were allowed to vaporize and pass through the tube. About 40 mg of methyleneoxetane **12** was pyrolyzed at 400°. Less than 5 min was required for passage, and longer pumping reduced the amount of trapped dienol ether **13**. Glpc assay revealed a ratio of 72:28 for **8**:**13**. The nmr of this mixture exhibited the absorptions of **13** at δ 6.14, 5.4, 4.3, 4.18, and 1.84 ppm, the remaining peaks being hidden by the spectrum of **8**. To *ca.* 0.1 ml of a mixture (47% **8**, 47% **12**, and 6% **13**) from photolysis of a 1% solution of **8** in redistilled 30–60° petroleum ether was added $\sim$1 μl of the above pyrolysis mixture. Glpc analysis of this sample on three different columns (10 ft 10% DEGS, 10 ft 15% Carbowax 20M, 5 ft 10% SE-30; all $^1/_8$ in. o.d.) showed only the three peaks originally present in the photolysis mixture.

Another 55-mg sample of **12** was pyrolyzed in the same manner as above. The trapped product mixture was transferred to an nmr capillary microtube and 1 drop of *p*-xylene was added. Integration of the nmr revealed an initial ratio of 6:1 for **8**:**13**. After 6 days at 25°, the corresponding ratio was 12:1; after 12 days, no **13** remained. Standardization against the added *p*-xylene demonstrated that the (**8** + **13**)/*p*-xylene ratio remained constant, thus indicating the conversion of **13** into **8**.

A sample of ketoallene **8** was recovered unchanged from pyrolysis at 400°.

Hydrolysis of 12.—A solution of 100 mg of methyleneoxetane **12** in 1 ml of ether was shaken with 5 ml of 1 *M* sulfuric acid for 5 min. To this was added 20 ml of ether, the mixture was shaken, and the layers were separated. The water layer was washed with two 15-ml portions of ether. The combined ether solutions were washed with 5 ml of saturated sodium bicarbonate solution and dried (Na_2SO_4). Removal of the ether gave 0.13 g of a colorless liquid which was collected by glpc to yield 48 mg (41%) of 2,6-heptanedione: glpc pure; mp 29–32° (lit.[24] mp 30–33°); ir (CCl_4) 5.83 μ (C=O); nmr δ 2.40 (m, 4, CH_2CO), 2.05 (s, 6, CH_3CO), and 1.76 ppm (m, 2, $CH_2CH_2CH_2$).

Ozonolysis of 12.—A solution of 1.00 g of vacuum transferred product mixture from photolysis of **8** ($\sim$45% **12** by glpc analysis) in 50 ml of methylene chloride containing 2 ml of pyridine was cooled to −80°. The output of a Welsbach Model T-408 ozonator was bubbled through the solution for 2 hr. The solution was flushed with oxygen for 30 min, allowed to warm to room temperature, and washed with three 25-ml portions of 10% hydrochloric acid. The combined aqueous washings were back extracted with 20 ml of methylene chloride. The combined methylene chloride solutions were shaken vigorously with four 15-ml portions of saturated sodium bicarbonate solution (an unidentified carboxylic acid was removed only with much effort) and dried (Na_2SO_4). The solvent was removed to give 0.24 g ($\sim$50%) of 1-methyl-2-oxa-3-oxobicyclo[2.2.0]hexane (**15**): ir 5.49 μ (vs, β-lactone); nmr δ 3.6 (m, 1, CHCO), 2.3 (m, 4), and 1.58 ppm (s, 3). Attempts at glpc analysis or purification of neat samples of **15** gave two peaks with very short elution times and only a relatively small peak with an elution time appropriate for β-lactone **15**. Presumably, decomposition of **15** to carbon dioxide and olefinic products is occurring on the glpc column.

Photolysis of 8 in Methanol.—Irradiation of 1% solutions of ketoallene **8** in methanol on several occasions revealed the presence of methyleneoxetane **12** after a few per cent conversion. However, further irradiation led to disappearance of **12** and formation of several unidentified products with glpc elution times longer than that of **8**. A buffered methanol–water mixture was prepared by adding 5 ml of saturated sodium bicarbonate solution to 105 ml of methanol. The mixture was stirred for 6 hr at 25° to allow equilibration, and the undissolved sodium bicarbonate was removed by gravity filtration. Irradiation of 1.00 g of **8** in this solvent for 28 hr gave 42% conversion (glpc assay) to **12** with only traces of other products. A sample of **12** isolated by preparative glpc gave infrared and nmr spectral data identical with those reported previously for **12**.

Registry No.—**8**, 20449-20-1; **9**, 20449-21-2; **10**, 20449-22-3; **11**, 20449-23-4; **12**, 20500-56-5; **13**, 20449-24-5; **15**, 20455-51-0; 2,6-heptanedione, 13505-34-5.

Acknowledgment.—Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation (J.K.C) for support of this work.

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Nuclear Magnetic Resonance Studies of Enol–Enol and Keto–Enol Equilibria in Substituted Benzoylacetones[1a,b]

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Nmr investigation of a series of *para*-substituted benzoylacetones has established that they exist largely (75–98%) as chelated *cis*-enols. Long-range coupling constants suggest that the benzoyl carbonyl group enolizes, forming the cinnamoyl chromophore, and that little benzoylethylene enol is present. Substituent effects on the keto–enol equilibrium are discussed. It has been found that the rule that electron-releasing groups stabilize adjacent carbonyl groups is valid in these systems.

The tautomerism of benzoylacetone and its derivatives has been investigated by a number of physical methods[2–6] and treated briefly by simple Hückel molecular orbital calculations.[7] Although it is generally accepted that the phenyl group increases the enol content, there is disagreement over the question of whether the stabilization derives from mesomeric electron delocalization[7,8] or inductive electron withdrawal.[9] In an attempt to shed some light on this question, we have undertaken a nuclear magnetic resonance study of substituent effects on the tautomeric equilibria in a series of six *para*-substituted benzoylacetones in chloroform-*d*. Study of the long-range couplings provides evidence for the direction of enolization, and consideration of the concentration and substituent dependence of the hydroxyl resonance position allows us to discuss the probable importance of *trans*-enols.[4,10]

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[1] (a) Supported by National Institutes of Health Research Grant GM-09143; (b) presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964; (c) presented by D. J. S. to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, Aug 1967; (d) Department of Chemistry, Boston College, Chestnut Hill, Mass.; (e) Physical Research Laboratory, Dow Chemical Co., Midland, Mich.; (f) Department of Chemistry, Texas A & M University, College Station, Texas.

[2] F. Iimura, *Nippon Kagaku Zasshi*, **77**, 1855 (1956).

[3] R. D. Campbell and H. M. Gilow, *J. Amer. Chem. Soc.*, **84**, 1440 (1962).

[4] J. U. Lowe, Ph.D. Thesis, Howard University, 1963.

[5] J. U. Lowe and L. N. Ferguson, *J. Org. Chem.*, **30**, 3000 (1965).

[6] M. Gorodetsky, Z. Luz, and Y. Mazur, *J. Amer. Chem. Soc.*, **89**, 1183 (1967).

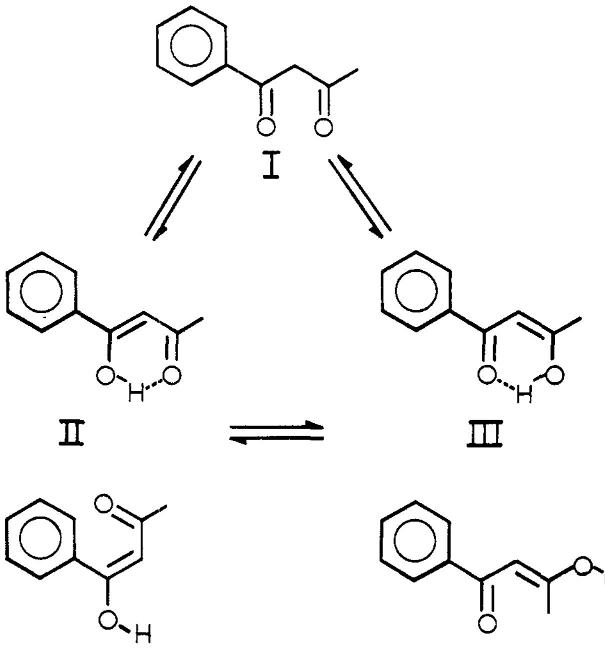
[7] S. Forsen, *Arkiv Kemi*, **20**, 1, 25 (1962).

[8] R. L. Lintvedt and H. F. Holtzclaw, *Inorg. Chem.*, **5**, 239 (1966).

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

[10] M. I. Kabachnik, S. T. Ioffe, E. M. Popov and K. V. Vatsuro, *Tetrahedron*, **12**, 76 (1961).

The complete tautomeric equilibrium consists of five possible species (neglecting other species with which they may be associated): diketone I, the pairs of *cis*- and *trans*-enols II (henceforth cinnamoylenol) and III (henceforth benzoylethyleneenol),[11] and the results thus far accumulated indicate the most stable species in solution to be a *cis*-chelated enol, probably II. The Hückel molecular orbital calculations of Forsen, neglecting the hydrogen bond, indicate the equilibrium constant for II ⇄ III to be about 12, favoring the cinnamoylenol.[7] Although these results probably reflect more truthfully the relative stabilities of the *trans*-enols, it seems unlikely that the hydrogen bonds in the chelated enols will be so different in strength as to invert the relative stabilities of the enols.



Results

A series of six substituted benzoylacetones (*p*-N,N-dimethylamino-, *p*-methoxy-, *p*-methyl-, *p*-bromo-, *p*-nitro-, and the parent benzoylacetone), examined over the accessible concentration ranges in chloroform-*d*, exhibit the following regularities: two peaks in the region characteristic of acetyl and unsaturated C-methyl groups, one each in the methylene, vinylic, and strongly hydrogen-bonded hydroxyl regions, and an aromatic multiplet. In addition, the substituent groups of *p*-CH_3-BA,[12] *p*-CH_3O-BA, and *p*-$N(CH_3)_2$-BA give rise to the characteristic aromatic C-methyl, O-methyl, and N-methyl resonances, respectively.

Assignment of peaks was unambiguous except for the methyl region of *p*-methylbenzoylacetone, which exhibits peaks at τ 7.64, 7.79, and 7.98. In this case, synthesis of *p*-(trideuteriomethyl)benzoylacetone in 90% isotopic purity established the lowest field methyl resonance (τ 7.64) to be due to the ring methyl, as might be expected from the great deshielding by the benzene ring.

Long-Range Coupling.—Couplings across four bonds are sensitive to the nature of the transmitting path, and it was anticipated that they might provide information on the nature of the species present in solution. Long-range proton–proton couplings have been discussed by Sternhell[13] and Burdett.[14] Under close examination, the methylene groups of *p*-H-BA, *p*-CH_3-BA, *p*-CH_3O-BA, and *p*-$N(CH_3)_2$-BA proved to be quartets, and the low-field methyl groups to be triplets.[15] The values for the couplings (at about 0.08-mol of fraction ketone) are summarized in Table I, along with the value reported by Burdett[14] for acetylacetone.

Table I

Long-Range Couplings in Diketones

Compd	Coupling, Hz
p-H-BA	0.44 ± 0.02
p-CH_3-BA	0.42 ± 0.03
p-CH_3O-BA	0.42 ± 0.03
p-$N(CH_3)_2$-BA	0.45 ± 0.03
Acetylacetone	0.44

Inspection of the vinylic resonances revealed no discernible splittings, nor was any splitting noticeable in the remaining methyl peaks. However, since it is possible that small couplings, though unresolvable, may manifest themselves by line broadening, we examined the unsplit methyl resonances of *p*-H-BA, *p*-CH_3-BA, *p*-CH_3O-BA, and *p*-Br-BA, comparing their line widths at half-height with the tetramethylsilane line width. The maximum couplings inferred in this manner are tabulated below.[16] In all four cases, the couplings are quite small (Table III). Similar examination of the substituent methyl resonances of *p*-CH_3-BA and *p*-CH_3O-BA indicated maximum couplings of 0.5 and 0.12 Hz, respectively. In no cases was there any evidence for discernible coupling between the hydroxyl proton and any other proton in the molecule, although Burdett[14] has reported a coupling of 0.71 Hz between the hydroxyl and vinyl protons of ethyl acetoacetate.

Table II

Long-Range Couplings in Enols

Compd	Maximum coupling, Hz
p-H-BA	0.07
p-CH_3-BA	0.00
p-CH_3O-BA	0.13
p-Br-BA	0.10

Chemical Shifts. Substituent Effects.—The chemical shifts of the six benzoylacetones are listed in Table III for concentrations in the region 0.05–0.08-mol fraction in chloroform-*d*. Since the work of Marcus, Reynolds, and Miller[17] has shown that, in many cases, good correlations exist between chemical shifts and substituent constants for series of related compounds,

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[11] The corresponding enols *cis* II and *cis* III with unchelated hydroxyl are considered to be unimportant in view of the ease with which the hydrogen bond could be formed and the large enhancement of stability which would accompany formation of the hydrogen bond.

[12] Henceforth, benzoylacetone will be abbreviated BA.

[13] S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

[14] J. L. Burdett, Ph.D. Thesis, Michigan State University, 1963.

[15] Undoubtedly the situation is the same in the remaining compounds; however, there is so little diketone present in these cases that noise obscures the couplings.

[16] The peak was assumed to be the enol methyl resonance, so to be an unresolved doublet. Hence the maximum value the coupling can have must be $W_{1/2}$ (obsd) − $W_{1/2}$ (TMS), where $W_{1/2}$ refers to the widths at half-height of the enol methyl and TMS, respectively.

[17] S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

TABLE III

CHEMICAL SHIFTS OF SUBSTITUTED BENZOYLACETONES (0.05–0.08-MOL FRACTION)

R	$N(CH_3)_2$	CH_3O	CH_3	H	Br	NO_2
σ	−0.83	−0.268	−0.17	0.00	0.232	0.778
CH_3 (enol)	7.90	7.85	7.87	7.85	7.84	7.74
CH_3 (keto)	7.77	7.72	7.73	7.72	7.73	7.63
CH_2 (keto)	6.05	5.98	5.95	5.93	5.97	5.70
CH (enol)	3.95	3.91	3.85	3.85	3.90	3.74
H (*ortho*)	3.37	3.10	2.86	...	2.31	1.61
H (*meta*)	2.22	2.17	2.19	...	2.31	2.10
OH (enol)	−6.52	−6.48	−6.26	−6.27	−6.00	−5.67
CH_3 (substituent)	7.00	6.18	7.61	...	...	...

we attempted to correlate the shifts of each type of proton (except the aromatic protons) with the Hammett σ constants of the substituents, hoping to derive information relating to transmission of electronic effects, especially to the hydrogen-bonded proton. The results of the correlations are summarized in Table IV. The significant datum is the slope obtained for the hydroxyl proton shifts. All other correlations are unexceptional; *i.e.*, resonances shift to lower field with greater substituent electron-withdrawing power. The aromatic protons (whose shifts were obtained by a pseudo-AB analysis of the four principal lines of the multiplet for the five substituted benzoylacetones) were not included in the correlation because it is likely that magnetic anisotropy effects, especially in p-NO_2-BA, override the normal electronic effects.

TABLE IV

PARAMETERS FOR HAMMETT-TYPE CORRELATIONS OF CHEMICAL SHIFTS

Peak	Slope	Intercept	Correlation coefficient	Standard deviation
CH_3 (enol)	−0.0939	7.838	0.929	0.0225
CH_3 (keto)	−0.0777	7.713	0.899	0.0226
CH_2 (keto)	−0.1990	5.921	0.890	0.0610
CH (enol)	−0.1174	3.862	0.864	0.0409
OH (enol)	0.5622	−6.174	0.945	0.1168

Chemical Shifts. Solvent Effects.—Each compound was examined over its entire solubility range in chloroform-*d*. In all cases except the hydroxyl resonances, the concentration dependence of the chemical shifts is unexceptional: downfield shifts with increasing dilution in chloroform-*d*. The small shifts most likely arise from the increased separation between the aromatic solute molecules with increasing dilution.

The behavior of the hydroxyl resonances is somewhat erratic: three compounds (p-H-BA, p-CH_3-BA, and p-CH_3O-BA) move upfield on dilution, p-$N(CH_3)_2$-BA remains the same, while p-Br-BA and p-NO_2-BA shift downfield. The data are consistent with either (1) the successive weakening of the intramolecular hydrogen bonds as the electron-withdrawing power of the substituents increases, or (2) a shifting of the *cis*-enol–*trans*-enol equilibrium toward the *trans*-enol side as the more electronegative substituents engage in a competition with the carbonyl group for the hydroxyl proton. Although a choice between these alternatives cannot be made from the data at hand, it is significant that infrared studies of acetylacetone and hexafluoroacetylacetone indicate a weakening of the hydrogen bond by electronegative substituents,[18] and that this weakening seems to be paralleled by an increase in shielding of the hydroxyl proton.[14] The presence of *trans*-enol in benzoylacetones has been inferred from the presence of bands in the 1708–1722-cm^{-1} region by Lowe.[4]

Keto–Enol Equilibrium. Concentration Effects.—The rate of keto–enol interconversion is sufficiently slow at room temperature on the nmr time scale that the position of the equilibrium can be determined by integration of peak areas. The data for the six benzoylacetones (Table V) indicate a moderate concentration dependence of the equilibrium, the percentage of diketone increasing with increasing dilution, consistent with the idea that the enol is less polar than the diketone.

TABLE V

CONCENTRATION DEPENDENCE OF KETO–ENOL EQUILIBRIA OF SUBSTITUTED BENZOYLACETONES IN CHLOROFORM-*d*

	Mol fraction	Per cent enol
p-N,N-Dimethylaminobenzoylacetone	0.095	77.4
	0.143	77.9
p-Methoxybenzoylacetone	0.059	87.7
	0.142	87.7
	0.221	89.0
	0.251	88.8
	0.338	89.8
	0.349	89.7
	0.479	90.1
p-Methylbenzoylacetone	0.065	89.6
	0.16	90.7
	0.35	93.0
	0.47	93.7
	0.71	94.6
	0.81	94.9
	1.00	95.2
Benzoylacetone	0.080	90.5
	0.118	90.7
	0.123	90.2
	0.169	90.4
	0.293	90.8
	0.316	90.4
p-Bromobenzoylacetone	0.071	91.9
	0.103	92.5
	0.223	93.4
p-Nitrobenzoylacetone	0.065	97.5
	0.082	97.8
	0.102	97.2
	0.152	97.8

Keto–Enol Equilibrium. Substituent Effects.—The position of the keto–enol equilibrium is influenced by the nature of the *para*-substituent, the percentage of

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[18] H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

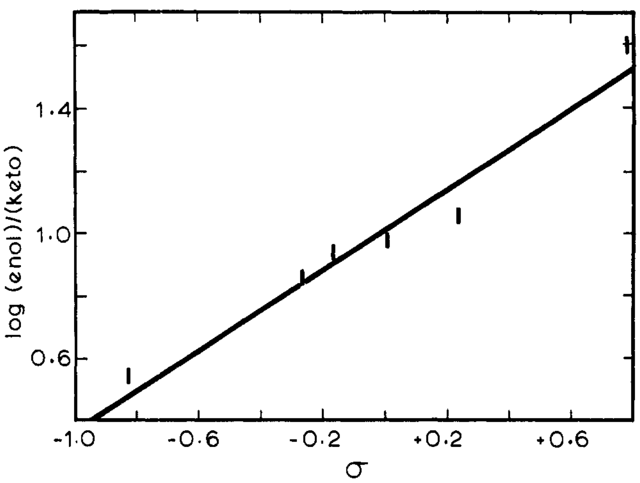


Figure 1.—Plot of log (enol)/(keto) *vs.* the Hammett σ for benzoylacetones.

diketone increasing with the electron-releasing power of the substituent. Figure 1 shows a graph of log (enol)/(diketone) *vs.* the Hammett σ constant for the six benzoylacetones in the concentration range of 0.06–0.10-mol fraction. The best straight-line fit corresponds to the equation

$$\log K = 0.629\ \sigma + 1.019$$

By comparison, application of the Hammett relation to the equilibrium constant data obtained by bromine titrations for series of *meta-* and *para*-substituted benzoylcyclohexanones and benzoylcyclopentanones yielded slopes of 0.70 and 0.93.[3,19]

Discussion

The observation of two methyl resonances, as well as both methylene and vinylic resonances, indicates the equilibrium mixture to consist of at least two species, the less abundant being unenolized β-diketone. This is borne out by the relative intensities of the diketone methylene and methyl groups and the magnitude of the cross-carbonyl coupling constant. Our data do not allow us to infer its conformation.

Nature of the Enol.—Although chemical shift data show clearly that the remainder of the equilibrium mixture is enolic, they cannot indicate the structure of the enol, which can be either II or III. The strongly downfield-shifted hydroxyl resonance indicates most, if not all, of the enol to be intramolecularly hydrogen-bonded, *i.e.*, *cis* II or *cis* III. We cannot, however, rule out the possibility that there may be a small amount of *trans*-enol in solution. Lowe[4] has interpreted the appearance of weak absorption at 3400–3700 cm^{-1} and 1708–1722 cm^{-1} in the infrared spectra of benzoylacetones as indicating the presence of a small amount of *trans*-enol.

Long-range couplings provide a method of estimating the position of the equilibrium *cis* II $\rightleftarrows$ *cis* III. In both cases, allylic couplings are possible: in *cis* II across a formal single bond; in *cis* III across a formal double bond. Couplings across formal single bonds, as in *cis* III are immeasurably small (methyl vinyl ketone <0.2 Hz;[20] methyl styryl ketone <0.2 Hz;[20] 4-methylaminopent-3-en-2-one <0.2 Hz[21]), whereas analogous couplings across formal double bonds are sizable (ethyl acetoacetate, J = 0.77 Hz;[14] 4-methylaminopent-3-en-2-one, J = 0.53 Hz[21]). Assuming rapid interconversion of *cis* II and *cis* III, the averaged allylic coupling constant is given by

$$J\ (\text{avg}) = N_{\text{II}}J_{\text{II}} + N_{\text{III}}J_{\text{III}}$$

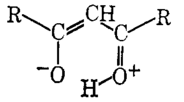
and, if we take J_{II}' = 0.1 Hz and J_{III} = 0.6 Hz, then for *p*-methoxybenzoylacetone [J (avg) = 0.13], N_{II} = 0.94. Even for the extreme case where $J_{\text{II}} = 0$, N_{II} = 0.78. Hence, we estimate the amount of *cis* III present in the equilibrium mixture at about 5–10%. This is in excellent agreement with the simple Hückel molecular orbital calculations of Forsen,[7] which indicate the equilibrium constant for the system *cis* II $\rightleftarrows$ *cis* III to be 12. By contrast, the ^{17}O nmr results of Gorodetsky, *et al.*,[6] indicate approximately equal amounts of *cis* II and *cis* III to be present in solution.

Campbell, *et al.*, have concluded on the basis of ultraviolet spectral studies of benzoylcyclohexanones and benzoylcyclopentanones that the dominant enol in both cases contains the cinnamoyl chromophore.[3,19]

Iimura[22] has reported *p*-methoxy- and *p*-nitrobenzoylpinacolone to enolize in the direction of the cinnamoyl chromophore. Paradoxically, the parent benzoylpinacolone is reported to enolize in the opposite direction.

The approximate nature of our discussion of the direction of enolization prevents us from discussing the substituent effect on the enol–enol equilibrium.

The Hydrogen Bond in the Enol.—The substituent effect on the position of the hydroxyl resonance of the enol is completely out of line with substituent effects on all the other resonances, both from the standpoint of its enormous sensitivity (slope = 0.56) and the fact that electron-releasing substituents produce a paramagnetic shift of the hydroxyl peak. The anomalous substituent effect has been noted by other workers,[23,24] and Nonhebel has ascribed it to the fact that "an electron-withdrawing substituent adjacent to a CO group causes the CO oxygen to be less electronegative with consequent strengthening of the bond between the other oxygen and the hydrogen-bonded hydrogen . . . and a consequent weakening of the hydrogen bond."[24] The weakening of the hydrogen bond by the introduction of electron-withdrawing substituents at the terminal positions of a β-diketone is indicated by normal coordinate analyses of the infrared spectra of acetylacetone and hexafluoroacetylacetone; the stretching force constants for the hydrogen bond are 0.300 and 0.128 mdyn/Å, respectively.[18] The corresponding hydroxyl shifts are τ −5.57 and −3.00.[14] The effect may be ascribed to destabilization of canonical forms such as



which are expected to contribute to the hydrogen-bond strength. Hence the anomalous variation in τ (OH)

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[19] R. D. Campbell and W. L. Harmer, *J. Org. Chem.*, **28**, 379 (1963).

[20] K. Takahashi, *Bull. Chem. Soc. Jap.*, **37**, 963 (1964).

[21] D. J. Sardella, unpublished observations.

[22] F. Iimura, *Nippon Kagaku Zasshi*, **77**, 1855 (1956).

[23] G. Allen and R. A. Dwek, *J. Chem. Soc., B*, 161 (1966).

[24] D. C. Nonhebel, *Tetrahedron*, **24**, 1869 (1968).

with substituent in our benzoylacetone series arises from the progressive weakening of the intramolecular hydrogen bond by increasingly electronegative substituents.

Substituent Effects on Keto–Enol Equilibrium.—The question of whether enol stability is due primarily to mesomeric electron delocalization[7,8] or inductive electron withdrawal[9] can be discussed in terms of our results. The ρ value, 0.63, is closely similar to the value of 0.70 found for benzoylcyclohexanones.[3] Although the magnitude suggests some steric hindrance to complete coplanarity, the fact of the correlation and the observed sensitivity of the strength of the hydrogen bond to substituent suggest strongly that there is appreciable overlap between the phenyl group and the remainder of the enol π system.

Experimental Section

Nmr Spectra.—Spectra were measured initially on a Varian Associates A-60 console coupled to a DP-60 power supply and magnet assembly, and later on a standard Varian A-60 instrument. Sample temperature was about 30°.

Chemical shifts, reported in τ values,[25] were obtained by direct reading from the 500-Hz scale and are considered to be accurate to better than 0.02 ppm.

Long-range coupling constants were measured directly from the 50-Hz scale. The values reported are the average of several values, obtained by sweeping in both directions at a sweep speed of 0.1 Hz/sec. The 50-Hz scale was calibrated daily against a 50.0-Hz side band.

Samples were weighed directly in nmr tubes and spectra measured as soon after preparation as possible. No samples were degassed.

Compounds.—All compounds used in this investigation were synthesized by standard methods or obtained commercially.

Melting points were determined with an electrically heated and stirred oil bath, using thermometers calibrated directly in units of 0.2°, and are uncorrected.

Microanalyses were performed in duplicate by Alfred Bernhardt Mikroanalytisches Laboratorium (Germany).

Deuteriochloroform was obtained from Merck Sharp and Dohme of Canada in isotopic purity of better than 99.5% and was used without further purification.

Tetramethylsilane (Anderson Chemical Division, Stauffer Chemical Co.) contained no detectable impurities.

Benzoylacetone (Eastman Organic) was purified by vacuum sublimation and recrystallization from Skellysolve B, giving long, flat needles, mp 55.8–56.5° (lit.[26] mp 57–58°).

p-**Methylbenzoylacetone.**—*p*-Methylacetophenone (Eastman Organic) was condensed with ethyl acetate by the method of Sprague, *et al.*,[27] using either sodium ethoxide (45.5% yield) or a sodium dispersion (20–25%). Double distillation was performed through a 200-mm vacuum-jacketed fractionation column packed with glass helices. The product had mp 23.3–24.4°; bp 118.0–118.5° (0.75 mm); $n^{25}\text{D}$ 1.5925 [lit.[28] bp 154–155° (14 mm)].

p-(**Trideuteriomethyl**)**acetophenone.**—Benzotrichloride (Eastman Organic) was reduced with zinc and acetic acid-*d* (prepared by hydrolysis of acetyl chloride with deuterium oxide) to toluene-α,α,α-d_3 in 80% yield by the method of Renaud and Leitch.[29]

To 5.8 g (0.06 mol) of toluene-d_3 in 20 ml of carbon disulfide and 14.8 g (0.11 mol) of aluminum chloride, 5.4 g (0.05 mol) of acetic anhydride was added, with stirring, over a 30-min period. The mixture was heated under reflux for 1 hr, then the complex was decomposed with 200 ml of ice and water and extracted with 200 ml of ether, and the solvent was removed *in vacuo*. The product was recovered by vacuum distillation in 58% yield.

The nmr spectrum of *p*-(trideuteriomethyl)acetophenone is identical with that of undeuterated material, except for loss of the peak at τ 7.75, assigned to the ring methyl group.

p-(**Trideuteriomethyl**)**benzoylacetone.**—To 2.8 g (0.12 mol) of powdered sodium under anhydrous ether was added a mixture of 4.1 g (0.02 mol) of *p*-(trideuteriomethyl)acetophenone and 5.1 g (0.06 mol) of ethyl acetate dropwise over a 30-min period with stirring and mild heating. The solution was allowed to sit, with stirring, for 3 hr. Ethanol was added to decompose the excess sodium and the resulting flocculent yellow precipitate was treated with ether and 30% sulfuric acid to effect solution. The aqueous layer was extracted with ether, the combined organic layers were dried ($CaSO_4$), and the solvent was removed *in vacuo*. Double distillation gave a fraction of bp 73–77° (0.01 mm), $n^{25}\text{D}$ 1.5906 (39%).

Nmr spectra indicated 90% deuteration. Calcd for 90% deuteration: C, 73.84; H, 8.28. Found: C, 73.43; H, 8.37.

p-**Methoxybenzoylacetone.**—*p*-Methoxyacetophenone (Eastman Organic) was condensed with ethyl acetate, using the same procedure as for *p*-CH_3-BA. The product sublimed with difficulty from the melt and was recrystallized from Skellysolve B: mp 54.5–55.2° (lit.[28] mp 53–54°).

p-(**N,N-Dimethylamino**)**benzoylacetone.**—*p*-N,N-Dimethylacetophenone (16.2 g, 0.099 mol) (Frinton Laboratories) was added slowly and with stirring to a sodium dispersion (4.7 g, 0.204 mol) in 300 ml of tetrahydrofuran (distilled from CaH_2 immediately before use) and allowed to stand overnight. To the resulting yellow solution was added over a 40-min period 27.0 g (0.306 mol) of ethyl acetate, and the reaction was allowed to proceed overnight with mild heating, during which time all the sodium disappeared. The solution was acidified to pH 6 with 20% H_2SO_4, extracted with methylene chloride, and dried ($CaCl_2$). Recrystallization from Skellysolve B gave either dark yellow plates, mp 114–118°, or lemon-yellow powder, mp 118–120°, depending on conditions. On standing after crystallization, the powder was transformed to plates, mp 118–120°. The uv spectra [λ_{max} (log ϵ) 240 (3.91), 247 (3.90), 354 mμ (4.60)] and nmr spectra of the 114–118° and 118–120° materials were identical.

Anal. Calcd for $C_{12}H_{16}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 69.50; H, 7.38; N, 7.05.

p-**Bromobenzoylacetone.**—A solution containing 25 g (0.125 mol) of *p*-bromoacetophenone (Eastman Organic) dissolved in 89.3 g (0.875 mol) of acetic anhydride at 0°, with stirring, was saturated with boron trifluoride. Boron trifluoride was bubbled in for 2 more hr, and the solution became a slurry and then solidified. Sodium acetate (87 g in 350 ml of water) was added, and the solution was heated under reflux for 30 min, cooled to 0°, filtered, and acidified with glacial acetic acid at 0°. The resulting white precipitate was washed with water and dried ($CaCl_2$). Double recrystallization from hexane, sublimation twice *in vacuo*, and recrystallization from benzene–hexane gave white needles, mp 96° (lit.[30] mp 92.5°). The procedure is a modification of that described by Hauser and Adams.[31] The yield was 44%.

p-**Nitrobenzoylacetone.**—*p*-Nitroacetophenone (Eastman Organic) was condensed with acetic anhydride in the presence of boron trifluoride by the method of Walker and Hauser.[32] Recrystallization twice from hexane, sublimation twice [110–118° (0.2 mm)], and recrystallization again from hexane gave pale golden yellow needles, mp 112.5–113.0° (lit.[32] mp 112.0–112.8°).

Registry No.—*p*-H-BA, 93-91-4; *p*-CH_3-BA, 4023-79-4; *p*-CH_3O-BA, 4023-82-9; *p*-N$(CH_3)_2$-BA, 20449-17-6; acetylacetone, 123-54-6; *p*-Br-BA, 4023-81-8; *p*-trideuteriomethyl)benzoylacetone, 20455-50-9.

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