in addition, possessed remarkable toxicity toward *Aerobacter aerogenes*. This property was also characteristic of 2-butoxyethyl vanillate, but was not exhibited by trichloro-*t*-butyl vanillate. The esters of orthovanillic acid appear to be less specific in their toxicity. Of the 5-chlorovanillic acid esters, only the methyl and ethyl esters exhibited any toxicity whatsoever. Toxicity data are given in Table I.

Acknowledgment.—The authors are indebted to John F. McCoy and to Virginia West Martin, respectively, for the microbiological and chemical analyses reported in this paper.

Summary

A large number of new esters of vanillic acid and the closely related acids, orthovanillic and 5-chlorovanillic, were prepared. The inhibiting concentrations of these esters were determined for representative microörganisms.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Infrared and Ultraviolet Spectroscopic Studies on Ketones[1]

BY R. S. RASMUSSEN, D. D. TUNNICLIFF AND R. ROBERT BRATTAIN

The infrared, Raman, and ultraviolet spectra of aldehydes and ketones have been the subjects of numerous studies in the literature.[2] Some further investigations, which were made in connection with the OSRD program on penicillin structure, are reported here. These studies were made in order to gain a better insight into the influence of structure on the spectra of carbonylic compounds.

The infrared spectra, from 2 μ to 15 μ, of the compounds studied are shown in tabular form in Table I; the ultraviolet spectra, from 2200 to 3500 Å., are given in Figure 1. All spectra are of pure liquids or solutions. The sources of samples and further spectroscopic experimental details are given at the end of this paper. Discussion of the infrared spectra is limited to the 3 μ region (NH, OH, and CH stretching vibrations) and 6 μ region (double-bond stretching vibrations). These were the regions actually used on the penicillin structure work and are the ones having an obvious correlation with structure. Thompson and Torkington, however, have noted several interesting regularities at longer wave lengths,[2] and such regularities are also present in Raman spectra.[2]

Infrared Work

Unconjugated Ketones.—Previous published infrared and Raman work[2] together with unpublished work from this laboratory, indicates that unconjugated ketones exhibit their C=O absorption very near 5.83 μ (1715 cm.$^{-1}$). The only compound of this type discussed here in detail, diacetone alcohol, was examined to determine the effect of simple hydrogen bonding on the band position. Badger and Bauer[3] have given evidence, based on studies of the third harmonic of the OH stretching fundamental, that intramolecular hydrogen bonding is present in this compound. The band at 5.84 μ (1712 cm.$^{-1}$) indicates that the effect of hydrogen bonding on the C=O band is small, in contrast to the large effects noted by many investigators on the OH band position (*e. g.*, the shifts of 0.1–0.2 μ noted by Gordy[4] between CH_3OD in benzene and in ketones and other proton acceptor solvents). An auxiliary experiment was carried out by examining a 10% (vol.) solution of methyl ethyl ketone in methanol. Under these conditions, where a large amount of hydrogen bonding of the type $CH_3OH \cdots O{=}CR_2$ is to be expected, the observed C=O band position was 5.86 μ (1706 cm.$^{-1}$), again indicating only a small effect.

The strong OH band is present in the diacetone alcohol spectrum at 2.87 μ (3484 cm.$^{-1}$), the usual position for hydrogen-bonded alcoholic OH groups.

Conjugated Ketones.—Two examples of ketone C=O conjugated to C=C, namely, isophorone and acetophenone, were examined. The strong bands at 5.98 μ and 5.93 μ, respectively, (1672 and 1686 cm.$^{-1}$) are to be attributed to the C=O vibration. These positions are in the range found by others from Raman[5] and infrared[6] work for this band type (roughly 1670–1690 cm.$^{-1}$). The factors influencing the exact amount of this conjugation shift are not yet understood, due to lack of data on a sufficient number of compounds. It is clear, however, that conjugation with C=C effects a shift of the order of 30 cm.$^{-1}$.

Other features of interest in the spectrum of isophorone are: (1) The weak band at 5.83 μ (1715 cm.$^{-1}$) which is probably caused by an unconjugated ketonic impurity (1 or 2% impurity would be sufficient to give a band of this intensity);

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[1] The major part of this work was done under contract between the Office of Scientific Research and Development, and the Shell Development Company (Contract OEM-cmr-445).

[2] *Infrared:* H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945); R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold, New York, 1944; R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, THIS JOURNAL, **70**, 2024 (1948). *Raman:* See J. H. Hibben, "The Raman Effect and its Chemical Applications," A. C. S. Monograph, Reinhold Publishing Corp., New York, N. Y., 1939. *Ultraviolet:* See H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

[3] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

[4] W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

[5] *E. g.*, K. W. F. Kohlrausch and A. Pongratz, *Z. physik. Chem.*, **B27**, 176 (1934).

[6] *E. g.*, Thompson and Torkington, ref. 2.

TABLE I

INFRARED SPECTRA OF KETONES

1. Diacetone alcohol (4-methyl-4-hydroxy-2-pentanone), 0.02 mm. pure liquid.
2. Acetophenone, 0.15 mm. 10% soln. in CCl_4.
3. Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one), 0.02 mm. pure liquid.
4. Biacetyl, 0.15 mm. 5% soln. in CCl_4.
5. Benzil (bibenzoyl), 0.15 mm. 5% soln. in $CHCl_3$.
6. Dibenzoylmethane, 0.15 mm. 10% soln. in CCl_4.
7. Acetylacetone, 0.15 mm. 10% soln. in CCl_4.
8. Acetylacetone acetate (4-acetoxy-3-penten-2-one), 0.15 mm. 5% soln. in $CHCl_3$.
9. 5,5-Dimethyl-1,3-cyclohexanedione, 0.15 mm. 3% soln. in $CHCl_3$. (Wave lengths in μ; intensity in units of 10% absorption; S = solvent interference.) Bands due to ketone C=O stretching vibrations are underlined.

1	2	3	3	5	6	6	8	9
2.87(9)	3.285(3)	3.36(7)	10.08(1)	3.2–3.4 S	3.22(3)	12.0–14.0 S	3.2–3.4 S	3.2-3.4 S
3.33(8)	5.12(1)	3.41(4)	10.52(1)	5.07(1)	3.72(1)	14.09(5)	5.68(7)	~3.8(2)
$\underline{5.84}$(9)	5.28(1)	5.83(2)	10.92(1)	5.22(1)	5.08(1)	14.53(8)	$\underline{5.90}$(5)	5.80(1)
6.80(3)	5.53(1)	$\underline{5.98}$(10)	11.085(7)	5.50(1)	5.23(1)	7	6.01(1)	$\underline{5.875}$(7)
~7.0(5)	$\underline{5.93}$(8)	6.10(4)	11.36(1)	$\underline{5.95}$(8)	5.50(1)	3.32(5)	6.125(7)	$\underline{6.23}$(8)
7.34(10)	6.25(3)	6.81(3)	11.625(5)	6.245(4)	5.64(1)	~3.7(3)	7.00(5)	6.83(2)
7.47(2)	6.315(2)	6.955(5)	12.18(7)	6.31(4)	$\underline{6.1–6.5}$(10)	5.85(5)	7.29(8)	7.30(1)
7.62(2)	6.915(2)	7.02(3)	12.51(1)	6.895(3)	6.75(10)	$\underline{6.1–6.3}$(10)	7.64(1)	7.45(3)
7.92(3)	7.00(1)	7.24(6)	4	7.545(3)	7.64(4)	7.02(10)	~7.9(3)	7.57(3)
8.20(6)	7.36(7)	7.305(6)	2.92(2)	7.77(1)	7.79(3)	7.34(10)	7.9–8.4 S	7.76(4)
8.44(7)	7.69(3)	7.59(2)	3.335(2)	7.9–8.4 S	8.155(7)	8.01(10)	8.48(8)	~8.0(4)
8.71(5)	7.925(8)	7.705(4)	5.69(1)	8.485(5)	8.435(5)	8.53(5)	8.665(4)	7.9–8.4 S
8.83(1)	8.04(2)	7.81(5)	$\underline{5.82}$(8)	8.60(1)	8.60(1)	9.97(5)	8.83(8)	8.59(3)
9.76(3)	8.485(3)	7.92(1)	5.95(1)	9.10(1)	9.035(2)	10.38(8)	9.77(7)	8.73(5)
10.00(3)	8.62(1)	8.025(6)	6.90(1)	9.31(1)	9.36(6)	10.60(8)	10.29(1)	8.89(1)
10.485(5)	9.08(1)	8.41(2)	7.05(5)	9.745(2)	9.72(5)	10.915(9)	10.54(4)	9.20(1)
10.91(5)	9.275(3)	8.69(3)	7.24(2)	9.995(1)	9.98(2)	>12.0 S	10.80(4)	~9.85(2)
12.275(3)	9.77(5)	8.89(2)	7.38(6)	11.44(5)	10.24(3)		11.36(4)	11.24(1)
12.93(2)	10.48(6)	9.67(1)	7.61(1)	>12.0 S	10.765(2)		>12.0 S	>12.0 S
13.185(2)	10.85(2)	9.78(3)	>8.0 run					
	>12.0 S	9.94(1)	discontinued					

(2) The moderately intense band at 6.10 μ (1639 cm.$^{-1}$) assignable as the C=C band shifted by conjugation. Other unpublished studies on this type of conjugated ketone reveal that the shifted C=C band falls in the range 6.07 μ to 6.17 μ (1647 to 1621 cm.$^{-1}$); published Raman data indicate the same thing.[5] Hence the shift from the unconjugated C=C position (*circa* 1660 cm.$^{-1}$) is of the order of 30 cm.$^{-1}$, about the same amount as the C=O shift noted above. In simple conjugated dienes, the shift is about the same in magnitude[7] so that it may be deduced that the amount of conjugation in the C=C—C=O system is about the same as in the C=C—C=C system.

The spectrum of acetophenone shows, in addition to the C=O band, the following features:

1. The three weak bands near 5.10 μ, 5.30 μ and 5.60 μ (1961 cm.$^{-1}$, 1887 cm.$^{-1}$ and 1786 cm.$^{-1}$) observed in compounds containing the phenyl ring.[8] From their wave-length region and weakness, these must be assigned to overtones of the ring fundamentals.

2. The two bands of weak-to-moderate intensity at 6.25 μ and 6.315 μ (1600 cm.$^{-1}$ and 1584 cm.$^{-1}$) which, from work on other benzoyl-containing compounds (to be described in later papers

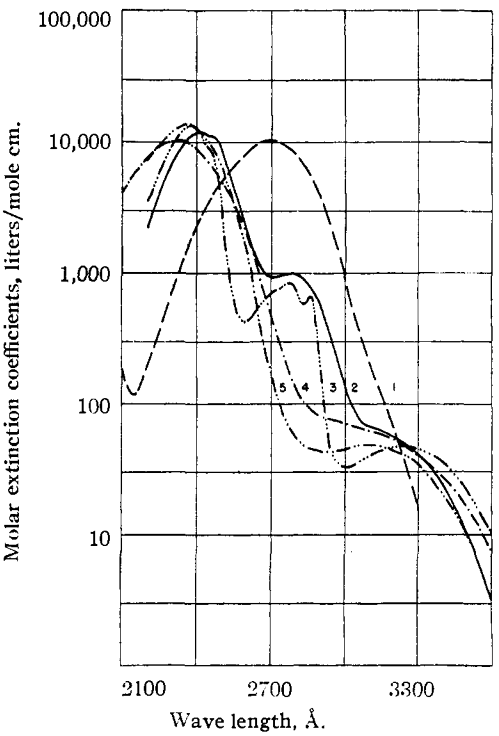

Fig. 1.—Ultraviolet absorption of conjugated ketones: 1, acetylacetone, in isoöctane; 2, acetophenone, in methanol; 3, hexadecanophenone, in isoöctane; 4, acetylacetone acetate (4-acetoxy-3-penten-2-one), in methanol; 5, isophorone, in methanol.

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[7] Actually, infrared and Raman spectra of conjugated dienes show the two C=C frequencies split considerably apart: R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947); K. Bradacs and L. Kahovec, *Z. physik. Chem.*, **B48**, 63 (1940). The splitting in this case is due to mechanical interaction, and as a measure of the shift due to electronic resonance alone the average of these values has been used.

[8] *E. g.*, see Barnes, *et al.*, ref. 2, Table 4, p. 24

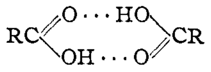
of this series), are universally found for the benzoyl group. The phenyl group itself, not conjugated to other groups, gives a single weak-to-moderate band near 6.25 μ (1600 cm.$^{-1}$).[8] Since one of the degenerate fundamental ring stretching frequencies of benzene lies at this position,[9] it is conceivable that in the unconjugated phenyl derivatives the analogous two ring frequencies are still very close even though the degeneracy is removed; but on conjugation with the C=O group, and the resulting change in character of the ring bonds, the two frequencies are split apart enough to exhibit themselves as the two bands at 6.25 μ and 6.31 μ (1600 cm.$^{-1}$ and 1584 cm.$^{-1}$) referred to above.

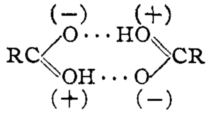
Spectra of two compounds in which one carbonyl is conjugated with another—biacetyl and benzil—are given in Table I. In each case only a single strong band attributable to C=O was found, at 5.82 μ and 5.95 μ (1718 cm.$^{-1}$ and 1681 cm.$^{-1}$), respectively. Since these positions are the ones expected for unconjugated and phenyl-conjugated C=O, respectively, it would seem that little or no conjugation between the adjacent C=O groups is present. Spectroscopic work on glyoxal[10] and electron diffraction work on biacetyl[11] indicate (not strongly) that the *trans* forms of these are the stable ones; benzil, by analogy and also because of repulsion of the phenyl groups, would be expected to be *trans*. Hence only one of the two C=O bands should be infrared active. Raman studies give 1725 cm.$^{-1}$ (5.80 μ) and 1683 cm.$^{-1}$ (5.94 μ) as the frequencies of the Raman-active vibration for biacetyl and benzil, respectively.[12] The small splitting between the infrared and Raman active frequencies is indicative of little mechanical interaction, and hence presumably indicates a weak central C–C bond and a low degree of conjugation. This result substantiates the conclusion made above from the C=O band position.

β-Diketones.—The Raman spectra of this class of compounds have been studied most intensively by Kohlrausch and collaborators,[13] who showed that the Raman spectrum of enolizable β-diketones is consistent with the usually formulated structure, R′C(OH)=CR″=CO—R‴, in some cases admixed with the keto form. Some further conclusions can be drawn from the infrared spectra. Spectra of acetylacetone and dibenzoylmethane are given in Table I. Both of these enolize almost completely as shown by chemical[14] and Raman spectral[13] methods.

Features of note in the 3 μ region are the lack of absorption near 3.0 μ (3333 cm.$^{-1}$) where simple hydrogen-bonded OH absorption occurs, and the weak band near 3.7 μ (2703 cm.$^{-1}$), an unusual absorption position. The latter absorption is very broad (not indicated in Table I), being in this respect reminiscent of the similar very broad OH band of fatty acid dimers[15]; the fatty acid dimer band is also shifted considerably beyond the normal hydrogen-bonded OH position ($\sim$3.0 μ) to about 3.4 μ (2941 cm.$^{-1}$), where it becomes superposed on the narrower CH stretching bands near 3.4 μ.

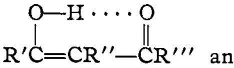
Pauling[16] has accounted for the greater strength of hydrogen bonds in fatty acid dimers on the basis of a large contribution of an ionic resonance structure along with the usual covalent structure





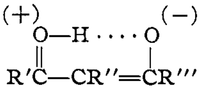
The ionic contribution is presumably increased in the dimer over its value in the monomer because of stabilization arising from the favorable position of the electropositive proton with respect to the negative carbonyl oxygen. The greater shift of the OH band in fatty acid dimers as compared with, for example, hydrogen-bonded alcohols, follows from this explanation as arising from the additional loosening of the OH bond due to the charges. It is clear that a similar explanation can be applied to the enolized β-diketones, since these can have contributions from the resonance structures

(I)



$$\mathrm{R'}\overset{\overset{\displaystyle \mathrm{O{-}H}\cdots\cdots}{|}}{\mathrm{C}}{=}\mathrm{CR''}{-}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R'''}$$

and



$$\mathrm{R'}\overset{\overset{\displaystyle \overset{(+)}{\mathrm{O}}\mathrm{{-}H}\cdots\cdots}{\|}}{\mathrm{C}}{-}\mathrm{CR''}{=}\overset{\overset{\displaystyle \mathrm{O}^{(-)}}{|}}{\mathrm{C}}\mathrm{R'''}$$

the latter being stabilized by the hydrogen bond. On this basis, the 3.7 μ (2703 cm.$^{-1}$) band may be accounted for as the OH vibration, extremely shifted and broadened in an analogous way to the fatty acid dimer band.

Enolized acetylacetone and dibenzoylmethane exhibit unusual absorption phenomena in the 6 μ region also. The former has a moderate band at 5.85 μ (1709 cm.$^{-1}$) which from its position is attributable to the keto form. No band is observed in the usual conjugated ketone region (5.90–5.98 μ) (1695–1672 cm.$^{-1}$) for either compound. Each, however, exhibits a tremendously strong band in the 6.1–6.5 μ (1639–1538 cm.$^{-1}$) region, which from the breadth of the region of total absorption is estimated to be stronger by a factor of 100 or more than usual ketone C=O bands. Since C=C bands are usually not very intense in the infrared, these bands must be assigned as due to C=O. Both their extreme shifts from the usual ketone C=O positions and

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[9] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules " D. Van Nostrand Co., New York, N. Y., 1945, p. 362.

[10] H. W. Thompson, *Trans. Faraday Soc.*, **36**, 988 (1940).

[11] J. E. LuValle and V. Schomaker, THIS JOURNAL, **61**, 3520 (1939).

[12] K. W. F. Kohlrausch and A. Pongratz, *Ber.*, **67B**, 976 (1934).

[13] *E. g.*, K. W. F. Kohlrausch and A. Pongratz, *ibid.*, **B67**, 1465 (1934).

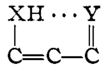
[14] *E. g.*, see J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932).

[15] R. Hofstadter, *et al.*, *J. Chem. Phys.*, **6**, 531, 534, 540 (1938); M. M. Davies and G. B. B. M. Sutherland, *ibid.*, **6**, 755 (1939).

[16] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell Press, Ithaca, N. Y., 1940, p. 306.

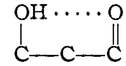
their extreme intensities may be explained reasonably in terms of the resonance structures written above. The enhanced participation of the ionic structure leads to a greater decrease in double-bond character of the C=O bond than would be the case with simple conjugation, thus resulting in the long wave-length shift; and the increased charge on the carbonylic oxygen results in the high intensity. If this interpretation is correct, the lack of an observed C=C band must be accounted for by its being hidden by the very strong C=O band, or by its being shifted out of the double-bond region because of loss of double-bond character.

It is clear that a conjugated system of the type

(II) 

$$\begin{array}{ccc} \mathrm{XH} & \cdots & \mathrm{Y} \\ | & & \| \\ \mathrm{C} & = \mathrm{C} - & \mathrm{C} \end{array}$$

where XH and Y can participate as a hydrogen bond donor-acceptor system, is necessary for this type of extreme shift. Examples other than enolized β-diketones which have also been found to exhibit this behavior will be described in ensuing papers. Since the structure II is a particular type of a chelate system, the name "conjugated chelate" system is suggested for it, to differentiate it from the type of structure represented by, say, diacetone alcohol, which is also a



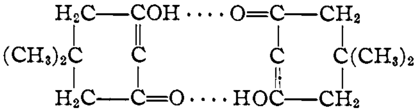
$$\begin{array}{ccc} \mathrm{OH} & \cdots\cdots & \mathrm{O} \\ | & & \| \\ \mathrm{C} & - \mathrm{C} - & \mathrm{C} \end{array}$$

chelate system but only by virtue of the ordinary sort of hydrogen bonding.

Resonance structures of the type I can be written for compounds in which the C=C is part of an aromatic ring. Thus Gordy[17] found the C=O bands of *o*-hydroxyacetophenone and salicylaldehyde, among other compounds, to be shifted to the 6.1–6.2 μ (1639–1613 cm.$^{-1}$) region, and he demonstrated that the hydroxyl group was necessary for the shift. On the basis of the above discussion, this shift is not to be attributed to simple hydrogen bonding, but to the existence of the conjugated chelate system. Also the early findings by Wulf, Liddel, and coworkers[18] that strongly intramolecularly hydrogen-bonded substances showed no absorption in the 7000 cm.$^{-1}$ region (second harmonic region of the usual 3.0 μ OH absorption) are attributable to the fact that all such compounds examined were of the conjugated chelate type, and hence the OH absorption was shifted completely out of the region examined. The second harmonic of this absorption should fall near 5000 cm.$^{-1}$.

The difference between ordinary conjugated systems and conjugated chelate systems is strikingly illustrated by the spectrum of acetylacetone acetate (spectrum 8, Table I). Acetylation of the OH group of enolized acetylacetone effectively removes the possibility of resonance indicated by formulae I, and reduces the system to the simple conjugated C=C—C=O type. The bands at 5.90 μ (1695 cm.$^{-1}$) and 6.125 μ (1633 cm.$^{-1}$) are attributable to conjugated C=O and C=C, respectively, being close to the regions noted above for such groups and being of the usual intensity for such bands. The somewhat enhanced intensity of the C=C band over its usually lower value may be ascribed to the oxygen substituent. The band at 5.68 μ (1761 cm.$^{-1}$) is at the position expected for the ester C=O of the vinyl ester grouping.[19]

The final spectrum of Table I, of 5,5-dimethyl-1,3-cyclohexanedione, illustrates a case in which the same resonance conditions as for acetylacetone can be realized in a different way. The moderately strong band at 5.875 μ (1702 cm.$^{-1}$) indicates that a good proportion of the molecules are in the keto form. However, the bands at 3.8 μ (2632 cm.$^{-1}$) and 6.23 μ (1605 cm.$^{-1}$) are indicative of the conjugated chelate type of enolization. Since the ring makes it impossible sterically for the OH of the enolized form to approach closely enough to the carbonylic oxygen of the same molecule to interact with it in the manner indicated by structures I, the necessary stabilization of the ionic structure must be accomplished through dimerization of the sort



Ultraviolet Work.—The conclusion drawn above as to the essential difference between a simple conjugated system (C=C—C=O) and the conjugated chelate system is well verified by ultraviolet spectra. Thus, spectra of the three simple conjugated ketones shown in Fig. 1 (isophorone, acetophenone, and hexadecanophenone) exhibit the characteristic strong band near 2350 Å. (molar extinction coefficient ~10,000) and the weak band or shoulder near 3200 Å. (molar extinction coefficient ~40) noted by many investigators[2] for the conjugated system and discussed theoretically by McMurry.[20] The two benzoyl-containing compounds show also the band or shoulder near 2800 Å. associated with the phenyl ring.

Acetylacetone gives a spectrum markedly different from the above cases, exhibiting a very strong band with a maximum at 2700 Å., and molar extinction coefficient ~10,000 (Fig. 1). This is at roughly the same position as the band of simple unconjugated ketones, but the latter band is much weaker (molar extinction coefficient ~20). Acetylation to acetylacetone acetate effects the same result here as it did in the infrared, converting the absorption from that of the con-

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[17] W. Gordy, *J. Chem. Phys.*, **8**, 516 (1940).

[18] U. Liddel, O. R. Wulf, *et al.*, THIS JOURNAL, **55**, 3574 (1933); **57**, 1464 (1935); **58**, 548, 1991, 2287 (1936).

[19] Barnes, *et al.*, ref. 2, spectrum 166, p. 72.

[20] H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941).

jugated chelate type to that of a simple conjugated ketone (Fig. 1), with maxima at 2300 and 3250 Å. (molar extinction coefficients ~13,000 and ~60, respectively).

Experimental

Infrared Spectra.—These were obtained by means of the recording rock-salt prism spectrograph of this laboratory, described elsewhere.[21] Each spectrum given in Table I was the result of a single run. Wave-length values as read directly from the record were corrected for temperature effects or mechanical shifts by observing the deviation of the CO_2 4.235 μ band, or of one of the known solvent bands, from its true position and correcting all wave lengths according to a standard correction curve. This curve was constructed from several calibration runs on CO_2, NH_3, and C_2H_4 vapors. The reproducibility for sharp bands is within ±0.02 μ. Intensities were estimated visually on a scale of 0 to 10. Solutions were made up (not highly accurately) on a weight-to-volume basis.

Ultraviolet Spectra.—The ultraviolet spectra were obtained from point-by-point readings on a Beckman quartz photoelectric spectrophotometer (Model DU). Solutions were made up accurately in the solvents noted in Fig. 1, using spectroscopically pure solvents. Molar extinction coefficients quoted are in units of liters/mole cm.

Sources of Samples.—The sources and purification procedures for the samples used were as follows:

Diacetone alcohol was obtained from a laboratory distillation of commercial material, the fraction boiling at 167.6–168.2° being used.

Isophorone was obtained from a careful laboratory distillation of commercial material, the resulting pure fractions being used also for determination of other physical constants.

Eastman White Label acetophenone and benzil were used without further purification.

The sample of biacetyl used was from an earlier laboratory preparation, and was not further purified.

Commercial acetylacetone was fractionated and the cut boiling at 139.0–139.1° used.

A dibenzoylmethane sample already on hand was used for this material (m. p. 77.5–78.0°, lit. 78°).

The sample of 5,5-dimethyl-1,3-cyclohexanedione had been prepared earlier in these Laboratories by the procedure of "Organic Synthesis," Collective Volume 2. The sample melted at 148.5–149.0° (lit., 148–150°).

Acetylacetone acetate was prepared by the method of Spence and Degering.[22] A cut of b. p. 95.1–95.6° (20 mm.), $n^{20}{}_D$ 1.4529, was used.

Hexadecanophenone was prepared from hexadecanonitrile plus phenyl Grignard reagent, and was purified by distillation at 1.5 mm. and crystallization from ether-alcohol mixture.

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Summary

1. Infrared absorption maxima in the 2–15 μ region are tabulated for diacetone alcohol, isophorone, acetopheonone, biacetyl, benzil, acetylacetone, dibenzoylmethane, 5,5-dimethyl-1,3-cyclohexanedione, and acetylacetone acetate. Ultraviolet spectra from 2100 to 3600 Å. are given for isophorone, acetophenone, hexadecanophenone, acetylacetone, and acetylacetone acetate.

2. Simple hydrogen bonding to the ketone C=O group has practically no effect on the C=O vibrational frequency, the infrared band appearing very near 5.83 μ (1715 cm.$^{-1}$) as in simple ketones.

3. Conjugation of C=C to the ketone C=O group gives rise to typical conjugation shifts in the infrared, the C=O band going to the region 5.90–6.00 μ (1695–1667 cm.$^{-1}$) and the C=C to 6.07–6.17 μ (1647–1621 cm.$^{-1}$) and also gives rise to the typical strong ultraviolet band near 2350 Å. (molar extinction coefficient ~10,000) and weak band near 3200 Å. (molar extinction coefficient ~40).

4. Simultaneous conjugation and chelation ("conjugated chelation") as in enolized β-diketones leads to an extreme shift of the C=O infrared band (to ~6.2 μ), (1613 cm.$^{-1}$) to a great enhancement of its intensity, and to the appearance of a broad weak band near 3.7 μ (2703 cm.$^{-1}$) attributable to an extremely perturbed OH vibration. The ultraviolet spectrum of one example of this class of compound exhibits a strong band at 2700 Å. (molar extinction coefficient ~10,000).

5. Conjugation of two ketonic C=O groups to each other has little or no effect on their observed infrared band positions.

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