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Effect of Substituents on the Keto-Enol Equilibrium of Alkyl-substituted β -Diketones

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β -Diketones are commonly used as extractants in the solvent extraction of many metals. In the elucidation of the mechanism of the extraction process, it is necessary to know the nature of the extractant. It is well known that β -diketones possess keto-enol tautomerism. Burdett and Rogers¹⁾ have determined the percentages of enol tautomers for acetylacetone and several β -diketones containing the trifluoromethyl group.

In a previous paper of this series,²⁾ the separation of various metals with the alkyl-substituted β -diketones was reported. In the present investigation, twenty-six alkyl-substituted β -diketones were used in order to establish the effects of substituents on the keto-enol equilibria.

Experimental

Materials. The alkyl-substituted β -diketones used in the present study were synthesized by the method of Hauser and Adams.³⁾ The compositions were confirmed by elemental analysis. Acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone were purchased from the Dojindo Co. and were redistilled before use.

Nuclear Magnetic Resonance Measurements. All the spectra of NMR were recorded at 60MHz with a Japan Electron Optics Model JNM C-60 spectrometer. During the measurements, the temperature was held at 24°C. The chemical shifts of the signal were measured with respect to the tetramethylsilane used as the internal standard, the peak positions are given in parts per million downfield from the internal TMS (δ). The accuracy of the measurement was within

1) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964).

2) H. Koshimura and T. Okubo, *Anal. Chim. Acta*, **49**, 67 (1970); **55**, 163 (1971).

3) C. R. Hauser and J. T. Adams, *J. Amer. Chem. Soc.*, **66**, 1220 (1944).

about ± 0.03 ppm. Equilibrium constants were obtained by the integration of the keto and enol resonance peaks. At least six integrations were performed; the percentage of the enol tautomer was accurate to within $\pm 2\%$. The spectra of these β -diketones were measured in the pure liquid state.

Results and Discussion

The identification of the resonance signal for the proton of the α -position in the enol and keto forms in β -diketone from the chemical shift has been possible. The percentages of the enol and keto tautomers have been determined by the integration of the relative intensities of these resonances for a given compound. While two possible enol structures can be postulated for unsymmetrically-substituted β -diketones, as, for example, by thenoyltrifluoroacetylacetone,⁴ these peaks for two enol forms can not be observed independently within the limits of this experiment.

The proton chemical shifts of the α -proton in the enol and keto tautomers, their percentages, and the corresponding equilibrium constants are summarized in Table 1 for each of the β -diketones.

From Table 1, it can be seen that the enolic content of these β -diketones increases considerably with an

increase in the branching of the alkyl chain near the donating oxygen atom. The enolic content of the alkyl group increases, to a certain extent, with the increase in chain length. However, the enolic contents of β -diketones containing methyl groups are slightly higher than those of β -diketones containing ethyl groups. The enolic contents of β -diketones containing a two-ethyl-group system are lower than would be expected from the effect of the ethyl group in this series. No explanation for the difference will be offered. However, a similar relation was observed with β -diketones containing the alkoxy group. Ness and McElvain⁵ have pointed out that the enolic content of β -diketones containing the ethoxy group was lower than that for methoxy and other alkoxy-group systems. In the presence of phenyl groups there is a greater tendency for an increase in enolization. Burdett and Rogers¹ have pointed out that the substitution of electron-withdrawing groups, such as the trifluoromethyl groups, and the aromatic ring in β -diketones results in an increase in enolization. Park *et al.*⁶ have

TABLE 2. THE CHEMICAL SHIFT OF THE ENOL OH PROTON AND THE ACID DISSOCIATION CONSTANT OF β -DIKETONES

No.	Substitution		pK_a	Chemical shift δ , ppm
	R	R'		
1	CF ₃	CF ₃	4.35 ^a	12.94
2	CF ₃	CH ₃	6.30 ^b	14.43
3	CH ₃	CH ₃	8.84 ^c	15.58
4	C ₂ H ₅	C ₂ H ₅	9.55 ^c	15.86
5	<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	9.82 ^c	16.15
6	CH ₃	<i>t</i> -C ₄ H ₉	10.00 ^c	16.30
7	<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	11.57 ^c	16.76

a) Ref. 7. b) Ref. 8. c) Ref. 2.

TABLE 1. THE CHEMICAL SHIFT OF THE α -PROTON OF KETO AND ENOL AND KETO-ENOL EQUILIBRIUM CONSTANT OF ALKYL-SUBSTITUTED β -DIKETONES

Substitution group		Chemical shift δ , ppm		Enol %	Equilibrium constant $\log K$ ([enol]/[keto])
R	R'	-CH ₂ -	-CH=		
CH ₃	CH ₃	3.62	5.56	81.2	0.636
C ₂ H ₅	C ₂ H ₅	3.55	5.52	80.0	0.602
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	3.50	5.49	91.7	1.045
<i>n</i> -C ₅ H ₁₁	<i>n</i> -C ₅ H ₁₁	3.47	5.45	91.7	1.045
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	3.61	5.51	95.8	1.358
<i>i</i> -C ₄ H ₉	<i>i</i> -C ₄ H ₉	3.41	5.43	95.3	1.308
<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	3.68	5.72	98.0	1.690
CH ₃	C ₂ H ₅	3.57	5.53	82.1	0.662
CH ₃	<i>i</i> -C ₅ H ₁₁	3.50	5.46	91.6	1.037
CH ₃	<i>s</i> -C ₄ H ₉	3.58	5.52	93.4	1.151
CH ₃	<i>i</i> -C ₃ H ₇	3.60	5.53	91.6	1.037
CH ₃	<i>t</i> -C ₄ H ₉	3.58	5.40	93.7	1.173
C ₂ H ₅	<i>n</i> -C ₃ H ₇	3.53	5.50	85.2	0.760
C ₂ H ₅	<i>i</i> -C ₅ H ₁₁	3.52	5.49	88.5	0.887
C ₂ H ₅	<i>i</i> -C ₄ H ₉	3.49	5.48	89.2	0.917
C ₂ H ₅	<i>i</i> -C ₃ H ₇	3.56	5.50	90.8	0.994
C ₂ H ₅	<i>t</i> -C ₄ H ₉	3.58	5.60	93.4	1.152
<i>n</i> -C ₃ H ₇	<i>i</i> -C ₄ H ₉	3.54	5.48	93.7	1.173
<i>n</i> -C ₅ H ₁₁	<i>i</i> -C ₄ H ₉	3.54	5.50	94.6	1.243
C ₆ H ₅	C ₂ H ₅	3.93	6.06	93.9	1.188
C ₆ H ₅	<i>n</i> -C ₃ H ₇	3.93	6.10	95.9	1.369
C ₆ H ₅	<i>n</i> -C ₄ H ₉	3.92	6.10	95.6	1.337
C ₆ H ₅	<i>i</i> -C ₃ H ₇	3.99	6.12	97.0	1.509
C ₆ H ₅	<i>i</i> -C ₄ H ₉	3.88	6.05	97.4	1.574
C ₆ H ₅	<i>i</i> -C ₅ H ₁₁	3.93	6.10	96.8	1.481
C ₆ H ₅	<i>t</i> -C ₄ H ₉	4.00	6.25	98.1	1.713

4) G. Pukanic, N. C. Li, W. S. Brey, Jr., and G. B. Savisky, *J. Phys. Chem.*, **70**, 2899 (1966).

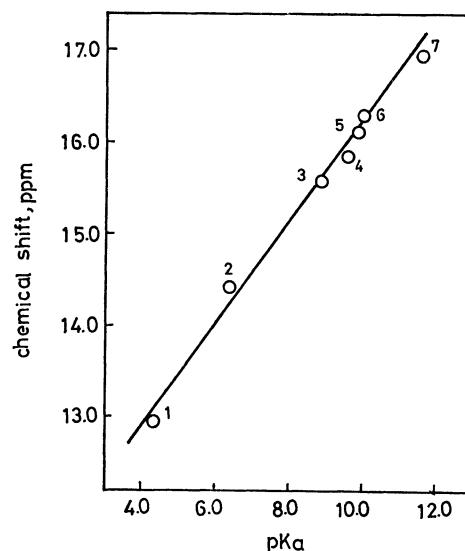


Fig. 1. Relative chemical shift of the enol OH proton *vs.* pK_a of β -diketones. Numbers correspond to entries in Table 2.

5) A. B. Ness and S. M. McElvain, *J. Amer. Chem. Soc.*, **60**, 2213 (1938).

6) J. D. Park, H. A. Brown, and J. R. Lacher, *ibid.*, **75**, 4753 (1953).

also suggested the stabilization of the enol tautomer in trifluoroacetylacetone by an F-HO intermolecular bond.

It would appear that the high enol content for a given compound is a result of electron release in the region of the oxygen atom in the carbonyl group. The correlation between the substitution group and the enolic contents of the β -diketones in this study suggests that the keto-enol ratio is probably dependent on the difference in the electron density of the alkyl groups.

It is known that the enol OH protons show a considerable variation in chemical shift, particularly among the β -diketones. Lintvedt and Holtzclaw⁷⁾ have pointed out that the chemical shift of the enol OH proton is shifted downfield on an increase in the basicity of the substituent with the β -diketones. The chemical shifts of the OH proton are given in Table 2 for β -diketones

7) R. L. Lintvedt and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 239 (1966).

whose acid-dissociation constant is known from the literature.^{2,8,9)} The results from the present study are plotted in Fig. 1; a linear relationship exists between the chemical shift of the enol OH proton and the acid-dissociation constant. A higher acid-dissociation constant corresponds to a lower chemical shift of the enol OH proton and, presumably, to a stronger intermolecular hydrogen bond. A similar relation was observed with thiazolylazophenol derivatives.¹⁰⁾

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8) L. G. Van Uitert, W. C. Fernelius, and B. F. Douglas, *J. Amer. Chem. Soc.*, **75**, 457 (1953).

9) J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

10) S. Kamata, S. Toda, and S. Nagata, *Nippon Kagaku Zasshi*, **88**, 24 (1967).