# β-Thioxo-ketones. Part 5.[1] Photo-induced Enol–Enethiol Interconversion of β-Thioxo-ketones †

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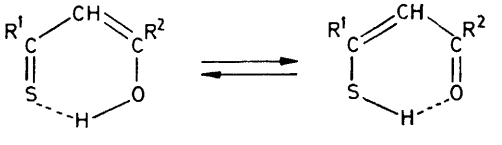
Thioacetylacetone, which exists in 2-methylbutane–methylcyclohexane (5 : 1) solution at 95 K exclusively as the intramolecularly hydrogen-bonded enol tautomer, is converted upon irradiation at 353 nm into the corresponding enethiol tautomer, characterized by its absorption at 288 nm. The reverse process takes place upon irradiation of the enethiol tautomer at 288 nm. Both processes are successively repeatable. Other isomeric and/or tautomeric forms have not been observed. Monothiodibenzoylmethane behaves similarly upon photolysis at 95 K.

It has recently been demonstrated that β-thioxo-ketones, which are not substituted unsuitably in the α-position, in solution at room temperature exist as rapidly interconverting intramolecularly chelated *Z*-enol (a) and *Z*-enethiol (b) tautomers,[1-3] the enol form usually being, thermodynamically, the more favoured isomer.[1]



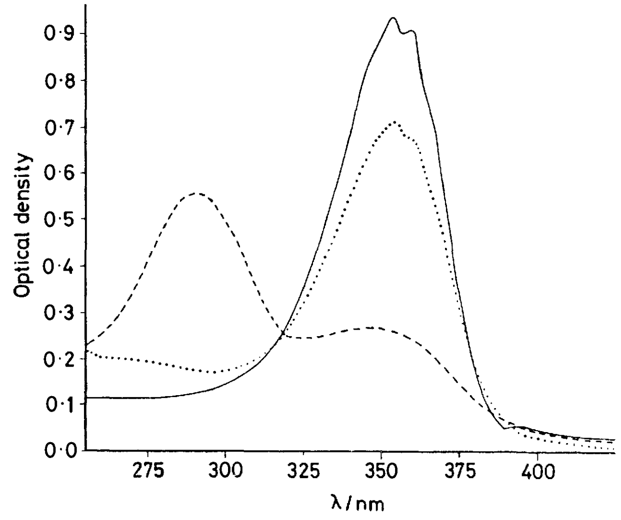
(a) (b)

(1) R$^1$ = R$^2$ = Me

(2) R$^1$ = R$^2$ = Ph

Parallel studies [4] of a variety of β-thioxo-ketones have shown that these compounds at 95 K exist as the enol tautomers exclusively. This fact constitutes an advantageous starting position for studying photolytic generation of thermally less-stable isomers. Recent reports on the photolysis of β-diketones [5,6] have demonstrated conversion of the chelated enol form into the diketo-isomer by photoisomerization. A flash photolytic study has proved the intermediacy of a thermally highly labile compound, suggested by the authors to be the non-chelated enolic structure.[6] Here we report on the photolyses of $10^{-4}$M solutions in MPH ‡ of thioacetylacetone (1a, b) [2] and monothiodibenzoylmethane (2a, b) [8] at 95 K in attempts to study possible intramolecular photoinduced transformations of the β-thioxo-ketone system.

At room temperature thioacetylacetone exhibits two absorption bands at 296 and 354 nm ($C_6H_{12}$), which are assigned to the π,π* HSC=CC=O and the π,π* S=CC=COH chromophores, respectively.[2] However, at 95 K only one transition was observed at 353 nm as a result of the exclusive existence of the enol tautomer (1a) at this temperature. Irradiation of (1a) at 95 K ($\lambda_{ex}$ = 353 nm ± 15 nm) resulted in a decrease of the 353 nm band with simultaneous appearance of a new absorption band with $\lambda_{max.}$ = 288 nm (see Figure). Upon prolonged irradiation the 353 nm band almost disappeared (Figure) whilst that at 288 nm increased. The weak absorption at 353 nm present even after prolonged photolysis is considered to be a result of concurrent photolysis of the new chromophore by excitation of the tail of the 288 nm absorption band;§ the absorption spectrum depicted in the Figure (b) thus reflects a steady-state situation. This assumption is, furthermore, confirmed by the fact that irradiation of the new absorption band ($\lambda_{ex}$ = 288 ± 15 nm) results in a decrease in the intensity of this band and, eventually, in the reappearance of the original spectrum of (1a) (Figure, c). The enol (1a) was hereby re-formed in 80% yield (based on the electronic absorption spectra). On the basis of the above we suggest that the spectrum depicted in Figure (c) reflects a steady-state situation due to unavoidable rephotolysis of the re-formed (1a). This probably also accounts for



a (—): electronic absorption spectrum of chelated enolic thioacetylacetone at 95 K (MPH); b (– – – –): spectrum after prolonged irradiation (50 min) into the 353 nm band; c (· · · ·): spectrum after prolonged irradation (45 min) of the new developed 288 nm absorption

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† The β-thioxo-ketones are named as such for simplicity, regardless of which of the possible tautomeric forms is dominant (in general these are the intramolecularly chelated enol and/or enethiol forms).

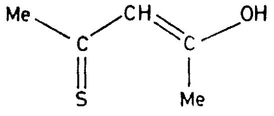
‡ MPH: 2-methylbutane–methylcyclohexane (5 : 1). This mixture stays liquid to 81 K.[7] At room temperature monothiodibenzoylmethane (2a, b) was found to be stable towards photolysis. The apparent stability can be explained by rapid thermal relaxation processes of possible formed labile products.

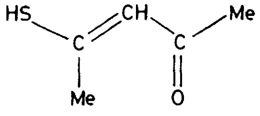
§ This rephotolysis is practically unavoidable due to the band width (±15 nm) of the exciting light.

the apparent discrepancy between the yield of (1a) upon irradiation of the 288 nm absorption, and the theoretical yield. The photoinduced interconversion between the enol (1a), absorbing at 353 nm, and the species absorbing at 288 nm can be continued by successive changes of the wavelength of the exciting radiation between 353 and 288 nm. The compound responsible for the 288 nm absorption was found to be thermally stable at 95 K.

Excluding the thioxo-ketone structure of thioacetylacetone, which is not expected to exhibit absorptions from $\pi,\pi^*$ chromophores above 250 nm, three structures apparently remain to be discussed as candidates responsible for the 288 nm absorption: the chelated enethiol (1b), the non-chelated enol (1c), and the non-chelated enethiol (1d).

The first candidate, the chelated enethiol (1b), seems to account well for the observed electronic absorption spectrum, since (1b) at room temperature exhibits an absorption maximum at 296 nm. The small blue shift observed at low temperature (8 nm) is explained fully by effects due to the difference in temperature.[9] On the other hand, compound (1c) scarcely seems to account for the observed spectrum. The absorption band of non-chelated enolic acetylacetone is reported to be 21 nm blue-shifted relative to that of the chelated enol form.[6] Thus the observation of a 65 nm blue shift on photolysis of (1a) (see Figure) suggests (1c) as a less obvious originator for the 288-nm absorption band. Further evidence against the candidature of (1c) was obtained by studying the electronic absorption spectrum of a sample photolytically converted into the species responsible for the 288-nm absorption upon heating. At temperatures around 130—150 K the 288-nm band was almost totally eradicated, in favour of that of (1a); this phenomenon is in complete agreement with the predicted very low activation barrier for the thermal enethiol–enol conversion (1b) $\longrightarrow$ (1a).[1] Unfortunately, activation parameters for the conversion from non-chelated enol to chelated enol in acetylacetone have not been reported; however, the half-life of the non-chelated enolic acetylacetone has been estimated at room temperature to be 2.6 s,[6] which, drawing a parallel to thioacetylacetone, most probably rules out the occurrence of a rapid *trans–cis* enolic conversion at 130 K. Furthermore, from current studies [10] of *cis*-enethiol–*trans*-enethiol interconversion of the related compound 2-thiobenzoylpentan-3-one, we have estimated the barrier of activation to be *ca.* 46 kJ mol$^{-1}$ for the *cis–trans* conversion. In view of these facts we rule out (1c) as well as (1d) as candidates responsible for the 288-nm absorption. Thus the observed photo-induced spectral changes most certainly reflect the enol–enethiol interconversion (1a) $\rightleftharpoons$ (1b). There was no evidence indicating the presence of other isomers and/or tautomers.


(1c)


(1d)

At still higher temperatures (>240 K) the enethiol spectrum reappeared (reflecting the higher enol to enethiol conversion barrier [1]) and, finally, the usual room-temperature spectrum [2] was obtained.

Upon photolysis of monothiodibenzoylmethane * a similar picture, as for thioacetylacetone developed. At 95 K the enol (2a) exhibited two absorption maxima at 335 and 416 nm, assignable [1,4] to the $\pi,\pi^*$ PhC=S and the $\pi,\pi^*$ HOC=CC=S chromophores, respectively. Irradiation of the HOC=CC=S chromophore (416 nm) resulted in a decrease of the 416 nm and the 335 nm absorptions, giving rise to a simultaneous development of a new absorption band at $\lambda_{max.} = 326$ nm. Irradiation of the PhC=S chromophore (335 nm) on the other hand caused no spectral changes. However, rephotolysis of the newly developed 326 nm absorption afforded the original enol (2a) in 70% yield. By drawing a comparison with the above discussion of the spectrally much simpler (1a, b) interconversion, we assign the 326-nm absorption band to the chelated enethiol (2b). Hence, the apparent photo-inactivity of the PhC=S chromophore can be explained by an immediate unavoidable rephotolysis of (2b), absorbing at 326 nm, back to (2a).

The results described above strongly support the occurrence of an intramolecular photoinduced enol–enethiol interconversion in the β-thioxo-ketone system, whereas evidence for concurrent transformations, *e.g. cis–trans* isomerization is lacking.

## EXPERIMENTAL

β-*Thioxo-ketones*.—Thioacetylacetone was prepared by action of hydrogen sulphide and hydrogen chloride on acetylacetone.[2] Monothiodibenzoylmethane was prepared by condensation of acetophenone with *o*-ethyl thiobenzoate.[8]

*Low-temperature Photolysis and Spectroscopy*.—The low-temperature u.v. cell used was constructed by the Inorganic Department, University of Copenhagen. It is, in principle, a three-walled Dewar made of steel. The six quartz windows are sealed to the steel with indium washers. The frozen solution is contained in the inner chamber, while high vaccum is maintained in the outer jacket. Heat transport is furnished by a helium atmosphere contained in the middle jacket in contact with liquid nitrogen as well as with the sample cell. The temperature was kept at 95 K except for cooling and heating periods. The electronic absorption spectra were recorded with a Cary 14 instrument. The samples of the β-thioxo-ketones in MPH were irradiated outside the spectrograph with a Bausch and Lomb SP200 mercury point source equipped with a monochromator (thioacetylacetone) or with interference filters (monothiodibenzoylmethane), respectively.

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* At room temperature monothiodibenzoylmethane exhibits three absorption maxima at 262 nm (PhC=O, PhC=C), 325 nm (PhC=S, HSC=CC=O), and 408 nm (S=CC=COH), respectively.[14]

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