Enol Content of Some Beta-Diketones

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Nuclear magnetic resonance data have been gathered on a series of beta-diketones which may be viewed as derivatives of 2,4-pentanedione in which the methyl groups are replaced by ethyl, isopropyl, and *tert*-butyl groups. These data are interpreted to identify the amounts of the keto and enol forms present in the pure liquids.

BETA-DIKETONES exist in a keto-enol tautomeric equilibrium. The position of this equilibrium may be dependent upon the temperature, the solvent, the concentration, and the structure of the compound (*8*). The relative amounts of keto and enol forms can be very easily obtained from NMR spectra. The per cent enol content of pure 2,4-pentanedione has been determined by NMR to be 75% (*2*), 81% (*3*, *7*), and 85% (*5*). The present study reports the effects of structure on the per cent enol content of a series of beta-diketones in which the methyl groups of 2,4-pentanedione are replaced by ethyl, isopropyl, and *tert*-butyl groups.

EXPERIMENTAL

Materials. All reagents used as starting materials were obtained commercially and were either distilled before use or used without further purification. 2,4-Pentanedione was commercially obtained and purified by distillation.

Preparation of Beta-Diketones. Beta-diketones were synthesized by a Claisen condensation reaction involving a ketone and an ester according to the general procedure of Adams and Hauser (*1*). Sodium amide was used as the condensation agent. 2,4-Hexanedione was prepared from 2-butanone and ethyl acetate, 3-methyl-2,4-hexanedione from 3-methyl-2-butanone and ethyl acetate, 3,5-heptanedione from 2-butanone and ethyl propanoate, 2-methyl-3,5-heptanedione from 3-methyl-2-butanone and ethyl propanoate, 2,2-dimethyl-3,5-heptanedione from 2,2-dimethyl-3-butanone and ethyl propanoate, 2,6-dimethyl-3,5-heptanedione from 3-methyl-2-butanone and ethyl methylpropanoate, and 2,2,6-trimethyl-3,5-heptanedione from 3,3-dimethyl-2-butanone and ethyl methylpropanoate. All these syntheses gave yields of 70% or better.

2,2,6,6-Tetramethyl-3,5-heptanedione (dipivaloylmethane) was obtained by Method B of Man, Swamer, and Hauser (*6*), since appreciable amounts were not obtained by the above method. The condensation reaction between 3,3-dimethyl-2-butanone and phenyl-2,2-dimethylpropanoate using sodium amide as the condensation agent produced an impure product which could not be purified by fractional distillation. The pure product was obtained by preparation of the copper chelate, then regeneration of the beta-diketone from the copper chelate, followed by fractional distillation in vacuo. The yield ran about 5%. The beta-diketones were characterized by chemical analyses, infrared spectra, and NMR spectra. Table I contains the analytical data and boiling points for the beta-diketones prepared for this study.

Physical Measurements. Infrared spectra were determined on liquid samples spread between sodium chloride plates with a Beckman IR-5A spectrophotometer. The proton NMR spectra of the pure beta-diketones were obtained on a Varian A-60 spectrometer operating at ambient probe temperature.

RESULTS AND DISCUSSION

The infrared spectra were used in identification of the compounds. Characteristic absorption regions of beta-diketones are sharp bands seen around 1700 and 1725 cm.$^{-1}$ (attributed to the free carbonyl absorptions of the keto form) and a strong band around 1510 cm.$^{-1}$ (associated with the six-membered ring structure of the enol form). The 1700- and 1725-cm.$^{-1}$ bands appeared in all compounds investigated in this study. The positions of these bands appeared to be insensitive to the nature of the alkyl groups outside the carbonyl groups. The intensities of these bands appeared to decrease with increasing molecular weight of the alkyl groups. In 2,2,6,6-tetramethyl-3,5-heptanedione, these bands were very weak. The intense broad absorption around 1510 cm.$^{-1}$ was also seen in all compounds, the position of the band being insensitive to the alkyl groups present. The hydroxyl absorption band of the enol form was not observed in any of the spectra.

The proton NMR spectra of the beta-diketones consisted of singlets for the protons on the carbon atom between the carbonyl groups, in both the keto and enol forms, and for the enolic proton. The enolic proton peak was generally very broad. The chemical shifts in parts per mil-

Table I. Analytical Data and Boiling Points of Beta-Diketones

	Boiling Point		Analysis,[a] %			
			Carbon		Hydrogen	
Beta-Diketone	°C.	Mm.	Calcd.	Found	Calcd.	Found
2,4-Hexanedione	28–31	1–5	63.12	62.28	8.85	8.78
5-Methyl-2,4-hexanedione	27–28	1	65.58	65.29	9.45	9.23
2,2-Dimethyl-3,5-hexanedione	68–70	16	67.58	67.87	9.94	10.21
3,5-Heptanedione	48–53	7–10	65.58	65.91	9.45	9.59
2-Methyl-3,5-heptanedione	57	5	67.58	67.26	9.94	9.68
2,2-Dimethyl-3,5-heptanedione	65–66	6	69.18	69.03	10.34	10.40
2,6-Dimethyl-3,5-heptanedione	54–55	1	69.18	69.12	10.34	10.47
2,2,6-Trimethyl-3,5-heptanedione	71–72	7–8	70.53	70.15	10.68	10.74
2,2,6,6-Tetramethyl-3,5-heptanedione	58–62	3–4	71.68	71.63	10.96	10.85

[a] Elemental analysis performed by G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England, or Galbraith Laboratories, Inc., Knoxville, Tenn.

Table II. Nuclear Magnetic Resonance Data on Beta-Diketones

Beta-Diketone	Chemical Shifts^{a,b} K	E	OH	% Enol
2,4-Pentanedione	3.58	5.50	15.34	79
2,4-Hexanedione	3.18^c	5.08^c	13.46^c	81
5-Methyl-3,5-hexanedione	3.57	5.50	14.92	89
2,2-Dimethyl-3,5-hexanedione	3.56	5.60	15.58	94
3,5-Heptanedione	3.66	5.66	15.04	76
3,5-Heptanedione	3.18^c	5.12^c	14.30^c	76
2-Methyl-3,5-heptanedione	3.57	5.50	14.92	88
2,2-Dimethyl-3,5-heptanedione	3.56	5.58	15.58	92
2,6-Dimethyl-3,5-heptanedione	3.60	5.50	15.50	94
2,2,6-Trimethyl-3,5-heptanedione	3.54^c	5.28^c	15.52^c	96
2,2,6,6-Tetramethyl-3,5-heptanedione	3.74	5.86	...	...

[a] Chemical shifts in p.p.m. from TMS as internal standards unless otherwise indicated. [b] K = keto; E = enol. [c] Chemical shifts in p.p.m. from TMS as external standard.

lion observed for the CH_2 (keto abbreviated K), CH (enol abbreviated E), and OH protons are presented in Table II. The spectra of the other protons were as expected for the methyl, ethyl, isopropyl, and *tert*-butyl groups. The characteristic patterns were seen for both the keto and enol forms with overlapping of the multiplets being observed.

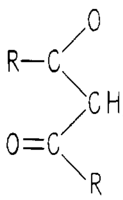
The per cent enol of the beta-diketones was calculated from the following relationship:

$$200E/(2E + K)$$

where E is the integrated intensity of the CH (enol) proton and K is the integrated intensity of the CH_2 (keto) protons. The calculated values are presented in Table II. No value was calculated for 2,2,6,6-tetramethyl-3,5-heptanedione because the value of K was very small, making an accurate figure difficult to obtain. Apparently this beta-diketone existed almost completely in the enol form.

The value for the per cent enol of 2,4-pentanedione obtained in this study (79%) is in agreement with the literature values listed above. No literature values are available for the per cent enol of the other beta-diketones used in this study. The values obtained indicate that in general the per cent enol increases as the alkyl groups become more complex. However, decreases are noted in going from 2,4-hexanedione to 3,5-heptanedione, from 5-methyl-2,4-hexanedione to 2-methyl-3,5-heptanedione, and from 2,4-dimethyl-3,5-hexanedione to 2,2-dimethyl-3,5-heptanedione.

The increase in the amount of enol as the alkyl group becomes larger is mainly attributed to a steric effect. The keto form may take on structures I, II, and III (*4*). Structures I and II minimize the resultant of the dipole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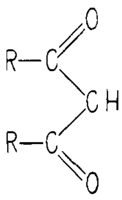
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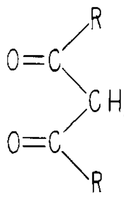
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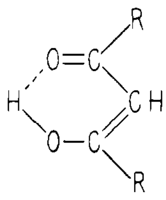
IV

moments of the carbonyl groups. However, when the R groups become large, these structures become strained and the keto form is forced into structure III. With 2,2,6,6-tetramethylheptane-3,5-dione a rotation of 30° to 40° away from III cannot take place without introducing some strain (*4*).

The enol form (IV) exists as the intramolecular hydrogen-bonded species (*3*). The hydrogen bond tends to decrease the dipole-dipole repulsion between the carbonyls and thus stabilizes the enol form relative to the keto form. The larger the alkyl groups, the greater the steric interaction forcing the carbonyls closer together and thus the greater the tendency to enolize to reduce the electrostatic repulsion between the carbonyls.

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Benzyltriethylammonium Salts

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A series of benzyltriethylammonium organic and inorganic salts was synthesized and characterized.

A SERIES of benzyltriethylammonium organic and inorganic salts was prepared to study the effect of the anionic species on the biological activity of benzyltriethylammonium salts. We report on the synthesis and characterization of several of these salts (*1*). Table I summarizes yields, melting points, and elemental analyses of the compounds prepared. Characteristic infrared

$$[C_6H_5CH_2N(C_2H_5)_3]^+Cl^- + AgY \rightarrow [C_6H_5CH_2N(C_2H_5)_3]^+Y^- + AgCl$$

absorption bands for each compound are listed in Table II. In all cases, absorptions at ~700 and ~750 cm.$^{-1}$ for five adjacent hydrogens on the benzene ring were noted.

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