

Acknowledgments. We thank Dr. T. G. Waddell for help in the synthesis of ^{14}C -labeled compounds. This research was supported in part by the National Institute on Drug Abuse and the Division of Biomedical and Environmental Research of ERDA.

References and Notes

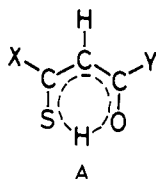
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Communications to the Editor

Conjugative Effects on the Enol-Enethiol Tautomerism of β -Thioxoketones^{1,2}

Sir:

Aliphatic and alicyclic β -thioxoketones^{3,4} are known to be rather unstable compounds, in contrast to the aromatic β -thioxoketones⁵ which can be stored for long periods without appreciable decomposition. This difference in stability may possibly originate from structural dissimilarities, since an electron-delocalized "quasi-aromatic" structure **A** may be of



importance in solution for the aromatic compounds. A structure of this type has been proposed recently for both aliphatic and aromatic β -diketones on the basis of ^1H and ^{13}C NMR spectroscopic studies.⁶⁻⁸ It has been shown^{3,4} that aliphatic and alicyclic β -thioxoketones exist as equilibrium mixtures of the tautomeric (Z)-enol (**B**) and (Z)-enethiol (**C**) forms which interconvert very rapidly (on the NMR time scale) by intramolecular chelate proton transfer. It seems reasonable to assume that the introduction of flanking aryl substituents (X, Y = Ar) may lead to enhanced stabilization of a central "quasi-aromatic" ring by conjugative effects. Structure **A** should, strictly speaking, be regarded as a borderline case of the equilibrium system $\text{B} \rightleftharpoons \text{C}$ at continuous lowering in the energy barrier for the interconversion. With this in mind we decided to investigate theoretically the influence of conjugative effects on this equilibrium (Scheme I).

We have calculated⁹ the energy barriers for the enol-enethiol interconversion of four model compounds, the hypothetical β -thioxocarbonyls **1-4**. The bonding energies for the enol and enethiol structures were minimized with respect to all internal atomic coordinates, and the energies of 13 intermediate states, corresponding to stepwise intramolecular chelate proton transfer from the energy-minimized structure **B** to the energy-minimized structure **C**, were determined for

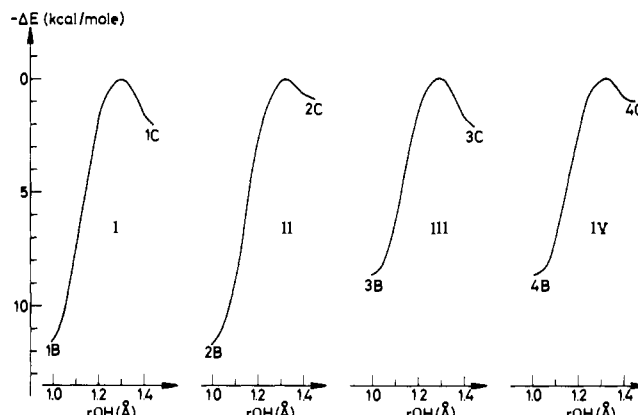
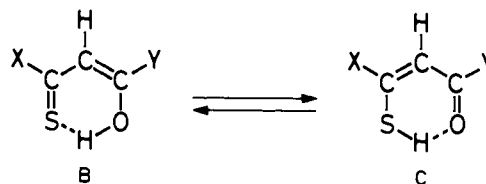


Figure 1. Theoretically derived energy profiles for the interconversions $1\text{B} \rightleftharpoons 1\text{C}$ (I), $2\text{B} \rightleftharpoons 2\text{C}$ (II), $3\text{B} \rightleftharpoons 3\text{C}$ (III), and $4\text{B} \rightleftharpoons 4\text{C}$ (IV).

Scheme I



- | | |
|-------------------------|--|
| 1 : X, Y = H, H | 5 : X, Y = CH_3 , CH_3 |
| 2 : X, Y = H, Vinyl | 6 : X, Y = CH_3 , C_6H_5 |
| 3 : X, Y = Vinyl, H | 7 : X, Y = C_6H_5 , CH_3 |
| 4 : X, Y = Vinyl, Vinyl | 8 : X, Y = C_6H_5 , C_6H_5 |

each pair of tautomers by continuous variation of all geometric parameters. The energy profiles found for the four interconversions are depicted in Figure 1, the transition-state energies being chosen arbitrarily as zero points.

It can be seen from Figure 1 that the enol form (**B**) is generally the more stable tautomer, a result which is in accord with work by Fabian.¹⁰ The introduction of a vinyl group instead of the hydrogen atom in the Y position effects a lowering of the energy barrier for the enethiol-enol conversion ($2\text{C} \rightarrow 2\text{B}$), whereas no apparent change with respect to the energy barrier

Table I. The Absorbances of the 262-nm and 408-nm Bands, Measured at Various Temperatures

Temp, °C	408 nm	
	262 nm ($\pi \rightarrow \pi^*$, PhCO)	($\pi \rightarrow \pi^*$, S=CC=CO)
20	0.540	0.990
-60	0.504	1.160
-100	0.428	1.184
-150	0.360	1.266

for the reverse process (**2B** \rightarrow **2C**) can be demonstrated. We interpret the effect of the vinyl group as being partly a conjugative stabilization of the enol structure (**2B**) and partly a destabilization of the enethiol structure owing to the possibility of vinylic conjugative stabilization of the carbonyl group competing with the SC=CC=O conjugation. The substitution of a vinyl group for the hydrogen atom in the X position (case III) has the opposite effect on the energy barriers, i.e., leads to a relative lowering of the barrier for the enol-enethiol conversion (**3B** \rightarrow **3C**). This effect may be interpreted as arising partly from a relative stabilization of the enethiol structure (**3C**) by extended vinylic conjugation and partly from a destabilization of the enol structure (**3B**) owing to the competitive possibilities for conjugative stabilization of the thiocarbonyl group. Finally, the introduction of two vinyl groups effects an unmistakable lowering of both energy barriers (case IV). On the basis of these results we conclude that the introduction of conjugating X,Y substituents will give rise to a more rapid tautomeric interconversion process and, in the extreme case, possibly a "quasi-aromatic" common structure.

To gain further information concerning the latter possibility we studied the UV spectrum of monothiodibenzoylmethane (**8**) at different temperatures. It should be noted, at this point, that the UV spectrum of **8** is not easily explicable on the basis of the "quasi-aromatic" structure, whereas an interpretation in terms of the existence of the tautomer mixture **8B** \rightleftharpoons **8C** is consistent with the spectral features. In nonpolar solvents (e.g., cyclohexane) the spectrum shows three bands of high intensity at 262, 325, and 408 nm, together with a further band of low intensity at \sim 520 nm. These bands may be assigned to the transitions $\pi \rightarrow \pi^*$ (PhCO),¹¹ $\pi \rightarrow \pi^*$ (PhCS)¹² + $\pi \rightarrow \pi^*$ (O=CC=CS),^{3,4} $\pi \rightarrow \pi^*$ (S=CC=CO),^{3,4} and $n \rightarrow \pi^*$ (C=S),¹² respectively. We found that progressive lowering of the temperature from room temperature to -150 °C leads to a simultaneous increase in the intensity of the 408-nm band and a decrease in the intensity of the 262-nm band, corresponding nicely to a shift in the equilibrium **8B** \rightleftharpoons **8C** in favor of the enol tautomer **8B** (Table I). Against this background we therefore reject the possibility of a "quasi-aromatic" structure for **8**.

The theoretically evaluated effects of conjugative X,Y substituents on the equilibrium position for the enol-enethiol tautomerism are reflected qualitatively by the ¹H NMR chelate proton chemical shifts (Table II) of the β -thioxoketones **5-8** (the ¹H NMR spectra of these compounds are all characterized by the apparent presence of only one single species^{3,13}). In reference to the UV spectroscopic findings above, the observed chelate proton shifts should be regarded as weighted average shifts of those for the chelate protons of the individual tautomers **B** and **C**; i.e., a relatively large δ value should correspond to a relatively large equilibrium concentration of the enol form (**B**) and vice versa (intramolecularly chelated enols exhibit their chelate proton shifts in the region δ 13–17 ppm,⁷ whereas the mercapto proton signals of intramolecularly chelated enethiols have been found at δ 6–8.5 ppm^{3,4,14,15}). It can be seen from Table II that the replacement of a methyl group by a phenyl group in the Y position (as in pairs **5** and **6** and **6** and **8**, respectively) gives rise to a general chelate proton shift displacement toward lower field, in accord

Table II. Observed ¹H NMR Chelate Proton Chemical Shifts for the β -Thioxoketones **5-8**^a

	Compd			
	5	6	7	8
δ (H ^{chel})	13.53	15.09	14.95	15.98

^a The shifts given are extrapolation shifts, referring to infinitely diluted tetrachloromethane solutions.^{3,13,14}

with the predicted increase in enol concentration (Figure 1; cf. pairs I and II and III and IV, respectively). Similar considerations hold for the pairs **6** and **7** and **5** and **8**, respectively. The apparent exceptions seen on comparison of results for **5** and **7** and **6** and **8**, respectively, does not necessarily reflect the breakdown of the above generalization, but emphasize rather its qualitative nature. Thus, for obvious reasons the model compounds and the β -thioxoketones actually investigated are not identical, and substituent screening effects on the chelate proton shifts have been totally neglected in this discussion.

Acknowledgments. The authors are grateful to Mr. B. Stillerkerieg and Mr. G. Lindner (Institut für Strahlenchemie, Mülheim/Ruhr, Germany), for their assistance with the low temperature UV measurements, and to the Danish Natural Science Research Council for financial support.

References and Notes

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Received April 1, 1977

1-Aza-1,2,4,6-cycloheptatetraene

Sir:

The photolysis of aryl azides has attracted attention because of the commercial interest in making photoresists, the use of aryl azides in photoaffinity labeling, and the intriguing mechanism problems posed. We wish to report a new primary photochemical process in the photochemistry of phenyl azide and the spectroscopic observation of 1-aza-1,2,4,6-cycloheptatetraene.

Irradiation of phenyl azide (**1**) in solution in the presence of nucleophiles such as diethylamine gives 2-diethylamino-3H-azepine (**2**) in 70% yield¹⁻³ and small amounts of aniline and related products.⁴ The quantum yield for formation of **2**