water was allowed to trickle through a 2.5 × 10 cm. column of Amberlite IR-400 resin (hydroxide form, prepared as described), and the resin was washed with 100 ml. of water. The water was removed from the eluate and washings on the steam-bath at 15–20 mm., and the residual base underwent decomposition to a clear oil as soon as the water was gone. The product was extracted with ether, the ether was removed and the residue distilled (10 μ, bath temperature 95–105°) to yield 0.71 g. of a colorless oil, n^{20}_{D} 1.5512.

An oxime, prepared by the pyridine method,[20] was a white solid, m.p. 185–187°, from ethanol.

Anal. Calcd. for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.23; H, 8.07; N, 5.28.

Hydrogenation of a sample of the oil, n^{20}_{D} 1.5512, in ethanol solution over Adams catalyst at 60 p.s.i. for 1 hour produced another oil, from which an **oxime** was also prepared by the pyridine method.[20] It was a fluffy white solid, m.p. 129–130° from cyclohexane.

Anal. Calcd. for $C_{16}H_{23}NO_2$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.59; H, 8.72; N, 5.80.

Preparation and Decomposition of the Oxide of XI (and/or XV).—A solution of the amine oxide in 20 ml. of water was prepared from 1.6 g. of XI (and/or XV) in accordance with the procedure of Cope, Foster and Towle.[15] Addition of a 3-ml. aliquot from this solution to a solution of 0.2 g. of picric acid in 15 ml. of water effected the precipitation of about 0.4 g. of a yellow solid which formed fine, light yellow needles, m.p. 133–134.5°, after three recrystallizations from aqueous ethanol.

Anal. Calcd. for $C_{24}H_{28}N_4O_9$: C, 55.81; H, 5.46; N, 10.85. Found: C, 56.13; H, 5.56; N, 10.95.

The remaining 17 ml. of amine oxide solution was concentrated at 40–50° (15–20 mm.); removal of all the water left a viscous sirup that crystallized to a waxy solid. This material was heated at 100° (15–20 mm.) for 1.5 hours, and an ether solution of the residual oil was extracted with 20 ml. of 10% hydrochloric acid, washed with water and dried over magnesium sulfate. Distillation of this oil at 10 μ (bath temperature 130°) gave about 0.5 g. (43%) of a colorless oil, n^{20}_{D} 1.5625. While its analysis did not accord satisfactorily with the formulation XII, it indicated that XII could indeed be the chief component.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 83.60; H, 7.71.

Hydrogenation of the amine oxide elimination product (0.8 g.) in 25 ml. of absolute methanol over 0.1 g. of Adams catalyst at 50 p.s.i. for 1.5 hours gave a solution from which a light yellow oil remained after removal of the catalyst and methanol. Distillation of this oil at 10 μ (bath temperature 90–100°) produced 0.7 g. of a mobile, faintly yellow oil, n^{20}_{D} 1.5182; infrared spectrum (pure liquid, 0.025-mm. cell): 3.32sh, 3.44i, 3.50i, 5.87i, 6.23w, 6.68m, 6.89i, 7.28m, 7.36sh, 7.62w, 8.08w, 8.52w, 8.90m, 9.10w, 9.32w, 9.50w, 9.72w, 9.96m, 10.16m, 10.48m, 11.62m, 11.88w, 13.32m, 13.66m, 14.34i.

The **oxime**, prepared by the pyridine method,[20] gave white needles, m.p. 114–115.5°, from ethanol.

2,6-Dimethyl-2-(β-phenylethyl)-cyclohexanone (XIII).—A warm, stirred suspension of 9.0 g. of powdered sodium amide in 150 ml. of dry benzene was treated with 23 g. of 2,6-dimethylcyclohexanone.[25] After ammonia evolution had ceased, 37 g. of β-phenylethyl bromide (Eastman Kodak Co.) was added, and the mixture was stirred at the boiling point for 18 hours. After addition of 100 ml. of water, the benzene solution was separated, dried over magnesium sulfate, and the benzene was removed. Distillation of the oily residue afforded three fractions: (1) b.p. 52–70° (12–13 mm.), 11.8 g. (52%) of unchanged 2,6-dimethylcyclohexanone; (2) b.p. 85–95° (12–13 mm.), 8.5 g. of an unidentified oil; (3) b.p. 145–155° (1–2 mm.), 17 g. (40%) of XIII. Redistillation of fraction 3 yielded a water-clear liquid, b.p. 143° (1–2 mm.), n^{20}_{D} 1.5205. Its infrared spectrum, determined on the pure liquid, was identical in every respect with that of the liquid derived by hydrogenation of the amine oxide elimination product.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.20; H, 9.66.

The **oxime**, prepared by the pyridine method[20] and recrystallized from petroleum ether (b.p. 65–110°) and then twice from ethanol, formed white needles, m.p. 115–116°. A mixture with the oxime formed from the liquid derived by hydrogenation of the amine oxide elimination product showed no m.p. depression.

Anal. Calcd. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.51; H, 9.28; N, 5.64.

Absorption Spectra.—Ultraviolet absorption spectra were determined by means of a Cary automatic recording spectrophotometer equipped with 1-cm. quartz cells. Infrared spectra were measured by a Perkin-Elmer model 21 infrared spectrophotometer equipped with sodium chloride optics.

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[CONTRIBUTION NO. 541 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Chelates of β-Diketones. I. Enolization, Ionization and Spectra

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Observations have been made concerning the properties of two series of β-diketones, one in which electronic factors are varied by the introduction of substituents in the *m*- and *p*-positions of dibenzoylmethane, and a second in which the steric requirements of the R-groups in $RCOCH_2COR$ are varied by progressive branching. Increasing the steric requirements of the R-groups in the aliphatic series increases the degree of enolization to such an extent that dipivaloylmethane has no detectable diketo form in the pure liquid. As the degree of *enolization increases*, the *acidity* of the enol *decreases*. Two series of β-diketones have been prepared and studied in order to observe the effects of electronic and steric effects upon properties such as acidity, enolization and spectra. In one series electronic effects were varied by introduction of *m*- and *p*-substituents in the dibenzoylmethane structure. The second series consisted of symmetrical aliphatic diketones in which the bulk of the terminal alkyl groups was varied.

Experimental

Diaroylmethanes.—All of the diaroylmethanes (1,3-diaryl-1,3-propanediones), except 3,3′-dinitrodibenzoylmethane, were prepared by Claisen condensations of ethyl benzoates with acetophenones using the procedure described by Adams and Hauser[4] with minor modifications. The physical constants and yield data are reported in Table I.

3,3′-Dinitrodibenzoylmethane.—1,3-Di-(3-nitrophenyl)-propenone (3,3′-dinitrochalcone) was prepared in 89% yield by the condensation of *m*-nitroacetophenone with *m*-nitrobenzaldehyde, m.p. 211–214°. The chalcone was converted to the dibromide in 44% yield by reaction with

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[4] J. T. Adams and C. R. Hauser, THIS JOURNAL, **66**, 1220 (1944).

TABLE I

PROPERTIES OF DIAROYLMETHANES

Compound, dibenzoylmethane	M.p., °C.	Yield,[a] %
Dibenzoylmethane	76–76.5 (78[5])	[b]
4,4′-Dimethyl-	126–127 (127–129[6])	41
3,3′-Dimethyl-	b.p. 167–171 at 2 mm.[c]	27
4,4′-Dimethoxy-	120–121 (116[7])	25
3,3′-Dimethoxy-	70–71	47
3,3′-Dibromo-	148–149	44
4,4′-Dichloro-	160–161 (159[7])	38
4-Methoxy-	130–131 (128[8])	33
3,3'-Dinitro-	238–240	15[d]

[a] Prepared by Claisen condensation unless otherwise indicated. [b] Material from stock, recrystallized from ethanol. [c] Compound did not crystallize. [d] Preparation described in Experimental section.

bromine in chloroform solution, m.p. 173–175°. The dibromide (0.05 mole) was heated under reflux for one hour with 0.15 mole of sodium methoxide in 150 ml. of methanol. The mixture was neutralized with aqueous hydrochloric acid and 2 ml. excess of concentrated acid was added along with 25 ml. of water. The hot solution was filtered and the precipitate was washed with hot methanol. The product was identified as 3,3′-dinitrodibenzoylmethane on the basis of its spectra and its ability to form a copper chelate when treated with a solution of cupric acetate in acetic acid; yield 2.3 g. (14.6%), m.p. 238–240°. Upon cooling, the mother liquor yielded 8 g. of an unknown compound, m.p. 140–142°.

Diisobutyrylmethane (2,6-Dimethyl-3,5-heptanedione) and Dipivaloylmethane (2,2,6,6-Tetramethyl-3,5-heptanedione).—The samples used in this study were made by the Claisen condensation of ethyl esters with methyl ketones in the presence of sodamide.[4] Higher yields have since been obtained by a procedure utilizing phenyl esters and lithium amide, the details of which will be published elsewhere. The crude condensation products were converted to cupric chelates by treatment with cupric acetate in acetic acid. The chelates were decomposed with hydrogen sulfide and the liquid ketones were then distilled through a 60-plate, glass center-rod column. Characteristic constants are: dipivaloylmethane, b.p. 94.0–94.5° at 20 mm. (lit.[4] 96–97° at 20 mm.), m.p. of cupric chelate, 190–191°; diisobutyrylmethane, b.p. 80.5–81.4° at 17 mm. (lit.[9] 62–63° at 3 mm.); m.p. of cupric chelate, 127–129°.

3-Methylacetylacetone was prepared by the acid-catalyzed condensation of ethyl methyl ketone with acetic anhydride, b.p. 75.0° at 30 mm.[10]

Materials.—Dioxane was purified by the method of Calvin and Wilson.[11] Samples were fractionally distilled immediately before use. Solutions of potassium hydroxide were prepared by the reaction of the metal with water in dioxane. About 2 g. of freshly cut metal was added to 750 ml. of purified dioxane under a stream of nitrogen. Water then was added cautiously under a blanket of nitrogen. After the metal had entirely dissolved, sufficient water was added to bring the volume to one liter. Carbonate-free tetramethylammonium hydroxide solutions were prepared by passing solutions of tetramethylammonium chloride through a column of Amberlite IR 401 resin in the hydroxide form. The chloride-free eluent was diluted with water and dioxane to give 0.01 N solutions in 75% dioxane. The solutions deteriorated rapidly unless they were stored under nitrogen. Solutions stored in contact with air for several days gave very poor end-points in titration, indicating that weakly acidic oxidation products were formed.

Standardization of the pH Meter.—The procedure used to relate pH meter readings to hydrogen ion concentrations was essentially that developed by Van Uitert and Haas.[12] All measurements were made in solutions of total ionic strength of 0.5 which was maintained with potassium perchlorate. The equation established at hydrogen ion concentrations between 0.1 and 0.0001 N was

$$\log [H^+] = \text{meter reading} + 0.37$$

A similar relationship was established by titration of potassium hydroxide with perchloric acid. Combination of the two relationships gave a value of $-\log [H^+][OH^-]$ for the medium of 16.9. The value may be compared with the value of pK_W of 17.85 for 70% (by weight) dioxane.[13] A crude extrapolation of the primary medium effect for the ionization of water in dioxane indicates that the value of K_W would be near 18.3 in 75% dioxane. To complete the comparison the value of the ion product should be corrected for the electrolyte effect on the ionic activity coefficients. It has been shown[14] that remarkably consistent corrections of this type can be made by using the mean ionic activity coefficients for hydrochloric acid in dioxane–water mixtures for all 1–1 electrolytes.[15] By interpolation the value of $\gamma_\pm$ for 0.05 M HCl in 75% dioxane at 25° is estimated as 0.168. Use of this value, and our value, for Q_W, the measured ion product for water, we estimate a value of pK_W of 18.4 for the medium at zero ionic strength.

Measurement of Acidity Constants.—Molarity quotients, Q_A, were determined using the pH meter calibrations in terms of $[H^+]$. The aliphatic diketones were titrated with 0.01 N potassium hydroxide in the presence of sufficient potassium perchlorate to give a total ionic strength of 0.05 at the half-equivalence points. In the case of the weakly acidic dipivaloylmethane, it is necessary to correct the values of $[A^-]/[HA]$ for free hydroxide present in the solutions. Values of Q_A, calculated from several points in the vicinity of the half-equivalence points, were constant.

Deuteration of the diketones was accomplished by dissolution of the compound in sodium deuteroxide (prepared by dissolution of sodium in 99% deuterium oxide), followed by acidification of the solution with deuteriosulfuric acid (prepared by the dissolution of sulfur trioxide in deuterium oxide). Since the sodium salt of dipivaloylmethane is sparingly soluble in water, the salt was dissolved in ether and shaken with the sodium deuteroxide solution. The ether layer then was shaken with deuteriosulfuric acid and the deuterated diketone was recovered by evaporation of the ether.

Infrared spectra were run with a Baird Associates infrared spectrometer or with a Perkin-Elmer model 13 spectrometer. The latter instrument was used with lithium fluoride optics for examination of the 3300–2000 cm.$^{-1}$ region. The spectra of the solid diketones were determined in Nujol mulls and in solution in chloroform and carbon disulfide. Those of the liquids were measured in carbon tetrachloride solutions and with capillary films of the pure liquids.

Ultraviolet spectra were variously determined with Beckman model DU and model DK-2 instruments.

Results and Discussion

Spectra.—It has long been realized that the stable form of dibenzoylmethane, which melts at 78°, is an enol.[5] There is also ample evidence that solutions of the compound are largely or completely enolic.[16] In order to investigate the possibility that there are small amounts of diketo form present in solution, we have measured the ultraviolet spectrum of this compound in hexane and acetonitrile, solvents of widely different polarity. Dimroth[17] first observed that the tautomerization constants of β-dicarbonyl compounds are quite solvent-sensitive and the phenomenon has since been discussed many times.[18] As may be calculated from the data of

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Table III, the keto enol equilibrium constant for acetylacetone decreases from 11.5 to 1.3 on going from cyclohexane to acetonitrile solution. As is shown by the data in Table II, all of the diaroylmethanes studied have intense absorption maxima between 3400 and 3610 Å. which must be attributed to $\pi \rightarrow \pi^*$ transitions of the enols. The maximum in the spectrum of dibenzoylmethane is slightly *higher* (*ca.* 2%) in acetonitrile than it is in hexane and also occurs at slightly longer wave length in the more polar solvent (3420 *vs.* 3390 Å.). The shifts are very small and in the opposite sense to those expected if there were a *measurable* increase in the keto content in the more polar solvent. The small shifts are consistent with those to be expected from solvent effects on the spectrum of a single species having an excited state which is more polar than the ground state[19,20] and show that the enol content of *at least the hexane solutions* must be no more than a fraction of a per cent.

Spectra of the enolate ions derived from diaroylmethanes were measured in ethanol containing 0.001 *N* sodium hydroxide and the maxima are also given in Table II. As has previously been noted,[21] the ionization process has relatively little influence on the spectra of diaroylmethanes. The effects of substituents on the positions of the maxima of both enols and anions are much smaller than are the effects of substituents on the spectra of most benzene derivatives.[22] For example, the introduction of a *p*-methoxy group produces a red shift of 310 Å. in the spectrum of acetophenone whereas one and two *p*-methoxy groups give bathochromic shifts of only 120 and 190 Å. in the dibenzoylmethane system. One would infer, therefore, that resonance interaction between *p*-substituents and the enolic group is quite weak. This implies that there is a large amount of interaction within the group. Since the effects of *p*-methoxy groups are roughly cumulative we infer that introduction of the first group does not introduce much asymmetry in the chelated enol group.

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS FOR DIAROYLMETHANES AND THEIR ENOLATE IONS IN ETHANOL

Compound, dibenzoylmethane	Neutral form λ_{max}, Å.	$\epsilon \times 10^{-4}$	λ_{max}, Å.	$\epsilon \times 10^{-4}$	Enolate ion[b] λ_{max}, Å.	$\epsilon \times 10^{-4}$
4,4′-Dimethoxy-	3610	3.77	2920	8.21	3560	3.05
4,4′-Dimethyl-	3510	2.94	2620	8.94	3520	2.29
3,3′-Dimethyl-	3450	2.04	2520	7.84	3500	1.54
Dibenzoylmethane	3420	2.38	2450	4.47	3480	2.23
4,4′-Dichloro-	3510	2.84	2610	11.0	3580	1.99
3,3′-Dibromo-	3450	2.34			3560	2.02
3,3′-Dinitro-	3400	?[a]			3560	?[a]
4-Methoxy-	3540	3.06			3520	2.48

[a] Spectra run with solutions of indeterminate concentration because of low solubility. [b] Measured in ethanol containing 10^{-3} *M* NaOH.

Table III summarizes the ultraviolet spectra of the aliphatic diketones. The spectra are quite solvent-sensitive and the intensities in the region of maximum absorption (*ca.* 2750 Å.) are decreased markedly with increasing polarity of the solvent, indicating extensive ketonization in polar media. The enolization of acetylacetone has been carefully studied by bromination[23] and quantitative infrared measurements.[24] Figure 1 shows that the apparent molar absorption coefficients of solutions of acetylacetone are a linear function of the fraction enolized in various solvents. The absorption characteristics of the enol are apparently almost independent of medium as is the case with the completely enolic diaroylmethanes. Measurement of the apparent molar extinction coefficients of solutions of β-diketones should, therefore, provide a rapid method for estimation of relative extents of enolization in various solvents. Absolute values can be obtained either by an independent chemical analysis of a single solution or by reference to solutions, in which, for one reason or another, enolization may be presumed to be complete. Extrapolation of the straight line in Fig. 1 to 100% enol gives a value of 1.11 × 10^4 as the true molar extinction coefficient of acetylacetone enol. This agrees closely with the value of 1.10 × 10^4 which is calculated from the values of degree of enolization[23] and the apparent absorption coefficient in cyclohexane, the solution in which enolization is most extensive. Belford, Martell and Calvin[25] estimated an appreciably higher value, 1.25 × 10^4, from the study of chloroform solutions alone. Using Kuratani's value[24] of 78% for the degree of enolization of acetylacetone in chloroform we estimate the absorption coefficient as 1.15 × 10^4 in that medium.

TABLE III

ULTRAVIOLET ABSORPTION OF ALIPHATIC β-DIKETONES

Compound	Solvent	λ_{max}, Å.	Apparent extinction coefficient, $\times 10^4$
Acetylacetone	Acetonitrile	2730	0.63
Acetylacetone	Chloroform	2720	.60
Acetylacetone	Isoöctane	2710	.99
Acetylacetone	Cyclohexane	2710	1.01
Acetylacetone	Water	2740	0.15
Acetylacetone	NaOH aq.	2940	2.0
Diisobutyrylmethane	Acetonitrile	2740	0.71
Diisobutyrylmethane	Cyclohexane	2740	1.11
Diisobutyrylmethane	Water	2740	0.16
Dipivaloylmethane	Acetonitrile	2760	1.09
Dipivaloylmethane	Isoöctane	2740	1.27
Dipivaloylmethane	Excess NaOH	2940	1.81
Dipivaloylmethane	Water	2780	0.18

Infrared spectra imply that dipivaloylmethane (DPM) and diisobutyrylmethane are nearly 100% enolic in the pure liquid state. We can safely assume that these compounds will be even more enolic in hydrocarbon solvents so that the apparent extinction coefficients in cyclohexane

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may be taken as the true values of the extinction coefficients of the enols. These values can then be used to calculate the tautomerization constants for more polar solvents which are shown in Table IV.

TABLE IV
ENOLIZATION OF DIKETONES AT 25°

Diketone	K_T[a] Acetonitrile	Water
Acetylacetone	1.4	0.15
Diisobutyrylmethane	1.8	.16
Dipivaloylmethane	6.1	.16

[a] K_T = enol/keto.

The general character of the infrared spectra of β-diketones is well known.[26,27] The spectra of all the diketones described in this paper have been measured and the results are very consistent with those of previous authors with one minor exception. The strong bands near 1600, 1500, 1450 and 1260 cm.$^{-1}$, which were assigned by Mecke and Funk to symmetric and antisymmetric deformation of the C–O and C–C bonds of the ring, can be picked out in all spectra of the diketones and their deuterio derivatives. The positions of the bands do not change with substitution in the diaroylmethane series and are at very nearly the same positions in the spectra of the aliphatic compounds. Again, the indication is that interaction of the enol ring with attached unsaturated groups is weak. Broad, low intensity absorption around 2700 cm.$^{-1}$ disappears in the spectra of deuteriodiketones and metal chelates containing the diketone enolate ions as ligands.[28] A new, weak band appears at about 1950 cm.$^{-1}$ in the spectra of the diketones. We have regularly found sharp, medium intensity bands at 1120–1230 cm.$^{-1}$ in the spectra of both the diketones and metal chelates. The band disappears on deuteration and a new band appears at 880–890 cm.$^{-1}$. The absorption is almost certainly due to bending of the C–H (or C–D) of the central methine carbon atom. Disappearance of the higher frequency band is a useful indication of the completeness of deuteration in exchange studies. Mecke and Funk reported that this band was found at 1170 cm.$^{-1}$ in acetylacetone enol and appeared at 875 cm.$^{-1}$ in dideuterioacetylacetone. It is possible that the C–H frequency in question actually falls at longer wave length in the spectrum of acetylacetone and is overshadowed by the strong, methyl-wagging frequency at 1247 cm.$^{-1}$. At any rate, the frequency ratio, 1220/880, is 1.39 which agrees well with normal expectations for the isotopic shift.

The "chelate carbonyl" band in the dibenzoyl methane spectrum can be resolved, in carbon disulfide solution, into a group of bands with the first, and strongest, member at 1570 cm.$^{-1}$. Another sharp maximum of equal or lesser intensity always appears at 1530 cm.$^{-1}$. The positions of these two bands are invariant with substitution in the aromatic nuclei.

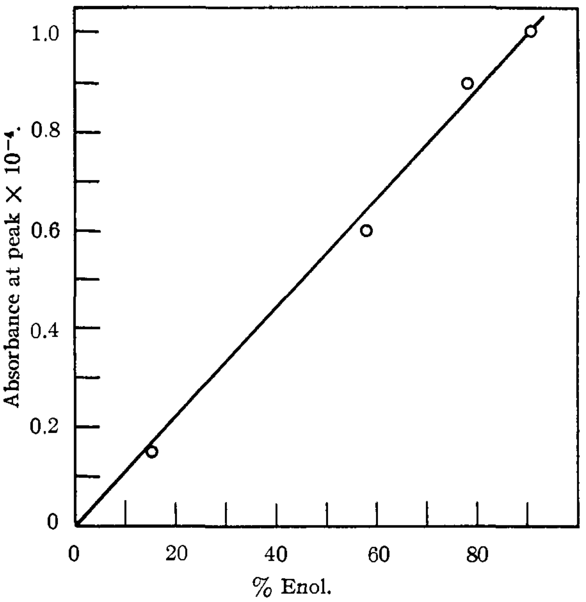

Fig. 1.—Apparent molar absorbance of acetylacetone as a function of enol content.

The spectrum of diisobutyrylmethane shows suggestion of a shoulder above 1700 cm.$^{-1}$, indicating the presence of a barely detectable trace of the dicarbonyl form in the pure liquid. The spectrum of DPM does not even have a shoulder in this region. The spectrum of 3-methylacetylacetone, which is known to be much less extensively enolized than acetylacetone,[29] has a very strong maximum at 1690 cm.$^{-1}$. The band is unsymmetrical and could, perhaps, be resolved into a doublet. The spectrum of this compound also shows a fairly strong maximum at 3400 cm.$^{-1}$. The latter band must be attributed to the presence of some acyclic enol in the neat liquid. The C=O stretching frequency in such a species should be expected below 1700 cm.$^{-1}$, and, coupled with normal carbonyl absorption due to the dicarbonyl form, may account for the unusual appearance of the 1690 cm.$^{-1}$ band.

Acidity.—The molarity quotients (Q_A, concentration acidity "constants") of the aliphatic diketones were determined in 75 volume per cent. dioxane–water in which the total ionic strength was maintained at 0.05 by the addition of potassium perchlorate. The results are shown in Table V. We may compare the values with the estimate of the thermodynamic acidity constant of acetylacetone.[30] If an interpolated value of the HCl activity coefficient at 0.05 *M* in 75% dioxane is used to correct the value of Q_A, the value calculated for pK_a of acetylacetone is 12.78. The value calculated from the equation of Van Uitert, *et al.*,[30] is 12.78. The data show that attachment of bulky alkyl groups to

TABLE V
RELATIVE ACIDITY CONSTANT OF ALIPHATIC β-DIKETONES IN 75% DIOXANE AT 25°

Diketone	$-\log Q_A$
$(CH_3CO)_2CH_2$	11.27
$[(CH_3)_2CHCO]_2CH_2$	12.48
$[(CH_3)_3CCO]_2CH_2$	14.48

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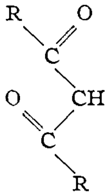
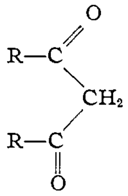
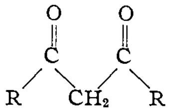
(30) L. G. Van Uitert, C. G. Haas, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 455 (1953).

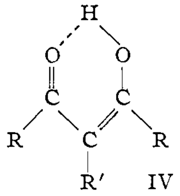
the pseudo carbonyl group decreases acidity markedly.

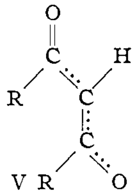
Structural Considerations.—The variation in the enol content of aliphatic diketones is attributed to steric effects. Acetylacetone probably has either configuration I or II, or both, since those arrangements minimize dipole–dipole repulsions. Examination of models indicates that both I and II would be strained in DPM in which the terminal R groups are *t*-butyl. In fact, no more than a 30-40° rotation away from configuration III can be accomplished without introducing some strain. The high degree of enolization of diisobutyrylmethane and DPM is, therefore, attributed to instability of the diketo forms which arises from a combination of classical steric strain and the electrostatic repulsion of the carbonyl group moments. It is understandable that substitution on the central carbon atom should have an opposite effect since compression of the three substituents would be at a maximum in the cyclic form of the enol IV.


I


II


III


IV


V

Steric strain is also an obvious factor in the variations in acidity. Large R groups would introduce considerable strain in the enolate ions in the planar *trans* form V, which should ordinarily be the most stable configuration. Another way of saying the same thing is to state that bulky terminal groups will tend to force the negatively charged oxygen atoms close together. The same steric effect is probably responsible for the fact that the phenyl group is an acid-weakening substituent in dibenzoylmethane[30,31] (compared with acetylacetone) whereas it is acid-strengthening in benzoic acid (compared with acetic acid). A model of the *trans* configuration of the dibenzoylmethide ion can only be constructed if the phenyl groups are turned perpendicular to the plane of the dicarbonyl system. The importance of steric hindrance to solvation[32] in determining the relative acid strengths cannot be sorted out since it would also be an acid-weakening influence. Measurements of relative acidities in widely varying solvent media would be required to distinguish between internal and external steric effects.

Acknowledgment.—We are indebted to Professor R. E. Rundle and Dr. A. W. Fort for stimulating and informative discussions of the structural possibilities in cyclic enols.

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(31) Measurements of the value of Q_A for dibenzoylmethane made in this Laboratory do not agree well with the value given in reference 30 but do confirm the fact that dibenzoylmethane is a weaker acid than acetylacetone.

(32) G. S. Hammond and D. H. Hogle, THIS JOURNAL, **77**, 338 (1955).

AMES, IOWA

[CONTRIBUTION NO. 554 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Chelates of β-Diketones. III. Steric Effects in the Formation Constants of Metal Chelates[2]

BY GERALD A. GUTER AND GEORGE S. HAMMOND[3]

RECEIVED AUGUST 28, 1958

The formation constants for several metal chelates of acetylacetone, diisobutyrylmethane and dipivaloylmethane were determined in order to study the effects of variation in the steric requirements of ligands on their chelating ability. A correlation of the constants indicated that the values for the second formation constants of the copper chelates of diisobutyrylmethane and dipivaloylmethane were low and the separation factors between the first and second constants were unusually large. Relatively small separation factors were found for metals which do not form square planar complexes.

Relatively few of the many studies of the stability of metal chelates have been designed to determine the effects of variation in the steric requirements of ligands on their chelating abilities.[4a,b] Symmetrical β-diketones appear to be a convenient group of compounds for use in such studies since the size of the R groups in I may be varied without materially affecting the electronic properties of the ligand. Furthermore, it is relatively easy to obtain an independent control of the sensitivity of diketone ligands to electronic influences by studying the coördination compounds derived from substituted dibenzoylmethanes. The indications are that electronic effects on the chelating abilities of the latter group of compounds are significant but not overpowering.[5] The extensive work of the group at Pennsylvania State University.[6-9] has provided much information

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Reference 19 is paper II in the series.

(3) Author to whom inquiries should be addressed: Division of Chemistry, California Institute of Technology, Pasadena, Calif.

(4) (a) For example, see H. Freiser and W. D. Johnston, THIS JOURNAL, **74**, 5239 (1952); H. Freiser, *Rec. Chem. Prog.*, **14**, 199 (1953); (b) H. Irving and H. S. Rossatti, *J. Chem. Soc.*, 2910 (1954).

(5) W. F. Borduin, unpublished observations in this Laboratory.

(6) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

(7) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*,