fully acknowledged. T. J. P. wishes to thank the Sprague Electric Co. for a predoctoral fellowship and the National Science Foundation for a summer fellowship. We also wish to thank Mr. Gorton Wood and Mr. James MacNeil for excellent maintenance of the n.m.r. spectrometers.

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Proton Magnetic Resonance Study of β-Diketones and Its Application to Thermodynamic Formation Constants of Various β-Diketone Metal Chelats.

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The proton magnetic resonance spectra of sixteen β-diketones were determined. The position and character of the chemical shift for the enolic hydrogen is dependent upon the nature of the substituent group at the 1 or 3 position. There is a correlation between the dissociation constant, K_d, of the β-diketone and the position of its enolic hydrogen magnetic resonance absorption peak. A correlation also exists between the position of this peak and the thermodynamic formation constants of the β-diketone metal chelates. The character of this peak is discussed in terms of the effects which substituents might have on the intramolecular hydrogen bond. There is strong evidence that in phenyl-substituted β-diketones the phenyl group is acting as an electron-supplying group.

Inasmuch as the basicities of the β-diketones are important in determining the stabilities of their chelates, it is of interest to determine whether a useful relationship exists between basicities and spectral data. In this paper the chemical shift of the β-diketone enolic hydrogen is compared with the pK_d of the β-diketone. The values of pK_d have been determined potentiometrically by Van Uitert.[1,2] The β-diketone enolic hydrogen chemical shift is also compared with the thermodynamic formation constants of numerous β-diketone chelates. The latter relationship is believed to be the first direct correlation between proton magnetic resonance data and chelate stability to appear in the literature.

The enolic form of a β-diketone contains a strong intramolecular hydrogen bond. Infrared spectra have been used to estimate the length of this bond.[3,4] Proton magnetic resonance should also be well suited for the study of the hydrogen bond. It was observed that the width of the magnetic resonance peak for the enolic proton varied greatly depending upon the groups substituted at the 1, 2, or 3 position. This peak width was used to draw conclusions about the placement of the enolic hydrogen between the two oxygens.

Recently, Burdett and Rogers[5] have stated that in phenyl-substituted β-diketones the phenyl ring is at no time coplanar with the enolic ring. Hence, they state that the only effect of the phenyl group is electron withdrawal by induction. The data given in the present article, however, seem to support the conclusion that the phenyl group is electron-supplying through resonance.

Experimental Section

All proton magnetic resonance spectra were obtained in 2.0 M solutions using reagent grade carbon tetrachloride as solvent.[6] A Varian A60 nuclear magnetic resonance spectrophotometer was employed. All resonance peaks are referred to tetramethylsilane (TMS) as an internal reference with $\delta = 0$ p.p.m.

The following β-diketones were obtained from commercial sources: 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione, 2,4-pentanedione, 1,1,1-trifluoro-3-(2-thienyl)-2,4-butanedione, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 2-furoylperfluorobutyrylmethane, 2-thenoylperfluorobutyrylmethane, and 6-methyl-2,4-heptanedione.

The β-diketones listed in Table I were synthesized by condensing the appropriate ethyl ester and methyl ketone using sodium amide as the basic condensing agent. The method of preparation is described by Levine, *et al.*[7]

All the β-diketones were sufficiently pure so that no extraneous, unidentifiable peaks occurred in the proton magnetic resonance spectra.

The 3-phenyl-2,4-pentanedione was prepared by other workers[8] in this laboratory by the method[9] described below. The

$$\mathrm{C_6H_5CH_2COCH_3 + (CH_3CO)_2O \xrightarrow{BF_3} CH_3CO\underset{\displaystyle C_6H_5}{\underset{|}{C}H}COCH_3 + CH_3COOH}$$

procedure is similar to the one submitted by Denoon[9] with a modified purification method. Phenyl acetone (134 g., 1.0 mole) and acetic anhydride (55 g., 2.5 moles) are placed in a three-necked flask. The mixture is cooled in an ice bath. An inlet tube which goes below the surface of the mixture is attached to one neck of the flask through which the boron trifluoride will

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[1] L. G. Van Uitert, "Solution Stabilities of Chelate Compounds," Ph.D. Thesis, The Pennsylvania State College, 1952.

[2] L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

[3] R. E. Rundle and M. Parasol, *J. Chem. Phys.*, **20**, 1487 (1952).

[4] K. Nakamoto, M. Margoshes, and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).

[5] J. L. Burdett and M. T. Rogers, *ibid.*, **86**, 2105 (1964).

[6] 1,3-Di(2-thienyl)-1,3-propanedione was run at a concentration of 1.0 M due to limited solubility in carbon tetrachloride.

[7] R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1510 (1945).

[8] A. H. Carlson, M.S. Thesis, University of Nebraska, 1952.

[9] C. E. Denoon, Jr., *Org. Syn.*, **20**, 6 (1940).

TABLE I

	Obsd. m.p., °C.	Lit. m.p., °C.	Cu(II) chelate Obsd. m.p., °C.	Cu(II) chelate Lit. m.p., °C.
1,1,1-Trifluoro-4-phenyl-2,4-butanedione	39–40	39.0–40.5[c]	241–242	243–244[c]
1,3-Di(2-furyl)-1,3-propanedione	72–73	70.5–72.0[d]	263–265	
1-Phenyl-3-(2-furyl)-1,3-propanedione			249–251	245–248[b]
1-(2-Thienyl)-1,3-butanedione	37	129–131 (8 mm.)[a,b]	230–232	228–230[b]
1,3-Di(2-thienyl)-1,3-propanedione	96–100	99–100[b]	261–263	259–263[b]
1,1,1-Trifluoro-4-(2-furyl)-2,4-butanedione	85 (10 mm.)[a]	60 (3 mm.)[e]	227–229	

[a] Boiling point. [b] S. R. Harris and R. Levine, *J. Am. Chem. Soc.*, **70,** 3360 (1948). [c] J. C. Reid and M. Calvin, *ibid.*, **72,** 2948 (1950). [d] G. S. Hammond and F. S. Schultz, *ibid.*, **74,** 329 (1952). [e] J. P. Collman, M.S. Thesis, University of Nebraska, 1956.

be introduced. An outlet tube is attached to the third neck of the flask. This outlet tube is connected to an alkali trap. The reaction is carried out in a well-ventilated hood. The boron trifluoride is passed through the mixture for 2.75 hr. The flask is kept cool (about room temperature) since the product has a melting point of 58°. A solid mass forms in the flask. The product is then steam distilled until the distillate is only slightly turbid. White crystals and a yellow oil separate when the mixture is allowed to stand overnight. The crystals are then collected by suction filtration.

The crystals are melted under water and stirred vigorously. They are then recrystallized three times from petroleum ether (b.p. 30–60°). The product melts at 58° (lit.[10] 58–60°). The yield is 41%.

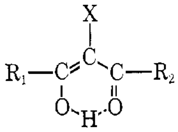
Results and Discussion

The fact that the basicities of the β-diketones change with the groups substituted at the 1 or 3 position is well brought out in the pK_d values obtained from potentiometric data.[1] The pK_d values which are reported in Table II for some substituted β-diketones show this effect clearly. In general, it can be seen that groups which are capable of decreasing electron density near the oxygens decrease the basicity of the β-diketone. Also, groups which are capable of increasing electron density near the oxygens increase the basicity of the β-diketone.

The chemical shift for the hydrogen-bonded proton varies depending upon the electronic effect that the substituent groups have on the oxygens. The magnetic resonance peak shifts to lower δ values relative to tetramethylsilane (δ = 0 p.p.m.) when a substituent group decreases the basicity of the β-diketone. When a substituent group causes an increase in basicity, the enolic hydrogen chemical shift of the resulting β-diketone has a greater δ value. Dilution of the 2.0 M samples did not cause shifts in the enolic hydrogen resonance peaks; therefore, it is concluded that the peak is due solely to an intramolecular hydrogen-bonded proton. The correlation between pK_d and the chemical shift of the enolic hydrogen is approximately linear. The validity of correlating chemical shifts to pK_d for compounds with widely varying structures is questionable. However, for a series in which structures are as closely related as in the one given above, the correlation is useful.

TABLE II

PROTON MAGNETIC RESONANCE CHEMICAL SHIFTS OF THE ENOLIC HYDROGEN FOR SOME SUBSTITUTED β-DIKETONES (2.0 M IN CCl_4 AT 25°) AND DISSOCIATION CONSTANTS.



	Substituents R1	Substituents R2	Substituents X	Chem. shift of enolic proton, δ[a]	pK_d[c]	Enol peak character[d]
1	CF_3	CF_3	H	13.0[b]	6.0	...
2	CF_3	CH_3	H	14.2	8.7	b
3	2-C_4H_3S	CF_3	H	14.9	9.1	fb
4	C_6H_5	CF_3	H	15.2	9.2	s
5	2-C_4H_3O	2-C_4H_3O	H	15.4	12.1	fs
6	CH_3	CH_3	H	15.4	12.70	vb
7	C_6H_5	CH_3	H	16.2	12.85	b
8	C_6H_5	2-C_4H_3O	H	16.3	12.95	s
9	C_6H_5	C_6H_5	H	17.1	13.75	s
10	C_4F_9	2-C_4H_3O	H	14.8	...	vs
11	C_4F_9	2-C_4H_3S	H	15.1	...	vs
12	$(CH_3)_2CHCH_2$	CH_3	H	*ca.* 15.0	...	vb
13	CH_3	CH_3	C_6H_5	16.8	...	vs
14	CH_3	2-C_4H_3S	H	15.7	12.35	fb
15	2-C_4H_3S	2-C_4H_3S	H	16.2	12.63	...
16	CF_3	2-C_4H_3O	H	14.3	8.5	vs

[a] P.p.m. *vs.* TMS. [b] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86,** 2105 (1964). [c] L. G. Van Uitert, "Solution Stabilities of Chelate Compounds," Ph.D. Thesis, The Pennsylvania State College, 1952. [d] vb, very broad; b, broad; fb, fairly broad; vs, very sharp; s, sharp; fs, fairly sharp.

The thermodynamic formation constants of many β-diketone chelates have been measured potentiometrically by Van Uitert[1] using a method developed by Calvin and Wilson.[11] In Figure 1, the formation constants of some chelates are plotted against the chemical shifts of the enolic proton for several β-diketones. The plot yields a series of straight lines for which the slopes and positions of the lines are characteristic of the central metal ion. The correlation between chemical shift and formation constant is better than that between chemical shift and pK_d. The slopes of the lines increase in the order Ba < Mg < Zn < Ni < Cu. The same order has been deduced from potentiometric and infrared spectral data and is attributed to an increasing tendency of the metal ions to form chelates.[12,13] A few proton magnetic resonance studies on the diamagnetic β-diketone chelates have been undertaken,[14,15] but as yet no systematic trends have been discovered which correlate the chemical shift of a particular proton to the stability of the chelate. The correlation shown in Figure 1 between the chemical shift of the

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(10) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 284 (1945).

(11) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(12) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *ibid.*, **75**, 2736 (1953).

(13) D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947).

(14) J. A. S. Smith and J. D. Thwaites, *Discussions Faraday Soc.*, **34**, 143 (1962).

(15) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

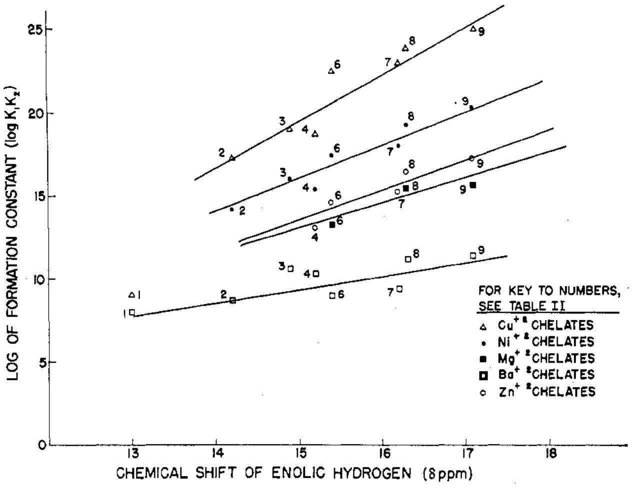


Figure 1.—Enolic hydrogen chemical shift for the unchelated β-diketones *vs.* the logarithm of the formation constants of some of the metal chelates.

enolic hydrogen on the unchelated β-diketones and the formation constants of the β-diketone chelates is apparently the first of this type to appear in the literature.

It is interesting to note the wide variations in the character of the enolic hydrogen peaks for the series listed in Table II. The peaks vary from exceedingly broad (*ca.* 50 c.p.s.) to very sharp (*ca.* 8 c.p.s.). In every case, β-diketones give sharp enolic peaks when substituted with electron-withdrawing groups and/or groups which enhance the resonance in the enolic ring. On the other hand, when groups are present which do not take part in extensive electron delocalization, broad and poorly defined peaks result. Broad peaks may be caused by averaging the chemical shifts of at least two unsymmetric tautomeric forms. Thus, for example, when R = $CH_2CH(CH_3)_2$ and R′ = CH_3 a broad, poorly defined enolic hydrogen peak results. When R = C_6H_5 and R′ = CH_3 a sharpening of the peak results. When R = R′ = C_6H_5 an even sharper peak results.

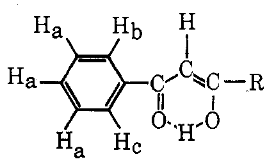
If coplanarity of the phenyl group and the enolic ring is assumed, the phenyl group should enhance the resonance of the enolic ring. The electron-supplying ability of the phenyl group increases the electron density of the adjacent oxygen. This results in a lengthening of the O–H bond and a shortening of the hydrogen bond. The result is a more symmetric placement of the enolic hydrogen with respect to the two oxygens. When both R and R′ are phenyl groups, the electron density on the oxygen atoms will be the same. This charge distribution would be expected to make the enolic proton symmetric with respect to the two oxygens. Due to the absence of widely different tautomeric forms and the shortening of the hydrogen bond, the enolic peak for the diphenyl derivative is sharp and well defined. Similar observations concerning hydrogen-bond length and absorption peak sharpening have been made using infrared spectroscopy. Rundle and Parasol[3] have reported a sharper band for the O–H stretching frequency absorption of a symmetric hydrogen-bonded O–H than of an unsymmetric one.

The above explanation of the proton magnetic resonance spectra of β-diketones depends upon the ability of the aromatic group to be coplanar with the enolic ring. Burdett and Rogers[5] have stated that the phenyl group is never coplanar and that it acts, by induction, as an electron-withdrawing group. However, potentiometric data, ultraviolet data, and proton magnetic resonance spectra seem to indicate that the phenyl group is electron-releasing through resonance.

Potentiometrically determined dissociation constants show that basicity increases in the following order: β-diketones substituted with electron-withdrawing groups < those substituted with weakly electron-releasing groups < those substituted with aromatic groups.[1] The trend in pK_d values is shown in the series 1,1,1-trifluoro-2,4-pentanedione, 8.7; 2,4-pentanedione, 12.7; 1-phenyl-1,3-butanedione, 12.9; 1,3-diphenyl-1,3-propanedione, 13.8. Inasmuch as the increasing basicity in the series results from an increase in electron density on the carbonyl oxygens, the phenyl group would seem to be acting as an electron-releasing group.

Resonance, which can arise only if the phenyl and enolic rings are coplanar, is evidenced by the increased wave length of maximum ultraviolet absorption (mμ) of the β-diketones[16] 2,4-pentanedione, 275; 1-phenyl-1,3-butanedione, 305; 1,3-diphenyl-1,3-propanedione, 340.

Proton magnetic resonance spectra may also provide evidence that the phenyl ring is coplanar with the enolic ring. In those β-diketones which are substituted with phenyl groups in the 1 or 3 position, the same pattern is observed for the phenyl hydrogens. The pattern consists of a triplet for which the area corresponds to three protons and two doublets for which the combined area corresponds to two protons. The doublets are separated by a chemical shift of 4.0 c.p.s. The high-field doublet has a splitting constant of 3.75 c.p.s. The lower field doublet has a splitting constant of 2.25 c.p.s. It is possible to rationalize three different proton environments on the phenyl ring by assuming coplanarity.



The triplet is assigned to the protons labeled H_a. The two doublets are assigned to H_b and H_c. The small chemical shift between the doublets is presumed to be due to a coplanar arrangement of the two rings. The proton labeled H_c is deshielded by the carbonyl group since H_c and the carbonyl group both lie in the same plane. Hence, the downfield doublet is assigned to H_c and the upfield doublet to H_b.

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(16) L. Lang, Ed., "Absorption Spectra in the Ultraviolet and Visible Region," Vol. 2 (1961) and 4 (1963), Academic Press, Inc., New York, N. Y.