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# Spectroscopic Studies on Enols

## Part 8.* Preferential Ring Enolisation of 2-Formylcyclopentane-1,3-dione

STURE FORSÉN**

*Research Group for NMR, Department of Physical Chemistry, Royal Institute of Technology, Stockholm 70, Sweden*

FERENC MERÉNYI and MARTIN NILSSON

*Department of Organic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden*

2-Formylcyclopentane-1,3-dione has been prepared from cyclopentane-1,3-dione *via* 2-anilinomethylenecyclopentane-1,3-dione. NMR spectra of 2-formylcyclopentane-1,3-dione show complete enolisation in deuterochloroform solution. The resonance field for the aldehydic proton ($\tau = 0.41$) indicates that the enol is best described as 2-formyl-3-hydroxycyclopent-2-en-1-one. Comparison of infrared and ultraviolet spectra of 2-formylcyclopentane-1,3-dione with those of other 2-acylcyclopentane-1,3-diones indicates that ring enolisation is also predominant for the latter group of compounds.

The previous communications in this series discussed the enolisation and hydrogen bonding in several 2-acetylcyclopentane-1,3-diones and related compounds on the basis of NMR and IR spectra.[1] Some problems, however, were left unsolved. 2-Acetylcyclopentane-1,3-diones, like other $\beta$-tricarbonyl compounds, can occur in several enolic forms, "internal tautomers" such as *1a* and *1b* or external tautomers like *1a* and *1c* ($R = CH_3$). Internal tautomers are rapidly interconverted and NMR spectra then show signals with chemical shifts and spin couplings, which are weighted averages of those of the tautomers. External tautomers are generally slowly interconverted and then, presumably, by intermolecular processes. Therefore the external tautomers often give separate NMR signals. For symmetrical $\beta$-tricarbonyl compounds the external enolic tautomers may be identical, but their slow interconversion

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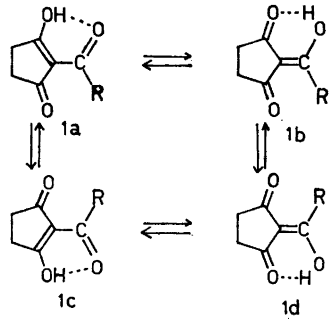
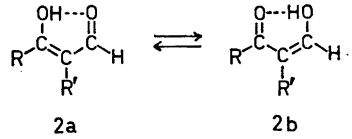
** Present address: Department of Physical Chemistry, Lund Institute of Technology, Lund, Sweden.

may still be manifest in the NMR spectra. For example in the enolic 2-acetylcyclopentane-1,3-dione, the slow interconversion of the two (identical) external tautomers is evident from the non-equivalence of the ring methylene protons. These give an $A_2B_2$ type pattern which collapses into a single line upon addition of small amounts of acids or bases which catalyse the interconversion.[1]




For the 2-acetylcyclopentane-1,3-diones no definite conclusions could be drawn from the NMR spectra regarding the internal tautomerism, due to the small differences between the presumed internal tautomers. The infrared spectra, however, showed unusual bands in the carbonyl region, which suggested that both enolic forms could be important.[1] It was therefore of interest to investigate a similar system where the internal tautomerism could be studied more readily.

In enolised $\beta$-oxo aldehydes spin couplings ranging from 0 to *ca.* 14 c/s have been observed between aldehydic and enolic protons showing the participation, in varying proportions, of both internal tautomers: formyl enols (*2a*) and hydroxymethylene ketones (*2b*).[2-4] Also the resonance field for the "aldehydic" protons varies in these compounds. A linear correlation between the spin-spin coupling constants and the resonance field for the aldehydic protons has been found by Garbisch for a series of enolised 2-formylcycloalkanones.[3] Compounds with a large enolic spin coupling constant and a high resonance field for the aldehydic proton are apparently best described as hydroxymethylene ketones and those with a low spin coupling constant and "normal" aldehydic signal as formyl enols.

2-Formylcyclopentane-1,3-dione should offer a proper system for investigation of the relative importance of ring enolisation and side chain enolisation of 2-acylcyclopentane-1,3-diones. Cyclopentane-1,3-dione is available *via* the 2-acetyl derivative.[5] However, it is not readily formylated by conventional methods; this is analogous to the findings for cyclohexane-1,3-dione.[6] The reaction of cyclopentane-1,3-dione with *N,N'*-diphenylformamidine (*cf.* Refs. 2, 6), however, proceeded more readily than corresponding reactions with cyclohexane-1,3-dione or dimedone and furnished 2-anilinomethylenecyclopentane-1,3-dione, which gave 2-formylcyclopentane-1,3-dione on alkaline hydrolysis.

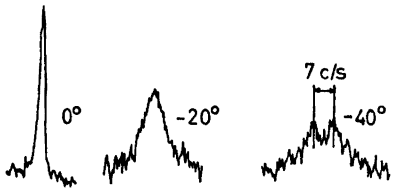



*Fig. 1.* The ring methylene signal at $\tau =$ 7.32 for enolised 2-formylcyclopentane-1,3-dione (deuterochloroform solution).

The NMR spectrum for 2-formylcyclopentane-1,3-dione in deuterochloroform solution recorded at room temperature showed complete enolisation and a signal of the aldehydic proton at a field "normal" for aldehydes ($\tau = 0.41$) as found also for 2-formyl-5,5-dimethylcyclohexane-1,3-dione. The hydrogen bonding as judged from the resonance field for the enolic proton ($\tau = -2.32$) was less marked than in the enol of 2-acetylcyclopentane-1,3-dione. This reflects the general tendency that intramolecular hydrogen bonds in enolised $\beta$-oxo aldehydes are weaker than those in the corresponding ketones.[1,2] No spin coupling was observed between the enolic and aldehydic protons.

The ring methylene protons of 2-formylcyclopentane-1,3-dione gave only one signal ($\tau = 7.32$) at room temperature. This contrasts to findings for other 2-acylcyclopentane-1,3-diones [1] and indicates a rapid interconversion of the (identical) external tautomers. However, in spectra recorded at lower temperatures the methylene signal broadened and at $-40°$ the signal appeared as a broad doublet with the maxima 7 c/s apart and presumably represented a badly resolved $A_2B_2$ pattern (Fig. 1). Poor solubility prevented studies at still lower temperatures. At the low temperatures there was a small shift of the signal for the enolic proton towards higher field whereas the signal for the aldehydic proton was not affected and no spin coupling between aldehydic and enolic protons was observed.

For comparison the NMR spectrum of the enolic 2-formyl-5,5-dimethylcyclohexane-1,3-dione [2] was also recorded at low temperatures. The aldehydic and enolic signals broadened below $-60°$, and at $-75°$ there was a distinct splitting due to a spin coupling of 1.9 c/s. This indicates some participation of the hydroxymethylene ketone form (solvent deuterochloroform with 20 % carbon disulphide).

These results demonstrate that 2-formylcyclopentane-1,3-dione in dilute deuterochloroform solution exists mainly as 2-formyl-3-hydroxy-cyclopent-2-en-1-one. This contrasts to the behaviour of 2-formylcyclopentanone which is only partly enolised and for which both internal tautomers seem to be important.[1]

The infrared and ultraviolet spectra of 2-formylcyclopentane-1,3-dione are largely similar to those of 2-acetylcyclopentane-1,3-dione [1] and thus indicate that the enolisation pattern is similar for these systems. Thus it appears that 2-acylcyclopentane-1,3-diones generally enolise preferentially in the ring to give 2-acyl-3-hydroxycyclopent-2-en-1-ones (*1a* = *1c*).

Apparently, the unusual type of infrared absorption of enols of 2-acylcyclopentanones with two bands in the carbonyl region and of 2-acylcyclopentane-1,3-diones and 2-acylcyclopent-4-ene-1,3-diones with three bands in

the carbonyl region [1] does not indicate the occurrence of comparable amounts of different internal tautomers. It seems more plausible that the phenomena are analogous to the occurrence of two bands in the carbonyl region of infrared spectra for enols of several cyclic β-oxo esters, and that the interpretation forwarded for these, namely that separate bands occur for the chelated carbonyl group and for the enolic double bond,[8] could apply also for other unsymmetrical enols.

2-Anilinomethylenecyclopentane-1,3-dione was obtained as an intermediate in the preparation of 2-formylcyclopentane-1,3-dione. The NMR data show that it is best described as the enaminoketone. This is essentially analogous to other findings for iminoketones.[2,9] 2-Anilinomethylenetetronic acid was also prepared from tetronic acid and *N,N'*-diphenylformamidine in an attempt to obtain α-formyltetronic acid.

## EXPERIMENTAL

NMR spectra were recorded on a Varian A 60 spectrometer, equipped with a Varian V-6040 temperature controller. Tetramethylsilane was used as an internal standard.

Infrared spectra were recorded on a Perkin-Elmer No 421 instrument, generally for 0.1 M solutions in 0.1 mm cells. Ultraviolet spectra were recorded on a Beckman DK 2 spectrophotometer.

*2-Anilinomethylenecyclopentane-1,3-dione.* A mixture of cyclopentane-1,3-dione [5] (20 mmole) and freshly recrystallised *N,N'*-diphenylformamidine (24 mmole) in a large test tube was heated with stirring in an oil bath kept at 125° for 4 min. (Prolonged heating gives tarry material.) The mixture melted and turned brown; after cooling the oily mass was stirred with hydrochloric acid (2 M, 3 × 10 ml) and the crystalline product collected, washed with dilute hydrochloric acid and water and dried. The crude product (3.2 g, decomp. from 174°) was recrystallised from ethyl acetate (charcoal) to give 2-anilinomethylenecyclopentane-1,3-dione as yellow prisms, m.p. 180–182° (decomp.) (2.3 g, 57 %). (Found: C 71.2; H 5.5; N 7.0. Calc. for $C_{12}H_{11}NO_2$: C 71.6; H 5.5; N 7.0.) The ultraviolet spectrum (ethanol) showed maxima at 351 nm ($\varepsilon$ = 26 700) and 235 nm ($\varepsilon$ = 17 700). The NMR spectrum (deuterochloroform, 0°) showed signals at the following τ-values: 1.65 (doublet, $-CH=$), −2.25 (broad doublet, NH) ($J$ = 13.8 c/s), *ca.* 2.65 (phenyl group), and 7.4 (ring methylene groups).

The infrared spectrum (potassium bromide disc) showed bands at 1680 $cm^{-1}$ (s), 1600 $cm^{-1}$ (vs), 1580 $cm^{-1}$ (m), and 1565 $cm^{-1}$ (s).

*2-Formylcyclopentane-1,3-dione.* 2-Anilinomethylenecyclopentane-1,3-dione (5 mmole) was hydrolysed in boiling sodium carbonate solution (*ca.* 0.2 M, 50 ml) with continuous steam distillation of the aniline formed. As judged from titration of the distillate the reaction was complete in about 3 h. The reaction mixture was acidified with dilute hydrochloric acid and extracted continuously with chloroform overnight. The extract was vacuum sublimed (120°, 0.01 mm) to give a pale yellow crystalline product decomposing from about 130° (0.4 g, 64 %). Resublimation and recrystallisation from ethyl acetate gave 2-formylcyclopentane-1,3-dione as colourless needles decomposing between 140 and 150°. (Found: C 57.2; H 4.8. Calc. for $C_7H_6O_3$: C 57.1; H 4.8.)

The ultraviolet spectrum (cyclohexane) showed maxima at 268 nm ($\varepsilon$ = 7720) and 214 nm ($\varepsilon$ = 15 000). The carbonyl region of the infrared spectrum (chloroform) showed bands at 1695 $cm^{-1}$ (s), 1630 $cm^{-1}$ (vs), and 1580 $cm^{-1}$ (vs). The NMR data are given in the text; *cf.* also Fig. 1.

Reaction of 2-formylcyclopentane-1,3-dione with *p*-nitroaniline gave *2(4-nitroanilinomethylene)cyclopentane-1,3-dione*, recrystallised from methanol, decomposing from about 243°. (Found: C 58.6; H 4.2; N 12.0. Calc. for $C_{12}H_{10}N_2O_4$: C 58.5; H 4.1; N 11.4).

*α-Anilinomethylenetetronic acid.* Tetronic acid [10] (20 mmole) and *N,N'*-diphenylformamidine (24 mmole) were heated to 120° for 2 min as described above. The crude product (3.55 g) was recrystallised twice from ethyl acetate (charcoal) to give α-anilino-

methylenetetronic acid as pale yellow crystals (1.6 g, 40 %), m.p. 174—176°. (Found: C 64.8; H 4.5; N 7.1. Calc. for $C_{11}H_9NO_3$: C 65.0; H 4.5; N 6.9.) The ultraviolet spectrum (ethanol) showed maxima at 340 nm ($\varepsilon$ = 8100) with a shoulder at 380—375 nm ($\varepsilon$ *ca.* 1000) and 228 nm ($\varepsilon$ = 5970). The infrared spectrum (potassium bromide disc) showed bands at 1730 $cm^{-1}$ (s), 1650 $cm^{-1}$ (vs), 1635 $cm^{-1}$ (vs, broad), and 1580 $cm^{-1}$ (m).

Alkaline hydrolysis of α-anilinomethylenetetronic acid as described above for 2-anilinomethylenecyclopentane-1,3-dione gave mainly anhydrotetronic acid and minute amounts of a product believed to be α-formyltetronic acid, decomposing from about 130°, with a transition point at about 80°. It gave a strong orange colour with iron(III) chloride.

The infrared spectrum (chloroform) showed strong bands at 1765, 1700, and 1605 $cm^{-1}$ and a shoulder near 1675 $cm^{-1}$ and was thus reminiscent to that of α-acetyltetronic acid.[1] Due to the small quantities available no analysis could be obtained and no NMR spectrum could be recorded. The ultraviolet spectrum (cyclohexane) showed a strong maximum at 265 nm and a moderate band at *ca.* 210 nm.

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