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## ENOL-ENETHIOL TAUTOMERISM OF $\beta$ -THIOXOKETONES

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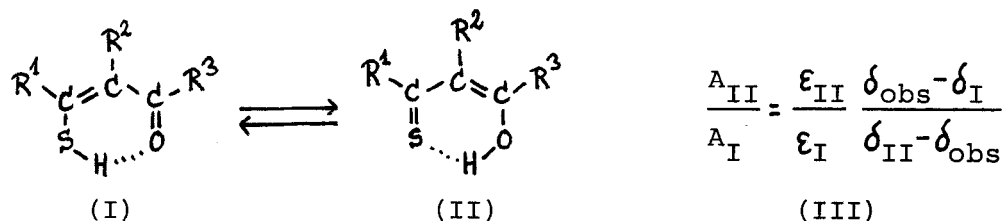
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## ENOL-ENETHIOL TAUTOMERISM OF $\beta$ -THIOXOKETONES

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Unless being unsuitably substituted at the  $\alpha$ -position,  $\beta$ -thioxo-  
ketones 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  $^1\text{H}$  n.m.r. spectra of  $\beta$ -thioxoketones are to be in-  
terpreted 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 se-  
ries of  $\beta$ -thioxoketones have been correlated to a theoretical  
model describing the tautomeric interconversion in terms of wei-  
ghted average chelate proton shifts and u.v.-absorbances of the  
 $\text{S}=\text{C}=\text{C}=\text{O}$  and  $\text{S}=\text{C}-\text{C}=\text{C}-\text{O}$  chromophores from (I) and (II), respec-  
tively. The correlation is expressed mathematically by equation



(III), where  $A_{\text{I}}$  and  $A_{\text{II}}$  are the measurable u.v.-absorbances men-  
tioned above,  $\epsilon_{\text{I}}$  and  $\epsilon_{\text{II}}$  are corresponding molar absorption co-  
efficients,  $\delta_{\text{obs}}$  represents the observable average chelate proton  
chemical shift, and  $\delta_{\text{I}}$  and  $\delta_{\text{II}}$  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 discus-  
sed.