[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA, IOWA CITY, IOWA]

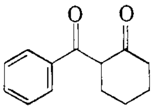
β-Diketones. II. Ultraviolet and Infrared Spectra of Some 2-Aroylcyclohexanones[1,2]

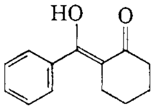
BY R. D. CAMPBELL AND H. M. GILOW[3]

RECEIVED JUNE 15, 1960

Ultraviolet and infrared absorption spectra of ten substituted benzoylcyclohexanones are presented. The Hammett correlation is applied to substituent effects on absorption bands. Comparison spectra of ten model compounds are presented and relationships are discussed. The scope of the relationship between spectra of the diketones and structure and tautomerism is discussed, the limitations are pointed out.

In the previous paper[2] in this series, the extent and direction of tautomerism of benzoylcyclohexanone was reported and discussed in terms of chemical behavior. In the course of that work, it seemed that infrared and ultraviolet spectra would be useful in determining the tautomeric character of the compounds studied. The conjugated systems (chromophores) in the three tautomeric structures I, II and III are, respectively, the benzoyl, cinnamoyl and phenylvinyl ketone structures. These chromophores show characteristic ultraviolet absorption patterns. The benzoyl group absorbs near 2500 Å. (ϵ 5–10,000), with weak ($\epsilon <$ 1000) absorption in the 2900–3300 Å. region.[4-6]


I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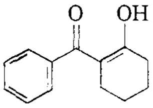
III

The cinnamoyl chromophore shows a variable band near 2400 Å. (ϵ 1–5,000) and a band with intense absorption (ϵ 7–15,000) in the 2800–3300 Å. region. The phenylvinyl ketone chromophore has an absorption pattern similar to that of the benzoyl chromophore, with a slightly greater intensity, and small bathchromic shift. Thus it was expected that the ultraviolet spectra of II and III should be substantially different.

In the infrared absorption spectra, Compound I should be distinguished from II and III by the presence of a carbonyl band above 1700 cm.$^{-1}$ in I, and the absence of the band in II and III. Differences between II and III in the infrared are not expected to be significant for assignable bands.

Thus, one might expect to distinguish the keto form I on the basis of infrared spectra from the enol forms, and to distinguish between enol forms II and III on the basis of the ultraviolet spectra, unless the influence of the OH group operates to remove the distinction.

The Hammett Correlation.—The Hammett equation[7] has been applied successfully to the correlation of *m*- and *p*-substitution and reactivity in reaction rates and equilibria. The application of this correlation to benzoylcyclohexanone keto–enol equilibria is shown by Fig. 1. From the enol percentage data reported previously[2] have been calculated equilibrium constants listed in Table I. The percentage error listed for each equilibrium constant represents the *maximum* deviation from the average of two to five determinations. The error limit is represented in Fig. 1 by a vertical line through each point. The horizontal limit line through each point represents the standard deviation for σ-values.[7] The σ-values for *o*-substituents were calculated from data for benzoic acid ionization constants. The only substantial failure of the correlation is with the *o*-fluoro compound. The slope of the line in Fig. 1 is 1, which is also the value of ρ for benzoic acid ionization.

TABLE I

BENZOYLCYCLOHEXANONE KETO–ENOL EQUILIBRIUM AND HAMMETT σ-PARAMETER

Compd.	Subst.	Enol,[a] %	K	log K/K_0	σ[b]
I	None	3.3 ± 0.4	0.034(12%)[c]	0.0	0
IV	*p*-CH_3O	2.6 ± .1	.027(16%)	− .097	−0.268 ± 0.063
V	*p*-CH_3	3.0 ± .4	.031(12%)	− .036	− .170 ± .080
VI	*p*-Cl	4.1 ± .5	.042(11%)	+ .097	+ .227 ± .054
VII	*p*-F	4.2 ± .5	.043(11%)	.107	.062 ± .065
VIII	*m*-Cl	6.9 ± .1	.074(1%)	.342	.373 ± .053
IX	*o*-CH_3	50.0 ± .1	1.0(1%)	.477	.392
XII	*o*-F	48.7 ± .5	0.97(1%)	.462	.936
XI	*o*-Cl	88.8 ± .4	8.0(4%)	1.38	1.26
X	*o*-Br	92.9 ± 1.3	13.1(18%)	1.46	1.35

[a] See ref. 2; error is maximum in 2 to 5 runs. [b] See ref. 7; values for *o*-substituents calculated from data for benzoic acid ionization. [c] Maximum percentage deviation in 2–5 determinations.

That *o*-substituents fit well in the correlation, may be understood in terms of the similarity of the solvation and structure characteristics of the two

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[1] Taken in part from the Ph.D. thesis of H. M. Gilow, August, 1959. Presented at the 137th Meeting, American Chemical Society, Cleveland, Ohio, April, 1960.

[2] Previous paper, THIS JOURNAL, **82**, 2389 (1960).

[3] Ethyl Corporation Fellow 1958–1959.

[4] N. H. Cromwell, H. H. Eby and D. B. Capps, THIS JOURNAL, **73**, 1224 (1951).

[5] R. D. Campbell and N. H. Cromwell, *ibid.*, **79**, 3456 (1957).

[6] W. B. Black and R. E. Lutz, *ibid.*, **77**, 5134 (1955).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186 ff.

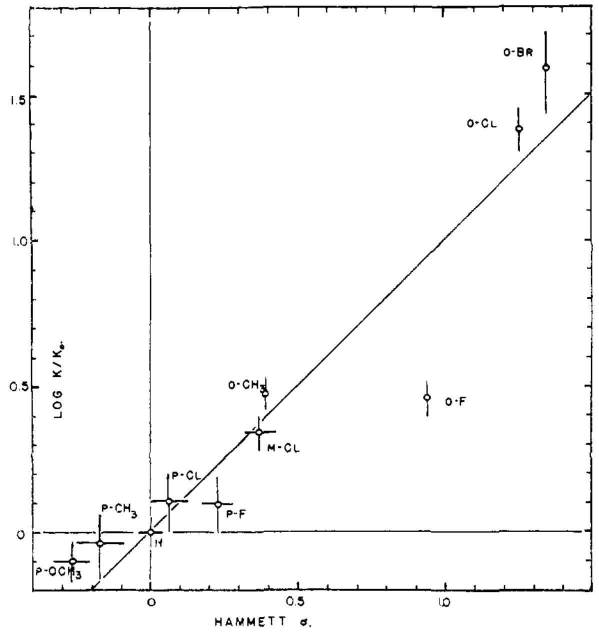
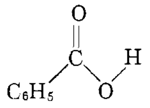
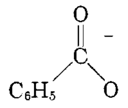


Fig. 1.—Log K/K_0 for keto–enol equilibria of benzoylcyclohexanones plotted for substituents indicated.

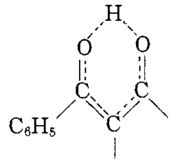
systems as indicated in structures I, A, B and R. The "*ortho* effect" due to steric and dipole effects is parallel in the two series. This is expected if



A



B



R

the enol form is structure II or a resonance hybrid (structure R). Thus the substituent effects upon solvation and stability are expected to be parallel in structures I and R, and also parallel in structures A and B.

That the value of $\rho = +1.0$ fits the data moderately well is of limited significance. One concludes from the positive value of ρ that substituents which are electron releasing by resonance stabilize the keto form to a greater extent than the enol structure, or, conversely that the keto group is more electron demanding than the enol structure. The absolute value of ρ is reasonable. In the absence of data for the *ortho* substituents, a value of $+0.7$ for ρ would fit as well.

The Hammett relation[7] may be applied to substituent effects in infrared and ultraviolet spectra. The relationship between Hammett σ-values and spectra shifts is given by eq. 1. This relationship is

$$\Delta\bar{\nu}\left[\frac{hc}{2.3RT}\right] = -\sigma\rho - \frac{\Delta(\Delta S)}{2.3R} \qquad (1)$$

derived from the Hammett eq. 2 with the assumption that $\Delta E = \Delta H$. Thus, systems in which solvent interaction effects are not negligible may not be expected to fit the correlation. The relation[8] between $\Delta(\Delta F)$ and the Hammett parameters along with the relation between internal energy

$$\log K/K_0 = \sigma\rho = -\Delta(\Delta F)/2.3RT \qquad (2)$$

change and wave number, (3), are inserted into the thermodynamic eq. 4, which gives, on rearrangement, eq. 1. Thus eq. 1 suggests that a linear rela-

$$\Delta E = h\nu = h\bar{\nu}c \qquad (3)$$

$$\Delta(\Delta E) = \Delta(\Delta F) + T\Delta(\Delta S) \qquad (4)$$

tionship is to be expected between Hammett σ-values and the spectral absorption bands expressed in wave numbers. The only prior attempt to correlate spectral band locations with σ-values was by Doub and Vandenbelt.[9] These authors correlated $\Delta\lambda$ with Price's (σ_p-σ_m).

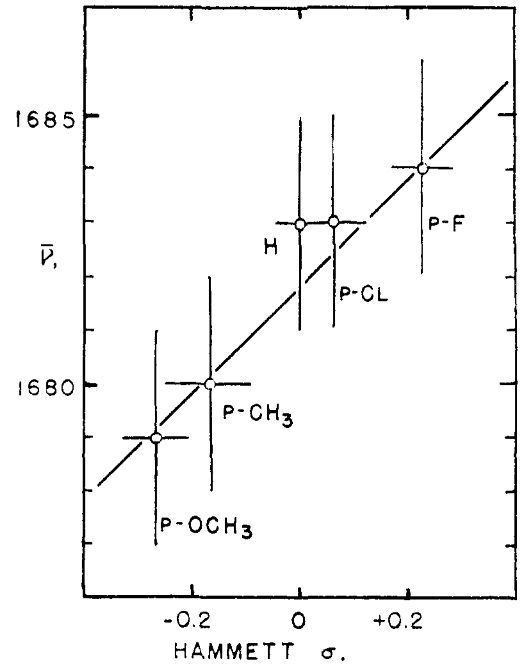


Fig. 2.—Wave number in cm.$^{-1}$ for the conjugated carbonyl stretching frequency.

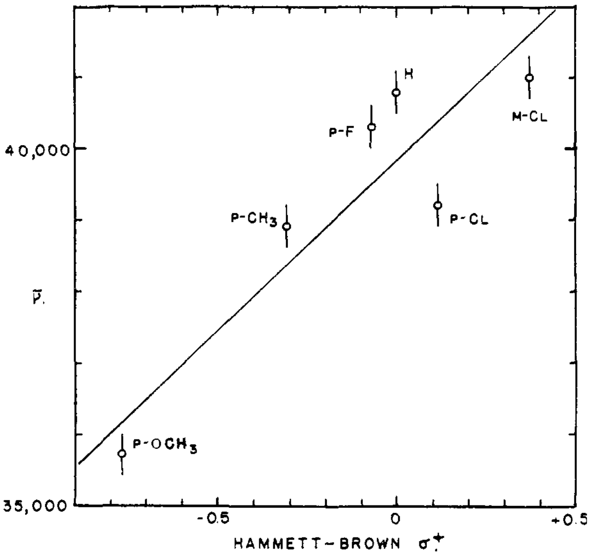


Fig. 3.—Wave number in cm.$^{-1}$ for the benzoyl chromophore in the 2400–2800 Å. region.

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(8) C. F. Prutton and S. H. Maron, "Fundamental Principles of Physical Chemistry," The Macmillan Co., New York, N. Y., 1950, Ch. 10, 11.

(9) L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

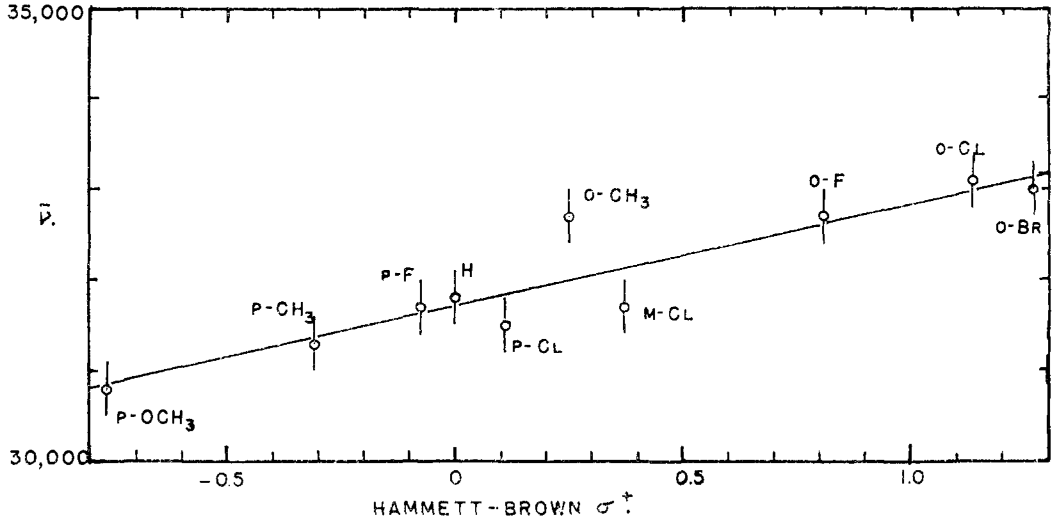

Fig. 4.—Wave number in cm.$^{-1}$ for the cinnamoyl chromophore in the 2800–3300 Å. region.

Figures 2, 3 and 4 show the result of the application of the correlation of eq. 1. In Fig. 2, the infrared carbonyl stretching frequency is plotted against σ-values. Probable error for σ-values is indicated as before. Probable error for $\bar{\nu}$-values is indicated as 2 cm.$^{-1}$, which is an arbitrary (and optimistic) estimate. The probable error for the slope of the line is extremely large. The slope shown indicates a shift of 10 cm.$^{-1}$ per unit of σ, which is a reasonable value. Further studies are planned in which modifications of standard techniques are used to obtain accurate values for small shifts of infrared absorption bands.

The two characteristic absorption bands in the ultraviolet spectra, *viz.*, the benzoyl and the cinnamoyl bands, are correlated with the σ^+-values[10] in Figs. 3 and 4, respectively. Since direct conjugative interaction is expected for *o*- and *p*-substituents, the σ^+-values are used. For the benzoyl band the shifts are substantial. The value for the methoxy compound shows serious deviation if σ-values are used instead of σ^+. The absorption band for the *p*-chloro compound appears at longer wave length than is predicted by the correlation. The deviation is not substantial, however.

The correlation of σ^+-values with the cinnamoyl band in the enols in Fig. 4 shows a smaller substituent effect. No significant deviations appear. The probable limit of error indicated on Figs. 3 and 4 for the wave number values is estimated reasonably as 1% (3 mμ or 330 cm.$^{-1}$ in the 300 mμ region). The band shift is shown in Figs. 3 and 4 as 4800 and 1100 cm.$^{-1}$ per unit σ^+ for the benzoyl and cinnamoyl chromophores, respectively. The observation that substituent effects are greater in a shorter conjugated system is reasonable. The resonance forms which contribute principally to the excited state of the cinnamoyl chromophore have a greater separation of charge, making the system less sensitive to influences of substituents; also, some of the stable resonance forms in the latter do not involve substituents.

Infrared Spectra.—The most significant characteristic of the infrared absorption is the presence and location of the carbonyl stretching band. In their keto forms, the diketones absorb at 1717–1724 cm.$^{-1}$ for the cyclic, unconjugated carbonyl group and at 1679–1684 cm.$^{-1}$ for the carbonyl group conjugated with the benzene ring.[11] The enols do not absorb in either region. Instead, a broad band appears in the 1600 cm.$^{-1}$ region.[11] In some cases a keto–enol equilibrium was established. In such cases, both of the ketone bands and the broad enol band appeared. One example, 2-(2-naphthoyl)-cyclohexanone (XIV), is shown in Fig. 5, showing the absorption curves in the 1500–1800 cm.$^{-1}$ region for the pure keto and enol forms, and the equilibrium mixture.

The pure enol forms of the *m*-chloro-, *p*-fluoro-, 2-(2-naphthoyl) and *o*-substituted compounds show in addition to the 1600 cm.$^{-1}$ enol band the absence of a band in the O–H region (see Table II). It is evident that strong hydrogen bonding is taking place. The OH stretching frequency may have been shifted to the 3000 cm.$^{-1}$ region. Thus it would not be discernible in the strong CH absorption band at 2920–2930 cm.$^{-1}$. Experimental evidence[2] (diazomethane reaction, solvent effect on enol content) has indicated that strong intramolecular (chelate) hydrogen bonding occurs in this series. The related methoxyl compounds (Table III) absorb normally in the carbonyl region. It is planned to replace the labile hydrogen atom with deuterium to aid in locating the OH stretching band.

Thus it is possible by means of infrared spectra to distinguish between keto and enol forms and tautomeric mixtures by the characteristic carbonyl and enol bands. That is, form I may be distinguished from II and III. No distinction between structures II and III is found in the infrared spectra, due to strong hydrogen chelation, with no carbonyl band in the spectrum of the enol.

Ultraviolet Spectra.—The two principal chromophores, *viz.*, the cinnamoyl and the benzoyl (and/or phenylvinyl ketone), show absorption in the spectra of the diketones of this series. The effect of sub-

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[10] H. C. Brown and Y. Okamoto, This Journal, **79**, 1913 (1957).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 142–143.

TABLE II

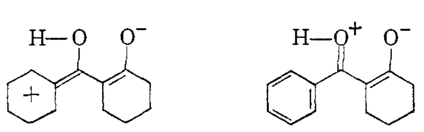
INFRARED SPECTRAL DATA FOR SUBSTITUTED BENZOYLCYCLOHEXANONES

Compd.	Subst.	Form	C = O Unconj.	C = O Conj.	Enol[a]
IV	*p*-CH_3O	K	1717s[d]	1679s	1602–1510m
V	*p*-CH_3	K	1718s	1680s	1610–1520m
		Eq	1719m	1680m	1610–1505s
I	H	K	1724s	1683s	1603–1589w
VI	*p*-Cl	K	1721s	1683s	1590w
VII	*p*-F	K	1721s	1684s	1600–1500m
		E			1600–1500s
VIII	*m*-Cl	E			1600s
IX	*o*-CH_3	E			1600s
XI	*o*-Cl	E			1600s
XII	*o*-F	E			1600–1500s
XIII	2,3-C_4H_4[b]	E			1635–1535s
XIV	3,4-C_4H_4[c]	K	1720s	1679s	
		Eq	1721m	1680m	1615–1500
		E			1615–1540s

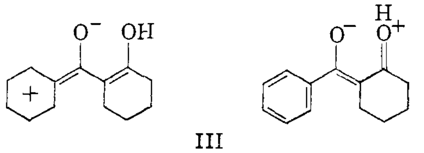
[a] No OH band appears in the 3100–3500 cm.$^{-1}$ region. [b] 2-(α-Naphthoyl)-cyclohexanone. [c] 2-(β-Naphthoyl)-cyclohexanone. [d] Numbers are in cm.$^{-1}$; letter indicates strong (s), medium (m) or weak (w) absorption.

stituents on these bands is discussed above and in Figs. 3 and 4. The member (XI) with *o*-chloro substitution may be compared with the corresponding model compounds in Table III, *o*-chlorobenzalcyclohexanone (XVIII) and *o*-chlorobenzoylcyclohexene (XVI) as well as the two enol methyl ethers (XVII, XIX) of the diketone XI.

The parent unsaturated ketones XVI and XVII absorb at 2400 and 2780 Å., respectively. Structural analogy might suggest that the corresponding enols of XI with forms III and II (respectively) should have spectra with a similar pattern. That is, structure II is expected to show strong cinnamoyl absorption while structure III should have a stronger band in the benzoyl phenylvinyl ketone region. The enol form isolated shows the cinnamoyl band, suggesting that the enol form exists in form II.



II



III

The spectra of the enol methyl ethers XVII and XIX illustrate a characteristic effect in the acrylophenone and cinnamoyl chromophores. Only a small (20 Å.) bathochromic shift is caused by introduction of the methoxyl group into the cinnamoyl structure (XVIII and XIX). However, the methoxyl group causes a shift of 500 Å. in the acrylophenone band (XVI and XVII). This gross difference in substituent effects has been noted in other cinnamoyl and acrylophenone compounds.[5] Thus the strong absorption of the enol form of XI at 3020 Å. does not provide evidence to choose structure II or III as the correct form, nor does it preclude the possiblity of a mixture of the two. Resonance forms such as those shown for II and III are expected to contribute to the stability of the excited state of the cinnamoyl and acrylophenone electronic transitions in the enol(s) and in the enol methyl ethers as well.

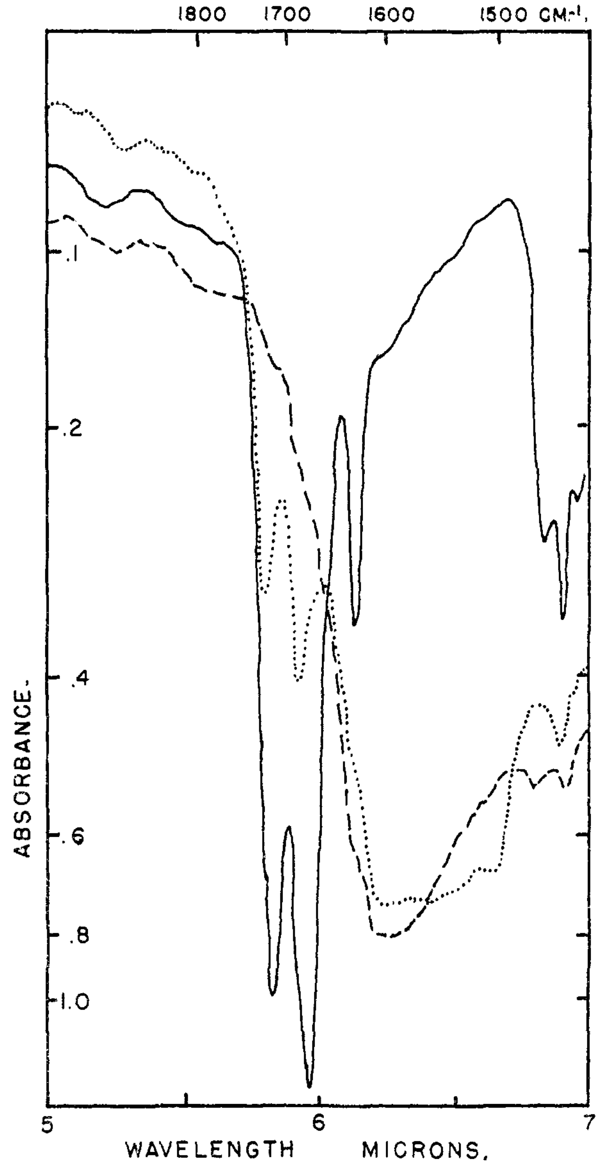


Fig. 5.—Infrared carbonyl region spectra: 2-(2-naphthoyl)-cyclohexanone (XIV), ———; the corresponding enol, - - - - - -; and the equilibrium mixture........

The same pattern of substituent effects is seen in the benzoylacetone series.[12] The parent diketone XV has a strong cinnamoyl absorption band (3100 Å.). Benzalacetone and ethylidene acetophenone have cinnamoyl and acrylophenone chromophores 2790 and 2500 Å., respectively, and show the expected absorption pattern. The spectra of the enol methyl ethers again show the large bathochromic shift (280 Å.) of the acrylophenone band and, in this case, a slight hypsochromic shift (−70 Å.) of the cinnamoyl band.

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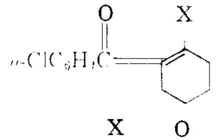
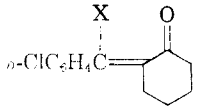
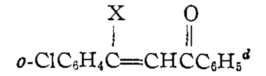
(12) B. Eistert and E. Merkel, *Ber.*, **86**, 895 (1953).

TABLE III

SPECTRA OF MODEL COMPOUNDS

Compound		X	Infrared bands^a C=O	C=C	Aromatic	Ultraviolet
	XVI	H	1661	1641		2400^b(9.4)^c
	XVII	OCH$_3$	1644	1613		2900(13.7)
	XVIII	H	1684	1609		2780(12.4)
	XIX	OCH$_3$	1682	1607	1550	2800(9.2)
 $o\text{-}ClC_6H_4\overset{\overset{X}{\vert}}{C}{=}CH\overset{\overset{O}{\Vert}}{C}C_6H_5$^{d}	XX	H	1670	1647	1580	2940(10.9)
	XXI	OCH$_3$	1680	1611	1550	2380(10.5) 2800(16.0)
	XXII	OH				3320(19.4) 2550(7.0)

^{a} In cm.$^{-1}$. ^{b} Wave length (Å.) of maximum absorption. ^{c} Extinction coefficient × 10^{-3}. ^{d} Prepared per C. L. Bickel, THIS JOURNAL, **68**, 865 (1946).

TABLE IV

ULTRAVIOLET SPECTRA OF SUBSTITUTED BENZOYLCYCLOHEXANONES

Compd.	Subst.	Tautomer Equilibrium	Keto	Enol	Enol, %^{c}	(σ^+)^d
I	None	2450^a(7.8)^b 3140(4.4)	2450(9.74)		20	......
IV	p-CH$_3$O$^-$	2800(14.9) 3250(3.5)^e	2800(16.3)		9	−0.764
V	p-CH$_3$	2570(12.7) 3190(3.3)	2570(15.3)		18	− .306
VI	p-Cl	2550(12.9) 3170(5.2)	2550(16.2)		21	.112
VII	p-F	2480(12.4) 3150(5.0)	2480(14.0) 3150(1.7)	2480(5.2) 3150(12.4)	25	.0714
VIII	m-Cl	2440(4.8) 3150(11.2)	2440(14.8) 2920(2.3)	2440(4.8) 3150(11.2)	100	.373
IX	o-CH$_3$	2300(1.6)^e 3020(11.6)		2300(1.1)^e 3020(11.8)	100	.25^g
X	o-Br	3030(11.6)		3030(11.7)	100	1.27^g
XI	o-Cl	2300(1.6)^e 3020(11.6)		2300(1.1)^e 3020(11.8)	100	1.14^g
XII	o-F	2410(5.2) 3060(9.2)		2450(3.4) 3060(12.1)	75	0.81^g
XIV	C$_4$H$_4$^{f}	2500(31.1) 2900(9.9) 3230(6.1)		2500(14.7) 2900(11.3) 3230(14.5)	42	−0.132
XV	Benzoyl acetone	2470(5.6) 3100(14.8)				

^{a} Wave length (Å.) of absorption maximum. ^{b} Extinction coefficient × 10^{-3}. ^{c} Calculated from spectral data. ^{d} From Brown, ref. 10. ^{e} Shoulder. ^{f} β-Naphthyl. ^{g} Calculated from σ; see ref. 10 and note b, Table I.

In the o-chlorobenzalacetophenone (XX) series, again, introduction of the methoxyl group to give XXI produces a small hypsochromic shift. The diketone XXII at tautomeric equilibrium (~ 100% enol) absorbs at 3320 Å., or 500 Å. toward longer wave length than the enol methyl ether. In the two previous series cited the enols absorbed at 200–400 Å. toward longer wave length than did the corresponding enol ether.

The ultraviolet absorption spectra of the benzoylcyclohexanones give a good indication of the extent of enolization (see Table IV). In two cases, VII and VIII, the pure keto and enol forms were isolated. The spectra of both tautomeric forms of each as well as the spectra of the equilibrium mixtures were determined. The absorbance data indicate the m-chloro compound VIII to be completely enolic at equilibrium. For the p-fluoro compound VII the enol content at equilibrium is 20% based on the benzoyl band, or 30% based on the cinnamoyl band. This discrepancy is probably due to the fact that the equilibrium contains both enol forms II and III, whereas the enol form of VII isolated is probably just one of the two forms possible. Also, variations in intensity due to polymorphic or stereoisomeric forms have been observed.[13]

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[13] B. Eistert, R. Weygand and E. Csendes, *Ber.*, **84**, 745 (1951).

The enol content of the equilibrium mixture for each member of the diketone series was estimated by assuming that the absorbance of the 2500–2800 Å. band is entirely due to the keto form, and that the 3000–3150 Å. band is entirely due to enol form. This assumption gives crude results, but permits an estimate of enol content in those cases in which only one pure tautomer is available. The enol content obtained by this method is listed in Table IV. The order of increasing enol content in 95% ethanol by the spectroscopic method agrees well with the order of increasing enol content found in methanol by bromine titration[2] (Table I).

Experimental

Materials.—The compounds studied were analytical samples as reported in the previous article,[2] or were prepared and purified according to literature methods as indicated in the tables in which the data appear. The solvents used were 95% ethanol (Commercial Solvents) for ultraviolet spectra and carbon tetrachloride (Brothers Chemical Co.) for infrared spectra and were used without further purification.

Measurement of Spectra.—The ultraviolet spectra were determined using a Cary recording spectrophotometer, model 11. Procedure used was according to the manufacturer's instructions. Matched quartz cells were used. The slit control was set at 10 and the fast scanning speed was used. The spectrophotometer was housed in a constant temperature room at 28°. The concentration employed was 10^{-4} molar in all cases. The solutions were freshly prepared and, for equilibrium data, were stored in the dark. Data obtained are listed in Tables III and IV.

The infrared spectra were measured using a Perkin-Elmer model 21 double-beam recording spectrophotometer, with a sodium chloride prism. The control settings were maintained constant at: resolution, 926; response, 1; gain, 5; speed, 4; suppression, 4. The concentration used was 10 mg./ml. Matched 1-mm. cells were used in standard double beam operation. Data obtained are listed in Tables II and III.

Acknowledgment.—The infrared spectrophotometer used in this study was purchased with the aid of a grant from the National Science Foundation.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Reactivity of Thiobenzophenone with Phenylhydrazine

BY JOHN C. POWERS AND F. H. WESTHEIMER

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Thiobenzophenone reacts with phenylhydrazine and with semicarbazide at *p*H 4 about ten times as rapidly as does benzophenone. However, since the reaction of the thio compound is catalyzed by bases, whereas the reaction for the ketone is catalyzed only by acids, the rates differ, at *p*H 6, by a factor of around 2000, and the difference becomes much larger in alkaline solution. Two mechanisms for the processes are discussed.

Thiobenzophenone is reduced non-enzymatically by DPNH (*i.e.*, diphosphopyridine nucleotide) and by N-benzyl dihydronicotinamide to benzhydryl thiol.[1] Since the corresponding reaction of benzophenone has not been observed, the thiocarbonyl group appears, in this particular oxidation–reduction system, very much more reactive than the carbonyl group. The present research was undertaken in the attempt to evaluate the general reacttivity of thiobenzophenone. Two reactions were studied: the reduction of the thioketone with sodium borohydride,[2] and the reaction of the thioketone with carbonyl reagents. The first of these processes is, presumably, a hydride ion transfer reaction. The second reaction is a complex one, where two separate steps are involved; the addition of the reagent to the carbon–sulfur double bond, and subsequent loss of hydrogen sulfide. Each of these reactions may in principle be catalyzed by acid or base, and the acidities and basicities of the reactants will influence the outcome of the reactions. Although in such a complex system the analogy with the reduction by the dihydropyridines is tenuous, the high reactivity of the thioketone, relative to that of the ketone, was here observed. The experiments are described below.

Experimental

Materials.—Benzophenone, recrystallized from ligroin, melted at 47.5–48.5°. Thiobenzophenone was prepared by the method of Staudinger and Freudenberger.[1,3] The compound, on recrystallization from ligroin under nitrogen, was obtained as blue crystals. The product was sealed in 50-mg. quantities in nitrogen-filled ampoules, and stored in a refrigerator prior to use; the compound assayed 95% or better on the basis of its absorption[1] at 600 mμ. Phenylhydrazine hydrochloride, recrystallized from 95% ethanol, melted at 244°; semicarbazide hydrochloride, recrystallized from ethanol-water, melted at 172°. Phenylhydrazinium *p*-toluenesulfonate, prepared from the crude base and acid in ethanol, and recrystallized from 95% ethanol, melted at 185–187°. *Anal.* Calcd. for $C_{13}H_{16}N_2SO_3$: C, 55.69; H, 5.76; N, 9.99. Found: C, 55.41; H, 5.78; N, 9.85.

Tris (*i.e.*, trishydroxymethylaminomethane), obtained from Sigma Chemical Co., melted at 171°; after recrystallization from ethanol–water it melted at 172°; no difference in the kinetic results from the two kinds of material was noted. *p*-Toluenesulfonic acid monohydrate, after recrystallization from aqueous hydrochloric acid, melted at 103–104° and had a neutralization equivalent of 188. Crude sodium *p*-toluenesulfonate was recrystallized three times from water; the final product was free of chloride ion. Salicylic acid melted at 158–159°, benzoic acid at 122°, *o*-chlorobenzoic acid at 140°, *p*-chloroaniline at 70–71°. *o*-Chloroaniline boiled at 109° (35 mm.), benzylamine at 81–84° (35 mm.), pyridine (dried over barium oxide) at 113° at atmospheric pressure, ethanolamine at 165–166° at atmospheric pressure, $n^{25}\text{D}$ 1.4533. The solvent was prepared by mixing four parts by volume of absolute ethanol (Gold Shield) to one part of distilled water; it is described hereafter as "80%" ethanol.

Products.—Approximately 0.7 g. of crude thiobenzophenone was allowed to react at room temperature overnight with 3 g. of phenylhydrazinium *p*-toluenesulfonate in 80% ethanol at *p*H 5–6 under nitrogen. After the solution was cooled in an ice-bath, 0.8 g. of benzophenone phenylhydrazone, m.p. 138–139°, was obtained; yield 83%.

***p*H Measurements.**—The "*p*H" was measured in 80% ethanol at an ionic strength of 0.2 with a Beckman model

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[1] R. H. Abeles, R. F. Hutton and F. H. Westheimer, THIS JOURNAL, **79**, 712 (1957).

[2] J. C. Powers, Thesis, Harvard University, 1958.

[3] H. Staudinger and H. Freudenberger, *Ber.*, **61**, 1576 (1928).