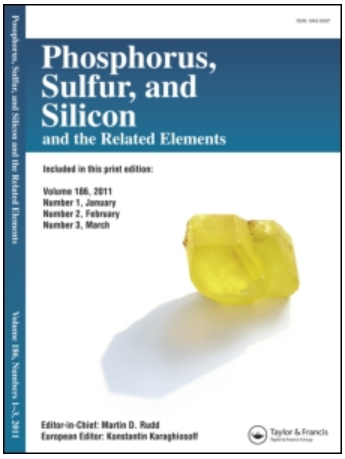

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ENOL-ENETHIOL TAUTOMERISM OF β-THIOXOKETONES

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ENOL-ENETHIOL TAUTOMERISM OF β-THIOXOKETONES

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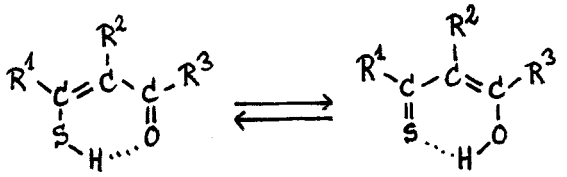
Unless being unsuitably substituted at the α-position, β-thioxoketones exist in the neat liquid state as well as in solution as equilibrium mixtures of two tautomeric forms, the cis-enethiol form (I) and the cis-enol form (II), the interconversion between these taking place by intramolecular proton-transfer at a rate so fast that ^{1}H n.m.r. spectra of β-thioxoketones are to be interpreted in terms of weighted average spectra of those of the individual tautomers (I) and (II). However, (I) and (II) are distinguishable by u.v.-spectroscopy. The spectral data of a series of β-thioxoketones have been correlated to a theoretical model describing the tautomeric interconversion in terms of weighted average chelate proton shifts and u.v.-absorbances of the S-C=C-C=O and S=C-C=C-O chromophores from (I) and (II), respectively. The correlation is expressed mathematically by equation



(I) (II)

$$\frac{A_{II}}{A_I} = \frac{\varepsilon_{II}}{\varepsilon_I} \frac{\delta_{obs}-\delta_I}{\delta_{II}-\delta_{obs}} \qquad \text{(III)}$$

(III), where A_I and A_{II} are the measurable u.v.-absorbances mentioned above, ε_I and ε_{II} are corresponding molar absorption coefficients, δ_{obs} represents the observable average chelate proton chemical shift, and δ_I and δ_{II} denote chelate proton shifts of a hypothetical reference enethiol, and a hypothetical reference enol, respectively.

The applicability of this model as a tool for the determination of the site of the tautomeric equilibrium displacements of actual enol-enethiol tautomeric systems will be illustrated and discussed.