and acidity should be kept low to minimise intermolecular condensations, without impractical dilution, however.

The hydrolysis of 2-acetylcyclopentane-1,3-dione can be monitored by UV spectrophotometry where the decrease of the characteristic bands of the enol at 227 and 256 nm and the appearance of the band at 247 nm for the enol of cyclopentane-1,3-dione are readily recognised in an acidic medium. The reaction can be followed also by TLC.

Solutions of 2-acetylcyclopentane-1,3-dione in water or dilute acids are rather stable at moderate temperatures and practical rates of hydrolysis are obtained only above 90 °C. Concentrated solutions, especially those above 0.5 M are then rapidly discolored, first becoming lemon-yellow and then turning brown or even black. The colouration is affected by acidity and hydrochloric or formic acids give more coloured solutions than does acetic acid. The hydrolysis of dilute solutions in 2 M hydrochloric acid[4,5] often works on a small scale but is not reliable.

The most practical method proved to be to keep an 0.1 M solution of 2-acetylcyclopentane-1,3-dione in 0.1 M aqueous acetic acid at 100 °C for 24 h. There was no indication for the formation of 4,6-dioxoheptanoic acid but several minor, fluorescent spots were observed on TLC. The yellow colour of the solution was due to a contaminant with a sharp absorption at 400 nm. It was readily removed by charcoal but otherwise stuck tenaciously to the crystals. The yield of recrystallised cyclopentanedione was 65 to 80 %. On melting, cyclopentane-1,3-dione immediately turns yellow and TLC then shows the formation of several coloured and fluorescent compounds; similar self-condensation has been described for cyclohexane-1,3-dione.[19]

Thus the acidic cleavage of 2-acetylcyclopentane-1,3-dione is rather selective under the conditions described. The cleavage of 2-acetylbicyclo[3.1.0]-hexane-2,4-dione in 2 M hydrochloric acid gives 78 % yield of bicyclo[3.1.0]hexane-2,4-dione,[20] whereas 2-acetylcycloheptane-1,3-dione gives at least 60 % of 6,8-dioxononanic acid.[5]

The present two-step pathway to cyclopentane-1,3-dione from succinic anhydride and 2-propenyl acetate[21] may be compared with the direct cyclisation of ethyl 4-oxopentanoate[7,8,10] in dilute solution and with the three-step syntheses from

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cyclopentadiene[6] or norbornadiene.[9]

Experimental. General methods. TLC were run on Silicagel 60 F_{254} (Merck) with ethyl acetate, pyridine, water and acetic acid (25:25:15:5) or with acetic acid. After inspection under UV light the chromatograms were sprayed with methanolic iron(III) chloride. UV spectra were recorded on a Beckman DK 2 instrument, the samples being diluted to convenient colume with 0.1 M hydrochloric acid to supress dissociation.

Materials. 2-Acetylcyclopentane-1,3-dione[21] was sublimed onto a large, cold finger at 60 °C and *ca.* 10 Pa. 4,6-Dioxoheptanoic acid[22] was obtained by hydrogenation[23] of (*E*)-4,6-dioxo-2-heptenoic acid.[24,25] Gram quantities of cyclopentane-1,3-dione are also commercially available.

Preparation of cyclopentane-1,3-dione. 2-Acetylcyclopentane-1,3-dione (7.00 g, 0.050 mol) was dissolved in 500 ml 0.1 M aqueous acetic acid and the solution kept at 100 °C in a thermostated oil bath under a reflux condenser for 24 h. The lemon-yellow solution was treated with a small amount of charcoal, filtered and evaporated at a water pump at 40 °C leaving a straw-coloured solid m.p. 130 – 145 °C, *ca.* 4.5 g. The evaporation removed any remaining starting material. The product was recrystallised from butanone (*ca.* 80 ml) to give 3.2 to 3.7 g almost colurless cyclopentane-1,3-dione, m.p. 148 – 150 °C (65 – 75 or occasionally up to 80% yield). Recrystallisation raised the m.p. to 151 – 153 °C; the melt immediately turned yellow. Butanone is preferred for recrystallisations. Ethyl acetate recommended in other publications gave slow dissolution and slow crystallisation. Moderate amounts can be sublimed at 120 °C and 10 Pa without appreciable decomposition.

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