

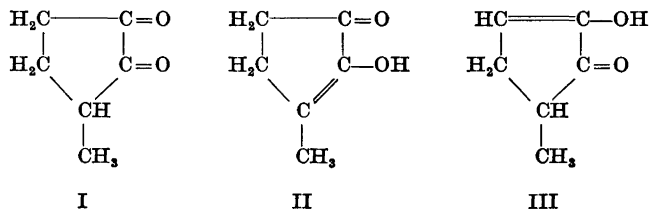
## The Enol Structure of 3-Methylcyclopentane-1,2-dione

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Nuclear magnetic resonance investigations show that 3-methylcyclopentane-1,2-dione occurs as the enol 3-methylcyclopent-2-en-2-ol-1-one.

The  $\alpha$ -diketone 3-methylcyclopentane-1,2-dione (I), a compound which has been found in soluble wood tar <sup>1</sup> and tall light oil <sup>2</sup> and which is formed by alkaline digestion of spruce wood or galactose <sup>3</sup>, has been shown to occur as a monoenol in the crystalline form as well as in solution <sup>4,5</sup>.



Two different enol structures (II, III) can be written for the compound. Both structures have been previously used <sup>4,6,7</sup>. Hesse and Breig <sup>8</sup> have recently tried to solve the problem of the direction of the enolisation by chemical methods. Halogenation and oxidation studies led them to advance structure III. The evidences are not, however, convincing, since the structures of the most important products were not unambiguously proven. In addition, it has to be remarked that substitution in the 5-ring has an influence that is not easily anticipated. The solution to the problem has therefore to be found in such physical methods as do not influence the tautomerism. An excellent method for this purpose is nuclear magnetic resonance spectrometry. The nmr spectrum of the compound in  $\text{CDCl}_3$  with tetramethylsilane as an internal reference is given in Fig. 1 a. This spectrum shows conclusively that the compound has the structure II. The methyl resonance appears as a single peak at a  $\tau$  value <sup>9</sup> of 7.97. The methylene groups are apparently nearly equivalent and give the resonance at  $\tau$  7.57. In view of the known influence of a keto

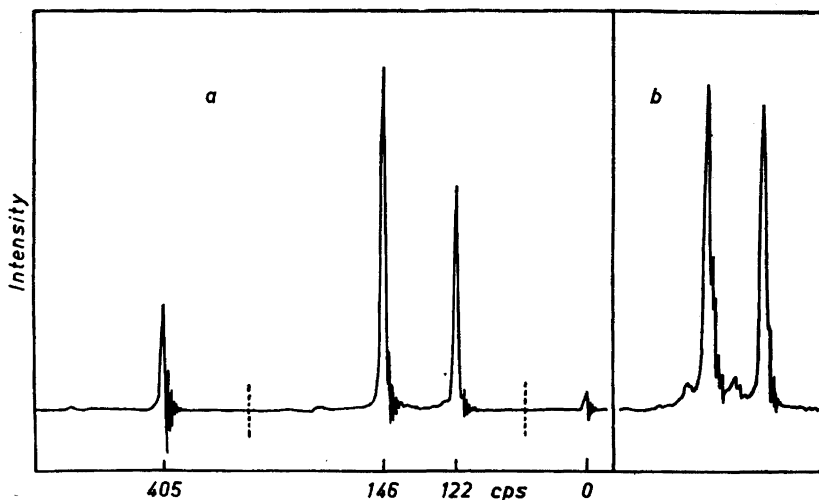


Fig. 1. Nuclear magnetic resonance spectra of 3-methyl-cyclopent-2-en-2-ol-1-one in *a*. CDCl<sub>3</sub> solution, internal reference tetramethylsilane (parts of the base line are omitted at the broken lines), *b*. pyridine solution.

group and a double bond, respectively, in  $\alpha$ -position to the methylene groups<sup>10</sup> the equivalence of the groups seems to be quite natural. The position at a  $\tau$  value of 3.25 confirms the enol nature of the single proton peak. The areas appear to be in the ratio 3:4:1 which also tallies with structure II. Structure III would have given a much more complicated spectrum, *inter alia* a doublet for the methyl resonance. The nmr spectrum in pyridine did not reveal any shift in the enol equilibrium. However, the solvent effect had made the two methylene groups slightly non-equivalent and the spin-coupling between them was beginning to appear as a number of weak satellites (Fig. 1 *b*). The temperature was varied from the freezing to the boiling point of CDCl<sub>3</sub> with no evidence of anything but the enol form. These results, as well as infrared and ultraviolet investigations, show that the compound does not occur as an equilibrium mixture between the different tautomeric forms. Hesse and Breig<sup>8</sup> arrived at the same conclusion. Structure II finds further support from the absence of bands in the olefinic C-H stretching region of the infrared spectrum in CCl<sub>4</sub> (Fig. 2 *b*).

The enol structure II is the sterically favoured form since the C-methyl bond is staggered in relation to the C—H bonds on the adjacent atom in contrast to structure III where the C-methyl bond is opposed to one C—H bond. Hyperconjugation also favours structure II. The inductive effect of the methyl group which Hesse and Böckmann<sup>7</sup> thought to be operative in the tautomerism can be observed in the ionisation of the enol. For the unsubstituted compound, cyclopent-2-en-2-ol-1-one, the pK value is 9.14, and for compound II it is 9.60<sup>5</sup>. This can be accounted for by structure II (compare phenol, pK 9.94, and *o*-cresol, pK 10.28<sup>11</sup>). It is not possible, however, that the methyl group

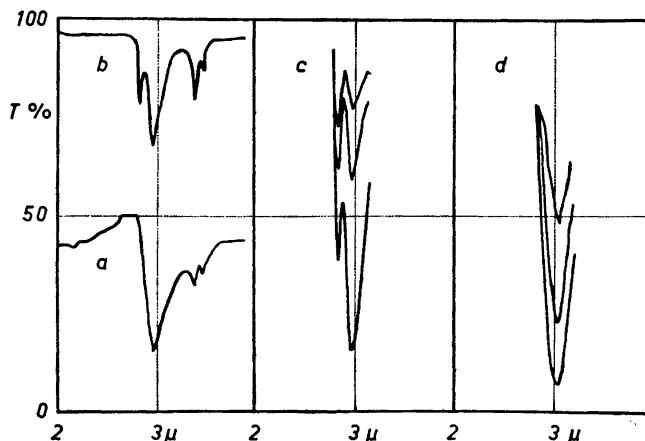


Fig. 2. Infrared spectra in the 2–4  $\mu$  region of 3-methylcyclopent-2-en-2-ol-1-one, *a*, pellet, 2 mg in 300 mg KBr, *b*, saturated solution in carbon tetrachloride, *c*, solutions in chloroform, 1 g in 10, 30, and 50 ml, *d*, solutions in dioxan, 1 g in 10, 30, and 50 ml. All solutions in 0.1 mm cell.

in structure III should have had such a strong influence on the ionisation constant. A similar difference in the  $pK$  values is found in cyclohex-2-en-2-ol-1-one and its 3-methyl homologue, the respective values being 10.30 and 11.23<sup>5</sup>. This also confirms the enol structure for the last-mentioned compound advanced by Wallach<sup>12</sup> in connection with his investigations of the structure of diosphenol.

Methyl cyclopentenolone is intermolecularly associated in the crystalline form, the OH stretching band absorbing at 3350  $\text{cm}^{-1}$  (Fig. 2 *a*). This band is also found in the carbon tetrachloride and chloroform solutions (Fig. 2 *b*, *c*). In these solutions there appears an additional band at 3530  $\text{cm}^{-1}$  which is strengthened upon dilution, the band at 3350  $\text{cm}^{-1}$  at the same time being weakened. The band at 3530  $\text{cm}^{-1}$  therefore corresponds to a chelate which, as a 5-ring hydrogen bridge, is rather weak. In dioxan the compound shows only one band at 3280  $\text{cm}^{-1}$  (Fig. 2 *d*).

#### EXPERIMENTAL

3-Methylcyclopent-2-en-2-ol-1-one, purum, Fluka A.-G., m. p. 106.5°, was used without further purification.

The nmr spectra were taken at Varian Associates, Palo Alto, California, with a 60 Mc High Resolution NMR Spectrometer. The infrared spectra were taken with a Beckman IR-5 spectrophotometer and the ultraviolet spectra with a Beckman DK-2 spectrophotometer.

*Infrared maxima.* Keto band,  $\text{cm}^{-1}$ , cryst. 1710, in  $\text{CHCl}_3$  1715, in  $\text{CCl}_4$  1715; double bond,  $\text{cm}^{-1}$ , cryst. 1650, in  $\text{CHCl}_3$  1667, in  $\text{CCl}_4$  1670.

*Ultraviolet maxima.* Water,  $\lambda_{\text{max}}$  256  $\text{m}\mu$  (log  $\epsilon$  4.14); ethanol,  $\lambda_{\text{max}}$  258–259  $\text{m}\mu$  (log  $\epsilon$  4.15); cyclohexane,  $\lambda_{\text{max}}$  251  $\text{m}\mu$  (log  $\epsilon$  4.15).

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