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# Spectroscopic Studies on Enols

## Part 7. NMR and IR Investigations of Hydrogen Bonding and Tautomerism in Cyclopentane Enols *

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Nuclear magnetic resonance and infrared measurements on 2-acetyl- and 2-formylcyclopentanone, 2-acetylcyclopentane-1,3-diones, 2-acetylcyclopent-4-ene-1,3-diones and *a*-acetyltetronic acid are reported. The tricarbonyl compounds are completely enolised but the resonance field for the enolic protons ($\tau = -2$ to $-5$) and the infrared spectra indicate that the intramolecular hydrogen bonds in the enols are weaker than those in analogous acyclic compounds or in cyclohexane and cycloheptane derivatives. The infrared spectra of the enols derived from five-membered rings show two bands in the 1600 $cm^{-1}$ region, generally separated by 30–40 $cm^{-1}$, which must be ascribed to the conjugated chelate system.

The results are discussed in terms of ring geometry. The equilibria between different "internal" and "external" tautomeric enolic forms are discussed.

The influence of ring size on enolisation of cyclic ketones has been the subject of several investigations.[1] Bromine titrations have shown that cyclohexanones are more enolised than cyclopentanones, which are in turn more enolised than acyclic ketones. Similarly, 2-acylcyclohexanones are more enolised than 2-acylcyclopentanones.[1] However, cyclopentane-1,2-diones [1] and cyclopentane-1,3-diones [2,3] are highly enolic, whereas cyclopent-2-ene-1,4-diones [4] and cyclopent-3-ene-1,2-diones [5] are not enolised at all.

Earlier papers in this series have demonstrated that *β*-tricarbonyl compounds are virtually completely enolised in solution as well as in the solid state (Refs.[6–11], partly summarised [12,13]). The hydrogen bonds in such enols

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are generally stronger than in enols of β-dicarbonyl compounds and hydrogen bonds in enols of 2-acylcyclohexane-1,3-diones are stronger than in acyclic analogues.

The present investigation concerns enolised di- and tri-carbonyl compounds with five-membered rings which form conjugated chelate systems. For reference some cyclohexane and cycloheptane derivatives are also considered. Nuclear magnetic resonance and infrared spectroscopy were used to investigate enolisation, hydrogen bonding and enol-enol equilibria. The triketones employed have become available by the reaction of isopropenyl acetate with anhydrides or chlorides of dicarboxylic acids.[3,14,15]

*Table 1.* Proton magnetic resonance shifts ($\tau$) and infrared absorption bands in the carbonyl region. Solvent carbon tetrachloride unless otherwise indicated by * for chloroform (or chloroform-*d*) or ** for carbon disulphide.

| | $\tau_{OH}$ | $\tau_{CH_3CO}$ (or CHO) | Infrared bands, $cm^{-1}$ |
|---|---|---|---|
| 1. 2-Acetylcyclopentane-1,3-dione | −4.75 | 7.56 | 1710, 1635, 1595 |
| | −4.60** | | |
| 2. 2-Acetyl-4-methylcyclopentane-1,3-dione | −472 | 7.56 | 1710, 1630, 1590 |
| 3. 2-Acetyl-4,4-dimethylcyclopentane-1,3-dione | −4.52 | 7.55 | 1700, 1630, 1585 |
| 4. *cis*-2-Acetyl-3a,4,7,7a-tetrahydroindane-1,3-dione | −4.67 | 7.55 | 1700, 1630, 1590* |
| 5. 2-Acetylindane-1,3-dione | −3.13 | 7.46 | 1710, 1660, 1620 (1596) |
| 6. 2-Acetylcyclopent-4-ene-1,3-dione | −2.10 | 7.62 | 1725, 1665, 1635 |
| | −2.12* | | |
| | −2.15** | | |
| 7. 2-Acetyl-4-chlorocyclopent-4-ene-1,3-dione | −1.83 | 7.58 | |
| | −1.94* | 7.56* | 1725, 1665, 1625 (1570) |
| 8. 2-Acetyl-4-methylcyclopent-4-ene-1,3-dione | −2.19 | 7.67 | 1720, 1660, 1630 |
| 9. 2-Acetyl-4,5-dimethylcyclopent-4-ene-1,3-dione | −1.90 | 7.67 | 1720, 1660, 1630 (1620 sh) |
| 10. 2-Acetylcyclopentanone | −3.08 | 8.06 (enol) | enol (60 %) 1660, 1615 |
| | | 7.78 (keto) | keto form 1745, 1710 |
| 11. 2-Formylcyclopentanone | −1.40 | 2.75 (enol) | enol (80−85%) 1680, 1610 |
| | −1.55* | 0.42 (keto) | keto form 1745, 1720 |
| | −1.80** | | |
| 12. 2-Anilinomethylenecyclopentanone | not seen | 2.19* | 1685 (1600) (KBr) |
| 13. α-Acetyltetronic acid | −3.10* | 7.47* | 1780, 1705, 1675, 1615 |
| 14. 2-Acetylcyclohexane-1,3-dione | −8.03 | 7.51 | 1670, 1565 |
| 15. 2-Acetyl-5,5-dimethylcyclohexane-1,3-dione | −8.06 | 7.47 | 1660, 1560 |
| 16. 2-Formyl-5,5-dimethylcyclohexane-1,3-dione | −5.60 | 0.68 | 1680, 1630, 1590 |
| 17. 2-Acetylcyclohexanone | −5.80 | 7.95 | enol (> 95 %) 1600 |
| | −5.82** | | keto *ca.* 1700 |
| 18. 2-Formylcyclohexanone | −4.25 | 1.30 | |
| 19. 2-Acetylcycloheptane-1,3-dione | −7.87 | 7.67 | 1670, 1550 |

## HYDROGEN BONDING

Spectra were recorded for the compounds on solutions in non-polar solvents. The resonance field for the enolic protons and the carbonyl region in the infrared spectra have received special attention. NMR and IR data are summarised in Table 1. The tricarbonyl compounds are all virtually completely enolised. 2-Acetyl- and 2-formylcyclopentanone are only partially enolic in contrast to their cyclohexane analogues, which are almost completely enolised.

The NMR signals for enolic protons in the cyclopentane tricarbonyl compounds were found in the region $\tau = -2$ to $-5$. 2-Acetylcyclopentane-1,3-diones gave the signals near $\tau = -5$ and the 2-acetylcyclopent-4-ene-1,3-diones near $\tau = -2$. 2-Acetylindane-1,3-dione, acetyltetronic acid and also 2-acetylcyclopentanone gave signals near $\tau = -3$, whereas 2-formylcyclopentanone gave the enolic signal at *ca.* $\tau = 1.6$. The positions and signal widths were somewhat sensitive to temperature and concentration.

The results should be compared with those recently obtained for some 3-acetylcyclopentane-1,2,4-triones (enolic signal at $\tau = -2$ to $-3$)[11] and for linderone (2-isovaleryl-4,5-dimethoxycyclopent-4-ene-1,3-dione)[16] which seems to give the enolic signal at $\tau = -1.5$ (literature data incomplete).

The resonance for enolic protons in cyclopentane tricarbonyl compounds thus occurs at markedly higher field than is usual for analogues which are acyclic or contain six- or seven-membered rings. The higher resonance field for the enolic proton in 2-formylcyclopentanone as compared to 2-acetylcyclopentanone corresponds to the difference between the enols of 2-acetylcyclohexanone and 2-formylcyclohexanone. The tendency of β-oxoaldehydes to enolise readily but to form fairly weak hydrogen bonds has been noticed earlier.[9] Moreover the hydrogen bonds in salicylaldehydes are weaker than those in *o*-hydroxyacetophenones.[17] This effect is probably related to the different electron releasing properties of hydrogens and methyl groups.

It is now fairly well established that hydrogen bonding causes displacement of proton resonance signals to lower field, the magnitude of the displacement being related to the strength of the hydrogen bonds.[18,19] On the assumption that the resonance field for the hypothetic "non-hydrogen-bonded" enolic protons is fairly constant, we will use the observed resonance fields for the enolic protons directly for comparing and relating the strengths of the hydrogen bonds.

Enols of β-dicarbonyl compounds generally show a very strong and broad infrared absorption near 1600 $cm^{-1}$. This is attributed to the conjugated chelate carbonyl group.[20] Usually no separate band is observed for the enolic double bond. In enols of β-tricarbonyl compounds the chelate carbonyl band may occur at still lower frequencies,[6] occasionally down to 1515 $cm^{-1}$. The displacement of the carbonyl band to lower frequencies can be related to the strength of the intramolecular hydrogen bond.[19] In the triketones the non-chelated, conjugated carbonyl group absorbs in the region 1660—1680 $cm^{-1}$.

The infrared spectra of the cyclopentane derivatives now investigated, however, differ from those of most other β-di- and β-triketones. Instead of the broad "conjugated chelate band", two narrower bands are observed in the 1600 $cm^{-1}$ region. The separation of the bands is fairly constant and of the

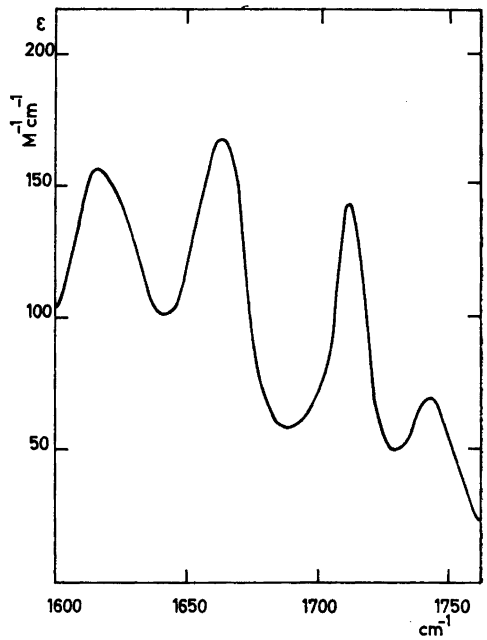


*Fig. 1.* Carbonyl part of the infrared spectrum for 2-acetylcyclopentanone. Carbon tetrachloride solution, *ca.* 0.2 M in 0.1 mm cell. The two right-hand peaks are due to the diketo form.

order of 30—40 $cm^{-1}$, although the frequencies vary. The splitting for 2-acetylcyclopentanone is shown in Fig. 1, where the distinct carbonyl bands for the diketo form are also seen. As for most other conjugated chelates the hydroxyl stretching absorptions for the enols are broad and weak and cannot be used in comparisons of hydrogen bond strength.

The "double" carbonyl band and its origin should be considered, because it may be related to some tautomeric phenomenon common to the cyclopentane derivatives.

Infrared spectra of cyclopentanone show a doublet near 1740 $cm^{-1}$. The separation of the two bands is *ca.* 20 $cm^{-1}$, but the shape of the double band is strongly affected by the solvent and the origin of the splitting is unknown.[21] For enols of some β-oxo esters two bands are observed in the 1600 $cm^{-1}$ region, one of which is ascribed to the chelate carbonyl group and the other to the enolic double bond.[22]

The splitting in the infrared spectra of the presently investigated cyclopentane derivatives is little affected by the experimental conditions. The pattern is rather the same for all compounds investigated, except for acetyltetronic acid, where apparently "external tautomerism" also comes into play (see below).

There are two plausible interpretations of the splitting in the infrared spectra. One is analogous to that advanced for β-oxo esters, *viz.* that the chelated carbonyl group and the enolic double bond give rise to separate absorption bands. The other interpretation would be that the two bands represent different chelated carbonyl groups. The high frequency band should then be due

to a carbonyl group on the cyclopentane ring and arise from the form in which the side-chain carbonyl group is enolised (*cf.* Fig. 3). Similarly the low-frequency band should be due to a chelated side chain carbonyl group. This interpretation is particularly favoured by the fact that the separation of the bands is fairly constant and of the order of 30—40 $cm^{-1}$, which is close to the difference between cyclopentanones and acyclic (or six-ring-) ketones.

In earlier papers we have demonstrated a correlation between the resonance field for enolic protons and the chelate carbonyl absorption frequency for several enolised $\beta$-tricarbonyl compounds.[6,12] The present NMR and IR data of di- and triketones are plotted in Fig. 2, which shows a fair correlation be-

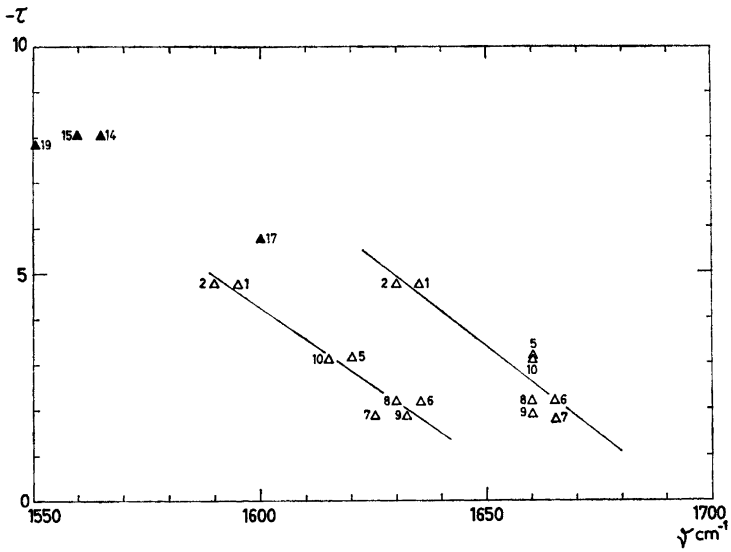


*Fig. 2.* Correlation of NMR and IR data for carbon tetrachloride solutions of di- and triketones. $\tau$ denotes resonance field for enolic protons and $\nu$ denotes IR absorption frequencies tentatively assigned to chelate carbonyl groups. Numbers refer to compounds as listed in Table 1. Filled symbols indicate compounds with a single chelate carbonyl band and the unfilled symbols compounds with "double chelate bands".

tween the resonance field for the enolic protons and the infrared absorption frequencies. Thus *both* infrared bands show the same dependence on structure and the correlation chart shows two approximately parallel lines for the cyclopentane derivatives. This seems to favour the second interpretation put forward above, namely that the infrared spectra represent the superimposed absorption of "internal tautomers" (see below).

Since there is a reasonable correlation between the NMR and IR data, fairly safe conclusions may be drawn regarding the strength of the hydrogen bonds. It is thus noticed that the hydrogen bonds in the enols of $\beta$-di- and $\beta$-tricarbonyl compounds derived from cyclopentane are weaker than those in acyclic analogues and those in cyclohexane or cycloheptane derivatives. This

difference seems to be related to the molecular geometry; the two chelate oxygen atoms at the five-membered ring are further apart. This should make the hydrogen bond weaker and, as has been pointed out by Hammond, should also render the enolic proton more acidic.[1] The effect of ring size on enolisation and acidity has recently been dramatically shown by Stetter, Krüger-Hansen and Rizk for bicyclic β-diketones.[23] Thus decaline-1,8-dione is completely enolic and a very weak acid ($pK_a$ = 11), hydrindane-1,2-dione is 80 % enolic ($pK_a$ = 8.64) and bicyclo [0.3.3] octane-2,8-dione is little enolised (1.4 %) and reasonably acidic ($pK_a$ = 7.04). Unfortunately, no IR or NMR data are as yet reported for these compounds.

The fact that the hydrogen bond in acetyltetronic acid is weaker than that in 2-acetylcyclopentane-1,3-dione may seem surprising. We have previously shown that hydrogen bonds in the enols of diacetoacetic esters are stronger than in the enol of triacetylmethane.[7] Since C—O bonds are shorter than C—C bonds, however, the ring should be more "contracted" in 2-acetyltetronic acid than in 2-acetylcyclopentane-1,3-dione, causing unfavourable geometry for the hydrogen bond. In accordance with this acetyltetronic acid is strongly acidic.[24] Thus the steric effect, which weakens the hydrogen bond, dominates over the electronic effect, which should strengthen the hydrogen bond.

Similarly, in 2-acetylcyclopent-4-ene-1,3-diones, the 4—5 double bond in the ring should weaken the hydrogen bond, as is found experimentally. Accordingly, 2-acetylindane-1,3-dione occupies an intermediate position. Ring current effects from the benzene ring may be estimated from the tables of Johnson and Bovey [25] to displace the signal of the enolic proton *ca.* 0.1 ppm towards lower field. 2-Acetylcycloheptane-1,3-dione is rather similar to 2-acetylcyclohexane-1,3-diones with regard to hydrogen bonding.

The present results thus indicate that steric effects are decisive for the strength of hydrogen bonds in enols of β-di- and β-tricarbonyl compounds.

## ENOL-ENOL TAUTOMERISM

In the discussion we have hitherto largely neglected the detailed structures of the conjugated chelates. However, there are several possibilities of enol-enol tautomerism which must be considered and may be studied by spectral methods.

For enolised β-dicarbonyl compound two chelated enolic forms are possible. The possible "internal tautomers"[13] differ by the location of the enolic proton near one or the other oxygen atom. Such enols may be rapidly interconverted. Fig. 3 shows the internal tautomers of 2-acetylcyclopentanone enol.

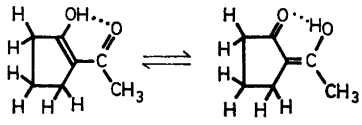

*Fig. 3.* The internal tautomers of enolic, chelated 2-acetylcyclopentanone.

For β-tricarbonyl compounds there are also possibilities for different "external" tautomers and therefore also for additional internal tautomers. Inter-

conversion of external tautomers is a comparatively slow process and the presence of external tautomers therefore shows up clearly in NMR spectra (Fig. 5, 7—10). The interconversion is accelerated by basic or acidic catalysts, *e.g.* triethylamine or trifluoroacetic acid. It is then possible to obtain an averaged spectrum of the external tautomers and thus to exclude the possibility that other types of isomerism cause the extra signals in the spectra.

The following discussion is largely limited to cyclopentane derivatives. It should be noted that the internal tautomers differ by having endocyclic or semicyclic enolic double bonds.

Internal tautomers may be interconverted by intramolecular displacement of the enolic proton along the hydrogen bond and concomitant rehybridisation. Proton transfer by tunneling should also be possible in these systems. Spectroscopic evidence for proton tunneling between hydrogen-bonded imidazole molecules has recently been presented by Zimmermann.[26] Interconversion of internal tautomers seems to be a rapid process and in NMR spectra separate signals from both of the limiting enols have not been observed.

Resonance fields and spin coupling constants observed for such rapidly interconverting tautomer mixtures should therefore be weighted averages of the "true values" for the limiting forms.[27] Studies of enolised aldehydes show that the resonance field of the "aldehydic" protons and the spin coupling between enolic and aldehydic protons exhibit the same trend.[10,27] Thus when the resonance field for the aldehydic proton approaches that found for *e.g.*, α-alkoxymethylene ketones, α-hydroxymethylene carbonitriles or β-hydrogens in α,β-unsaturated ketones (*i.e.* $\tau$ *ca.* 3), and the spin coupling reaches high values (above 10 c/s), one may conclude that the "hydroxymethylene forms" predominate.

The resonance for the enolic proton of 2-formylcyclopentanone occurs at distinctly higher field than in the enols of 2-formylcyclohexanone or 2-formyl-5,5-dimethylcyclohexane-1,3-dione which indicates the prevalence of 2-hydroxymethylenecyclopentanone (*cf.* Ref.[9]). However, no spin coupling between enolic and aldehydic protons is observed even at low temperatures. This is presumably due to intermolecular proton exchange accelerated by the acidity of the enol and also by traces of water from inevitable self-condensation. On the other hand, we have now observed a long-range spin coupling between the aldehydic proton and a methylene group in the ring (Fig. 4). Such coupling is also observed in 2-anilinomethylenecyclopentanone ($J$ = 1.9 c/s) but not in the enol of 2-formylcyclohexanone and provides additional evidence for the preponderance of 2-hydroxymethylenecyclopentanone form. This result should be compared with the generalisation by Brown, Brewster and Schechter that in simple compounds with five-membered rings semicyclic double bonds are favoured over those within the ring.[28]

The markedly different shifts observed for "aldehydic" protons in enolised β-oxo aldehydes indicate that it would be possible to evaluate the importance of internal tautomers in other enolic systems as well. For unsymmetrical diketones one would thus expect different resonance fields for signals from the limiting forms. A comparison of separate acetyl signals from ketonic and enolic forms of acetylacetone and acetoacetic esters indicates that the resonance fields for enolised and non-enolic acetyl groups differ by only *ca.* 0.1—0.2 ppm,

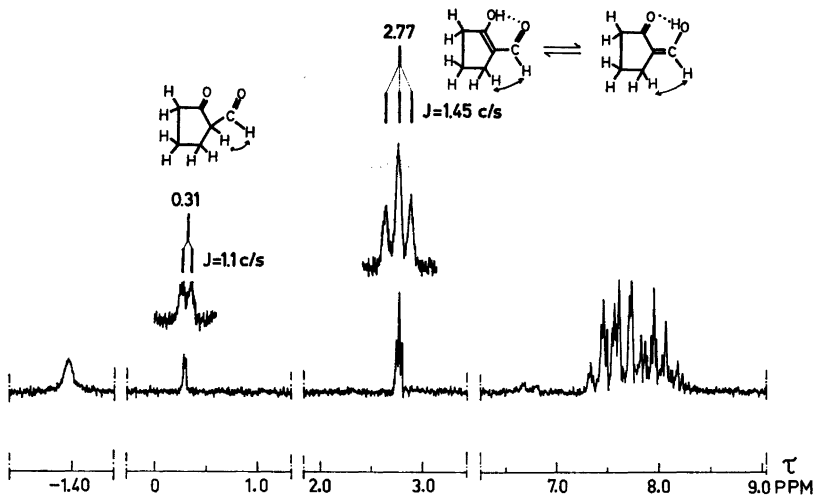


*Fig. 4.* NMR spectrum of 2-formylcyclopentanone, carbon tetrachloride solution.

signals from the enolised acetyl group occurring at higher fields. Spin coupling between enolic protons and adjacent alkyl protons is generally not observed. Recently, however, long-range couplings have been observed between enolic, acetylic and "olefinic" protons in the enol of ethyl acetoacetate.[29]

A comparison of the triketones shows slight differences between the resonance field for the acetyl groups; the 2-acetylcyclohexane-1,3-diones give the acetyl signal at *ca.* $\tau = 7.50$, 2-acetylcyclopentane-1,3-diones near 7.55 and 2-acetylcyclopent-4-ene-1,3-diones near 7.70. However, the diamagnetic anisotropy effect of the non-chelated carbonyl group may be expected to give similar differences, and therefore safe conclusions cannot be drawn.

In 2-acetylcyclopentanone and 2-acetylcyclohexanone no such anisotropy effect disturbs the comparison and other anisotropy effects should be nearly equal. The acetyl signal for the enol of 2-acetylcyclopentanone is found at $\tau = 8.06$, whereas 2-acetylcyclohexanone gives the signal at $\tau = 7.95$. In this case it seems reasonable to assume that the difference is due to the preponderance of the enolic form with a semicyclic double bond for the cyclopentane derivative.

The fact that the infrared spectra show two bands in the lower carbonyl region for the enolised 2-acetylcyclopentane-1,3-diones, 2-acetylcyclopent-4-ene-1,3-diones, and for 2-acetylcyclopentanone, as discussed above, could be interpreted in terms of two concurrent internal tautomers. The extinction coefficient for the carbonyl absorption in cyclopentanone is *ca.* 50 % higher than that for acetylcyclopentane. A corresponding difference is found between the two carbonyl bands from the diketo form of 2-acetylcyclopentanone (Fig. 1). If this were also true for chelated carbonyl groups the approximately equal intensities of the two bands would indicate that the tautomers with semicyclic enol double bonds are somewhat favoured.

In this connection it should be noted that molecular orbital calculations of the Hückel type on the enolised 2-acetylcyclopent-4-ene-1,3-dione system predict the highest delocalisation energy for $\pi$-electrons in the enolic form where the enolic double bond is semicyclic.[30]

The presence of external tautomers was noted for all the unsymmetrical $\beta$-triketones and for $\alpha$-acetyltetronic acid. Fig. 5 shows how the two forms of

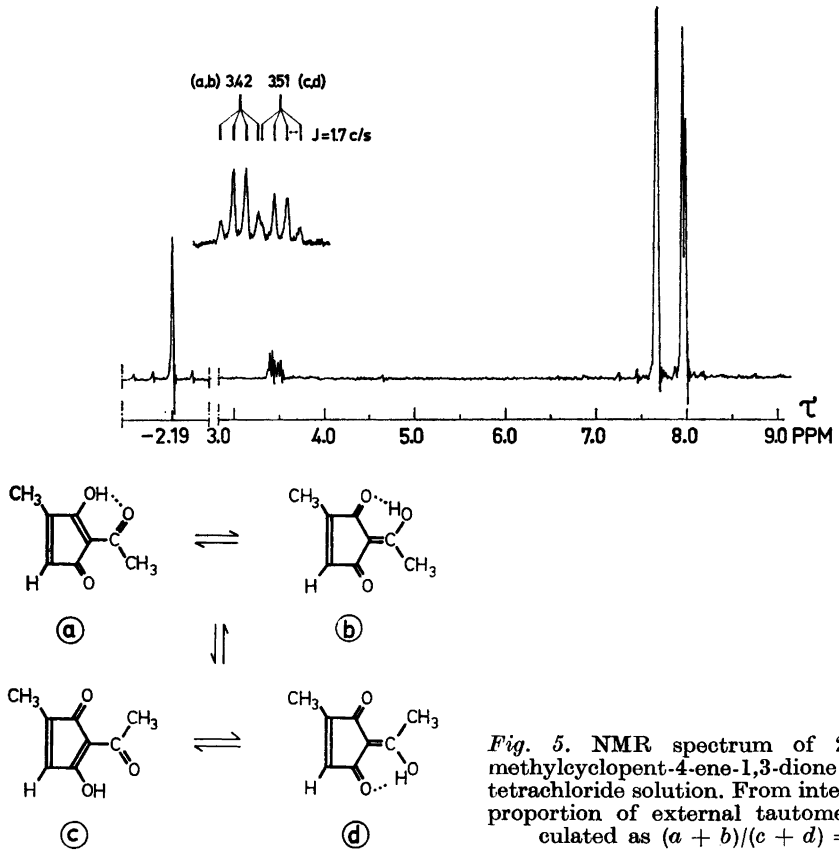


*Fig. 5.* NMR spectrum of 2-acetyl-4-methylcyclopent-4-ene-1,3-dione in carbon tetrachloride solution. From intensities the proportion of external tautomers is calculated as $(a + b)/(c + d) = 1.6$.

2-acetyl-4-methylcyclopent-4-ene-1,3-dione give superimposed spectra. For the symmetrical compounds, *e.g.* 2-acetylcyclopentane-1,3-dione and 2-acetylcyclopent-4-ene-1,3-dione, the external tautomers are identical. However, in the NMR spectra the non-equivalence of the protons in positions 4 and 5 show that the interconversion of the identical, external tautomers is a slow process (Fig. 6).

In contrast to other splittings due to external tautomerism only single hydroxyl signals were observed. For compounds with strong intramolecular hydrogen bonds the signals for the enolic protons in the external tautomers have been separated.[7,9] Indication has also once been obtained for separate

hydroxylic signals for external tautomers of cohulupone.[11] In the present series intermolecular proton exchange seems to proceed faster than the interconversion of external tautomers. This was demonstrated by an NMR spectrum

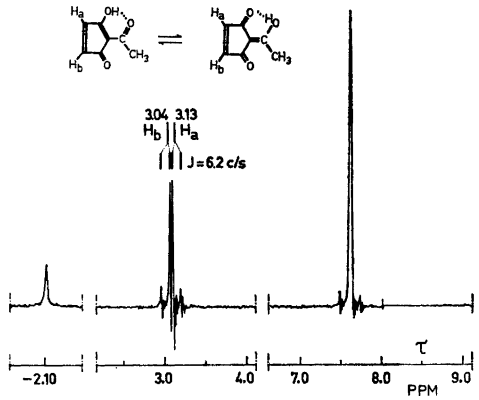


*Fig. 6.* NMR spectrum of 2-acetylcyclopent-4-ene-1,3-dione in carbon tetrachloride solution.

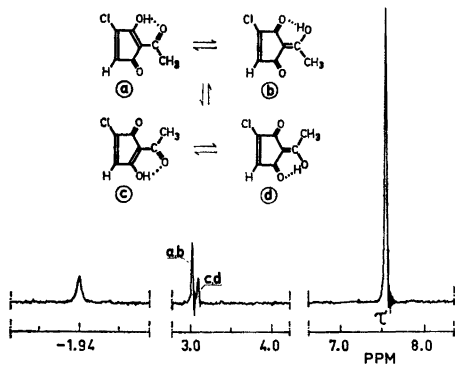


*Fig. 7.* NMR spectrum of 2-acetyl-4-chlorocyclopent-4-ene-1,3-dione in chloroform-*d* solution; $(a + b)/(c + d) = 2.4$. In carbon tetrachloride this ratio is reversed to 0.22.

recorded for a mixture of 2-acetylindane-1,3-dione and 2-acetyl-4-methylcyclopent-4-ene-1,3-dione in carbon disulphide. Here only *one* signal was observed for the enolic protons at a resonance field half-way between those found in the spectra of the separate compounds. At the same time the occurrence of *two* quartets (*cf.* Fig. 5) from the olefinic hydrogen in 2-acetyl-4-methylcyclopent-4-ene-1,3-dione shows that two external tautomers are present. The interconversion of these is in turn accelerated by catalytic amounts of triethylamine as shown by the averaging of the spectrum.

Some information about the relative stability of the external tautomers may be obtained from the NMR spectra albeit the assignment of the forms is not as certain as for acyclic β-tricarbonyl compounds in which two of the acyl groups are identical.[7]

Some conclusions regarding the equilibria between external tautomers are given in Figs. 5 and 7—10, and are briefly commented upon below.

For 2-acetyl-4-methylcyclopent-4-ene-1,3-dione (Fig. 5) it seems reasonable to assign the C—H quartet at the lowest field to the tautomeric pair *a*—*b* and the high-field quartet to the forms *c*—*d*. The diamagnetic anistropy of carbonyl groups is known to cause deshielding of neighbouring protons situated in the trigonal C—C=O plane. The anisotropy effect can be expected to be more pronounced in the forms *a*—*b* than in the forms *c*—*d* since it is unlikely that the equilibrium $c \rightleftharpoons d$ is completely in favour of form *d*. Similar arguments apply for 2-acetyl-4-chlorocyclopent-4-ene-1,3-dione (Fig. 7).

The carbonyl group should also have a deshielding effect on protons at adjacent saturated carbon atoms when the C—C=O plane approximately

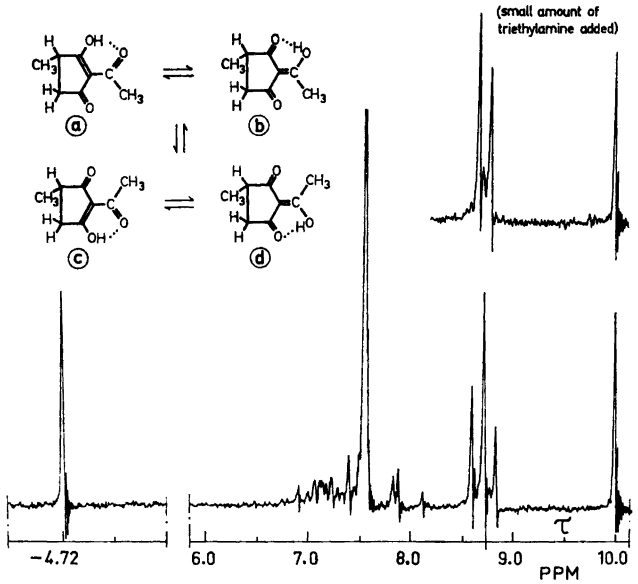


*Fig. 8.* NMR spectrum of 2-acetyl-4-methylcyclopentane-1,3-dione in carbon tetrachloride; $(a + b)/(c + d) \sim 1$.

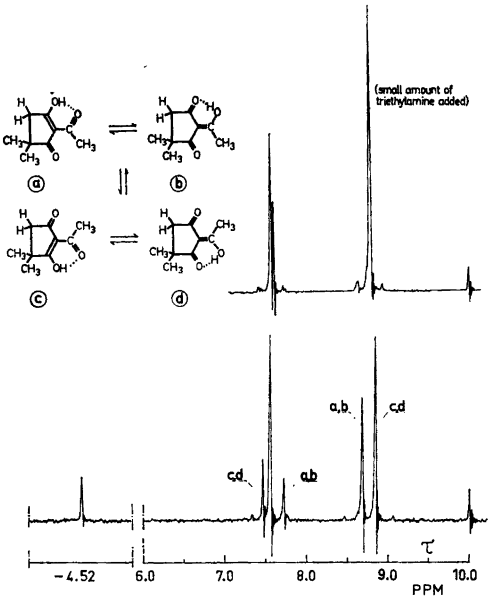


*Fig. 9.* NMR spectrum of 2-acetyl-4,4-dimethylcyclopentane-1,3-dione in carbon tetrachloride; $(a + b)/(c + d) = 0.70$.

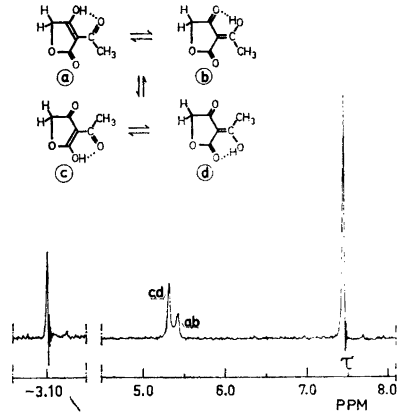


*Fig. 10.* NMR spectrum of α-acetyltetronic acid in chloroform-*d*; $(a + b)/(c + d) = 0.45$.

bisects the H—C—H angle as in 2-acetylcyclopentane-1,3-dione. Similarly, there is a slight deshielding of 4-methyl groups in these systems (Figs. 8 and 9). On the other hand the anistropy effect on methyl protons in 2-acetylcyclopent-4-ene-1,3-diones seems to be very small.

For α-acetyltetronic acid (Fig. 10) the presence of external tautomers was deduced from the splitting of the ring methylene signal in the NMR spectrum. The splitting was similar to that found for the two methylene groups in 2-acetylcyclopentane-1,3-dione or for the external tautomers of 2-acetyl-4,4-dimethylcyclopentane-1,3-dione. The assignment is facilitated by the fact that the aniostropy of the lactone carbonyl group on the methylene protons should be negligible. We therefore conclude that the signal at low field is due to the dominant pair *a*—*b*. The infrared spectrum of α-acetyltetronic acid has been discussed by Duncansen, who pointed out that the spectrum of the solid compound was similar to those from solutions.[31] There are some differences, however: thus, the solid gives three bands; in solutions the "central carbonyl band" is split into two at *ca.* 1675 and 1700 $cm^{-1}$, the intensities of which vary with the solvent. The high-frequency band, which is apparently due to the non-chelated lactone carbonyl, occurs near 1770 $cm^{-1}$ in solution. The splitting in the IR solution spectra could well be due to both internal and external tautomerism as the high-frequency band is relatively weaker in solution. Far-reaching conclusions should not be drawn, however, since it is known that unsaturated lactones and similar compounds often show a complex IR pattern, which is solvent-dependent and not well understood.[32]

It should be pointed out that molecular orbital calculations with the Hückel method indicate that the delocalisation energy for forms 13 *a*—*b* is higher than for 13 *c*—*d*, and thus that the former should be more stable, in accord with the experimental findings.

## EXPERIMENTAL

*Methods.* The NMR spectra were recorded on a Varian A-60 spectrometer operating at 60.007 Mc/s for 5—8 % solutions. Tetramethylsilane was used as internal standard and the resonance fields are reported as τ-values.[33] The sample temperature was 34 ± 1°. The calibration of the spectrometer was frequently checked with modulation side bands generated by a Hewlett-Packard Model 200 CD audio oscillator. The modulation frequencies were measured with an electronic counter, Hewlett-Packard model 5512 A.

The IR spectra were recorded on a Perkin Elmer No. 21 instrument equipped with a sodium chloride prism. The calibration was frequently checked towards air and frequencies should be accurate within 5 $cm^{-1}$. Solvent absorption was compensated with a variable path-length cell.

*Materials.* The triketones were prepared from anhydrides of dicarboxylic acids and isopropenyl acetate as described in separate papers where physical constants, etc., are also given. Di- and triketones were purified *via* the copper salts and sublimed or distilled. The numbering of the compounds corresponds to that in Table 1 and in the figures.

1. 2-Acetylcyclopentane-1,3-dione.[14]
2. 2-Acetyl-4-methylcyclopentane-1,3-dione.[3]
3. 2-Acetyl-4,4-dimethylcyclopentane-1,3-dione.[3]
4. *cis* 2-Acetyl-3a,4,7,7a-tetrahydroindane-1,3-dione.[15]
5. 2-Acetylindane-1,3-dione.[3]
6. 2-Acetylcyclopent-4-ene-1,3-dione.[15]
7. 2-Acetyl-4-chlorocyclopent-4-ene-1,3-dione.[15]

8. 2-Acetyl-4-methylcyclopent-4-ene-1,3-dione.[15]
9. 2-Acetyl-4,5-dimethylcyclopent-4-ene-1,3-dione.[15]
10. 2-Acetylcyclopentanone; from the pyrollidine enamine of cyclopentanone in analogy with compound (17)[34], b.p. 77–78°/10 mm, lit. b.p. 82–86°/12 mm.[35]
11. 2-Formylcyclopentanone; from cyclopentanone and ethyl formate with sodium hydride/sodium ethoxide in ether. M.p. 76–77°, lit. m.p. 76–77°.[36]
12. 2-Anilinomethylenecyclopentanone from compound (11) with aniline. Recrystallised from methanol and sublimed, m.p. 176–178° (thermochromic). (Found: C 76.7; H 7.1; N 7.5. Calc. for $C_{12}H_{13}NO$: C 77.0; H 7.0; N 7.5).
13. α-Acetyltetronic acid.[37] M.p. 81–82°, lit. m.p. 81–82°.[37]
14. 2-Acetylcyclohexane-1,3-dione.[14]
15. 2-Acetyl-5,5-dimethylcyclohexane-1,3-dione.[3] *Cf.* also Part I.[6]
16. 2-Formyl-5,5-dimethylcyclohexane-1,3-dione, data taken from Part 5.[10]
17. 2-Acetylcyclohexanone according to Stork *et al.*[34]
18. 2-Formylcyclohexanone, data taken from Part 5.[10]
19. 2-Acetylcycloheptane-1,3-dione.[3]

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