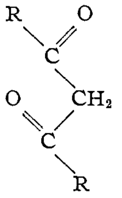
the pseudo carbonyl group decreases acidity markedly.

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.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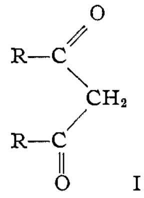
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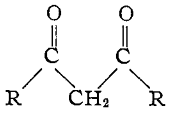
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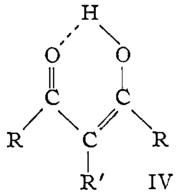
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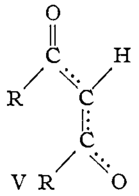

V

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.

(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

(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).

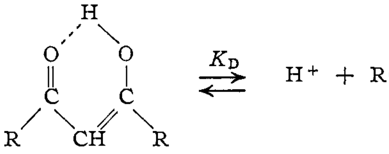
(7) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*,

TABLE I

FORMATION CONSTANTS OF β-DIKETONES IN 75 VOLUME PER CENT DIOXANE CONTAINING 0.05 *M* POTASSIUM PERCHLORATE

	Acetylacetone			Diisobutyrylmethane			Dipivaloylmethane		
Metal	log Q_1	log Q_2	log Q_1/Q_2	log Q_1	log Q_2	log Q_1/Q_2	log Q_1	log Q_1	log Q_1/Q_2
Cu(II)	11.57	9.64	1.90	12.29	9.99	2.30	13.91	11.55	2.36
Ni(II)	8.24	6.39	1.25	8.73	7.56	1.17	9.90	9.10	0.80
Co(II)	7.86	6.19	1.67	8.37	7.31	1.01	9.60	8.77	.83
Mn(II)	6.81	5.18	1.63	7.23	6.07	1.16	8.34	7.44	.90
Mg(II)	6.13	4.52	1.61	6.45	5.44	1.01	7.44	6.59	.85

concerning the dependence of chelate stability on the nature of the metal involved. Van Uitert, Fernelius and Douglas[7] showed that there is a limited relationship between formation constants and the values of pK_D for various diketones. In particular, they found that log K_f is a linear function of pK_D



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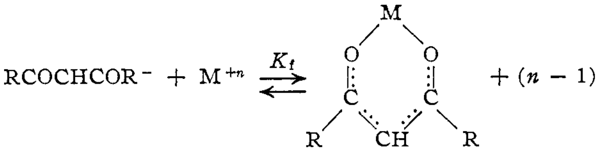

for a series of diaroylmethanes and that aroylacetylmethanes fit another linear relationship with virtually the same slope. Such observations suggest the incursion of steric effects since variations in electronic factors might be roughly the same in the protonation of diacylmethide ions[10] and in the formation of coördination compounds from them.

Experimental

Diisobutyrylmethane and dipivaloylmethane (DPM) were prepared as described in Paper I.[11] **Acetylacetone** (Eastman Kodak Co.) was purified by fractional distillation. A center fraction, b.p. 127°, was used in all experiments.

Dioxane was purified by the method of Calvin and Wilson[12] and standard solutions of potassium hydroxide in 75 volume % dioxane were made up as described previously.[11]

Potassium perchlorate, reagent grade, was recrystallized at least once from water to free it of acidic impurities.

Metal perchlorates were G. F. Smith Co. reagent grade materials. Stock solutions of approximately 0.0125 *M* concentration were prepared in 75% dioxane.

Apparatus for Titrations.—The titrations were carried out in a jacketed beaker having a capacity of about 250 ml. The stopper of the beaker contained nitrogen inlet and outlet, a delivery tube through which the titrant was added, and a stirring apparatus. The micro-buret used for measuring the titrant had a 5-ml. capacity and could be read to 0.001 ml. Titrations were followed with a Beckman model G *p*H meter.

Measurement of Formation Constants.—The Bjerrum method[13] was used for the measurement of formation constants. All measurements were made in the presence of sufficient potassium perchlorate to maintain ionic strength very close to 0.05. Titrations were monitored with a *p*H meter using the previously-established relationship[11] between hydrogen ion concentration and the meter readings. Two to four ml. of the metal perchlorate stock solution was placed in the titration cell with 0.6925 g. of potassium perchlorate. Five to 50 ml. of a 0.01 *M* solution of the diketone in dioxane and sufficient water and dioxane to bring the total volume to 100 ml. were added. The mixture was stirred until the potassium perchlorate was entirely dissolved and the mixture then was titrated with 0.05 *N* potassium hydroxide. Readings were taken at 0.10 ml., or smaller, intervals. The formation functions were calculated in the usual manner.[12,13] Values of log K_1 and K_2 were calculated from the formation curves at $\bar{n} = 0.5$ and $\bar{n} = 1.5$ wherever possible. Values of the concentrations of the ligand anions were calculated using the values of pQ_A determined in the same medium.[11] Since considerable excesses of the chelating agents were used (to minimize hydrolysis), the points $\bar{n} = 0.5$ in the formation of copper chelates occurred at such high acidities that the values of $[H^+]_{\bar{n}=0.5}$ could not be determined accurately. The value of log Q_1Q_2 then was determined from accurate measurements in the region $\bar{n} = 1.0$.

Hydrolysis.—As has been pointed out previously,[8] the formation of hydroxychelates, MCh(OH), is a major source of error in the determination of formation constants by Bjerrum's method. For this reason all titrations were carried out using varying excesses of chelating agent, *e.g.*, $[HCh]_0/[M^{+2}]_0 = 2, 4, 8$. Since increasing the ratio causes chelate formation in more acidic solutions, constancy of the values of Q_1 and Q_2 determined in such a series ensures the elimination of significant error. When values of Q_1 and Q_2 for determinations at different reactant ratios varied by more than 0.05 log unit the data were rejected. Such a situation was encountered in the case of titrations of zinc perchlorate. A summary of formation constants is given in Table I.

All "constants" reported in this paper were measured in a solvent consisting of three volumes dioxane to one of water containing sufficient potassium perchlorate to maintain ionic strength at 0.05. The chief disadvantage of the use of inert electrolytes is the lack of any rigorous basis for the comparison of results with those obtained under other conditions.[14] However, Van Uitert and Haas have shown that remarkably consistent approximations to thermodynamic equilibrium constants can be made by merely using the mean ionic activity coefficients for hydrochloric acid in dioxane–water mixtures.[15] We can use the same assumption to obtain at least a rough comparison between our values of Q_f for acetylacetonates with values of K_f obtained by extrapolation from lower electrolyte concentrations.[7] Table II shows the comparison of log Q_f (0.05 *M* $KClO_4$) with log K_f, both measured in 75% dioxane. The differences listed in the last two columns are remarkably consistent except for the first formation constant for copper. Since log K_{f1} for copper was not measured but is a minimum estimate based upon measurements made in the presence of nitrate, the discrep-

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75, 2736, 2739 (1953); L. G. Van Uitert and W. C. Fernelius, THIS JOURNAL, **75**, 3862 (1953).

(8) W. C. Fernelius and L. G. Van Uitert, *Acta Chem. Scand.*, **8**, 1726 (1954).

(9) R. M. Izatt, W. C. Fernelius and B. P. Block, *J. Chem. Phys.*, **59**, 80 (1955).

(10) We suggest the use of diacymethide as a generic name for the enolate ions derived from β-diketones. There seems to be no point in changing the well established term acetylacetonate but similar names for ions derived from other diketones are not euphonious in addition to being unsystematic.

(11) G. S. Hammond, W. G. Borduin and G. A. Guter, THIS JOURNAL, **81**, 4682 (1959).

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

(13) J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941; A. E. Martell and M. Calvin, "The Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, p. 87.

(14) L. G. Van Uitert and C. G. Haas, THIS JOURNAL, **75**, 451 (1953).

(15) H. S. Harned and B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950 p. 548.

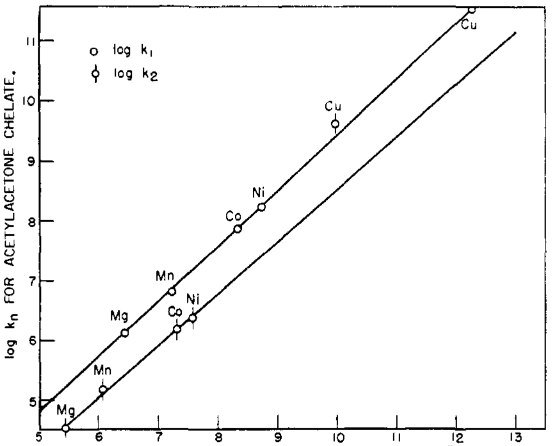

Fig. 1.—Correlation of formation constants of acetylacetone and diisobutyrylmethane chelates.

ancy is not surprising. The values of log K_{f2} − log Q_{f2} average 1.68 ± 0.08. If the interpolated value of 0.168 is used for $\gamma\pm$, the predicted difference is 1.55. The agreement is remarkably good and indicates excellent consistency in the numbers actually measured in the two studies. Excluding copper, the values of log K_{f1} − log Q_{f1} average 1.79 ± 0.10. That the correction is larger is not surprising since a 2-1 electrolyte is involved.

TABLE II

COMPARISON OF LOG Q_f (25°) FOR ACETYLACETONATES WITH ESTIMATED LOG K_f (30°, REFERENCE 8) IN 75% DIOXANE

Metal ion	log Q_{f1}	log Q_{f2}	log K_{f1}	log K_{f2}	log K_{f1} − log Q_{f1}	log K_{f2} − log Q_{f2}
Cu(II)	11.57	9.64	12.78 (est.)	11.24	1.21	1.60
Ni(II)	8.24	6.39	10.19	8.21	1.95	1.82
Co(II)	7.86	6.19	9.68	7.92	1.82	1.73
Mn(II)	6.81	5.18	8.50	6.84	1.69	1.68
Mg(II)	6.13	4.52	7.81	6.09	1.68	1.57

One is inclined to look for three types of steric effects in the formation of metal chelates from a ligand, such as the dipivaloylmethide (DPM), having bulky terminal groups: (1) The large R groups will hold the oxygen atoms of the ligand close together. The basicity of the ligand will be increased[11] but large ions may not fit well in the space between the oxygen atoms. (2) The region around the M–O bonds will be shielded from solvation. (3) If the R groups are large enough, F-strain[16] will arise, making it difficult to attach two or more ligands to the same ion.

We have previously reported[17] the high specificity of DPM for the lithium ion and have attributed the ability of the ligand to select lithium while rejecting the larger alkali metals to compatibility of the small size of the ion and the short O–O distance in the ligand. While tighter binding of lithium would also be predicted on the basis of electronegativity, the difference in affinities is larger than would normally be expected on that basis alone. Similarly, it has been reported[7,9] that beryllium ion is bound more strongly by diketone ligands than would be predicted on the basis of its electronegativity.

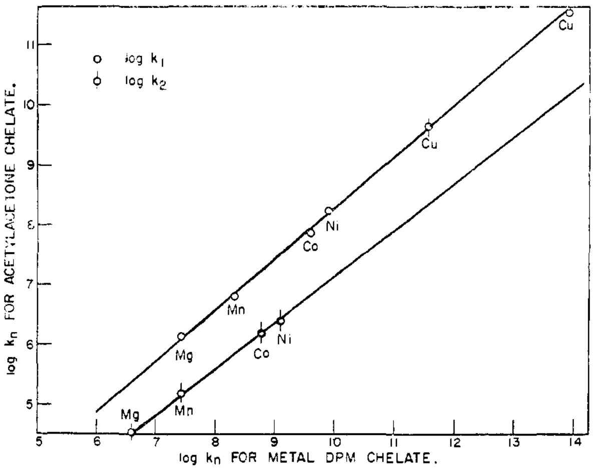

Fig. 2.—Correlation of formation constants of acetylacetone and DPM chelates.

Furthermore, the difference between the affinities of acetylacetonate and the sterically-hindered dibenzoylmethide ion for sodium is unusually large. This suggests that acetylacetonate, because of its small terminal groups, is better able to spread and allow the entrance of the sodium ion.

The clearest indication of the shielding effects of bulky ligands is found in the separation factors, Q_1/Q_2, listed in Table I. With the exception of the copper compounds, all separation factors are smaller for diisobutyrylmethide complexes than for acetylacetonates. Separation factors for dipivaloylmethides are smaller still. Since negative F-strain is an unattractive notion, the effect must be due to steric hindrance to solvation of the monochelated species, MCh^+. This effect is of some interest as an aid in effecting separations of metals, preparation of pure, neutral chelates, and the measurement of higher formation constants for polyvalent metals. Some of the advantages will, however, be partially lost because of the increase in formation constants for hydrolyzed species, such as MCh(OH). Shielding is probably also responsible for the fact that diisobutyrylmethides and dipivaloylmethides are very soluble in hydrocarbons.

Figures 1 and 2 show the values of log Q_f for the first and second formation constants for diisobutyrylmethide and DPM with a series of bivalent metals plotted against the similar data for acetylacetone complexes. The results are quite striking. The linear relationships are observed with two exceptions. The *second* formation constants for the cupric complexes of the two sterically hindered ligands are smaller by greater than an order of magnitude than would be expected on the basis of the otherwise-general correlation. The explanation for the deviation cannot be attributed straightforwardly to any simple feature of the Edwards parameters[18] for the ligands because the *first* formation constants fit the established linear relationships in both cases.

There must be some specific factor associated with the second chelation step with copper. Copper acetylacetonate is known to have the square planar

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[16] H. C. Brown, H. Barthalomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[17] G. A. Guter and G. S. Hammond, *ibid.*, **78**, 5166 (1956).

[18] J. O. Edwards, *ibid.*, **76**, 1540 (1954).

configuration.[19-21] Nickel acetylacetonate has been judged to be tetrahedral since it is paramagnetic.[22] However, it has been pointed out by Calvin and Melchior[23] that one can conceive of paramagnetic, square complexes of nickel(II). However, the specific case for which such a hybrid configuration was suggested, nickel disalicylaldehyde, was shown beyond reasonable doubt to have the tetrahedral configuration since it had an X-ray powder pattern resembling that of the corresponding zinc complex but very different from that of the square copper disalicylaldehyde.[24] All of the other metals included in the present study almost certainly form tetrahedral complexes. There is a possibility that the discontinuity in the relationship between the linear free energy relationship is associated with the tendency of copper to form square complexes with β-diketones. Lateral interference between the two ligands may be more serious in the planar configuration although models do not indicate that the tertiary butyl groups of DPM would be uncomfortably close together in square planar chelates. Alternatively, the sterically hindered ligands may give serious interference with the normal interaction of the metal in a square complex with nucleophilic solvent molecules. This line of argument also must be considered with reservation since coördination compounds of nickel, *rather than copper*, are notoriously prone to accept solvent molecules and change to an octahedral configuration.[25] Since Q_1/Q_2 for the copper–acetylacetone system is only a little larger than for other metals, the effect is almost certainly steric in origin. Since the first formation constants for copper fit the linear free energy relationship well it is unlikely that effect can be attributed to errors in measurement.[26]

Acknowledgment.—We gratefully acknowledge the help of Dr. Wilfred Borduin, both in the form of experimental suggestions and by way of discussion of theory.

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(19) E. G. Cox and K. C. Webster, *J. Chem. Soc.*, 731 (1935).

(20) E. A. Shugam, *Doklady Akad. Nauk S.S.S.R.*, **81**, 853 (1951).

(21) H. Koyama, Y. Saito and H. Kuroyo, *J. Inst. Polytech Osaka City Univ., Sec. C*, **4**, 43 (1953); *C. A.*, **48**, 3097 (1954).

(22) F. P. Dwyer and F. P. Mellor, THIS JOURNAL, **63**, 81 (1941).

(23) M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

(24) D. H. Curtiss, F. K. C. Lyle and E. C. Lingafelter, *Acta Cryst.*, **5**, 388 (1952).

(25) A. E. Martell and M. Calvin, ref. 13, p. 283 ff.

(26) K_1 for copper was determined by measuring K_1K_2 and K_2; see Experimental.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

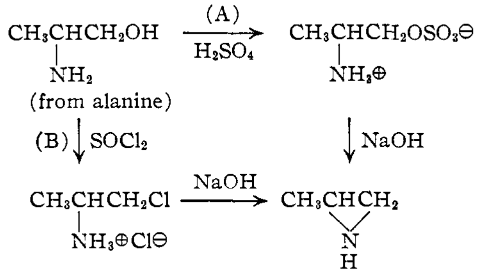
Preparation and Polymerization of D- and L-Propylenimine and N-Methylpropylenimine[1]

BY YUJI MINOURA, MATSUJI TAKEBAYASHI AND CHARLES C. PRICE

RECEIVED FEBRUARY 9, 1959

D- and L-Propylenimine have been prepared from D- and L-alanine. N-Methylpropylenimine has been prepared from propylene oxide and from alanine. Polymerization of the DL-monomers by a wide variety of catalysts has so far produced only oily polymers. The D- and L-monomers gave solid, optically active polypropylenimine of relatively low molecular weight.

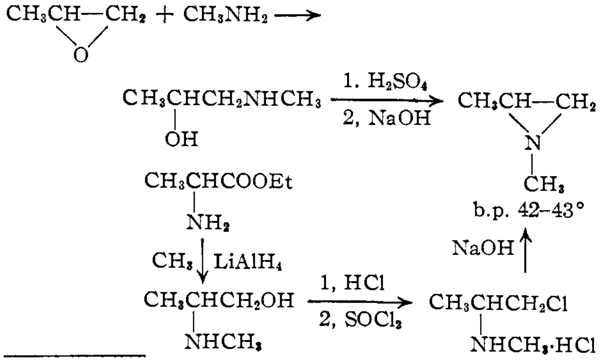
Our interest in propylene oxide polymerization[2] has stimulated an interest in analogous polymers from propylenimine and related monomers. We wish here to report on synthetic work designed to prepare optically active propylenimine and its N-methyl derivative, as well as attempts, so far unsuccessful, to prepare high molecular weight crystalline polymers from these monomers.



b.p. 67°, $[\alpha]^{21}\text{D}$ + 12.4° (D-), −12.8° (L-)

Propylenimine has been prepared in racemic form by many investigators. The successful reduction of alanine esters to alaninol with lithium aluminum hydride[3] suggested the following routes (A and B) for the preparation of D- and L-propylenimine. Cyclization through the sulfate ester gave superior yields and purer imine.

N-Methylpropylenimine has apparently not been reported in the literature. We have prepared it by the following alternate routes.



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[1] Presented in part at the Delaware Valley Regional Meeting, Amer. Chem. Soc., Feb., 1958, and 135th American Chemical Society Meeting, Boston, Mass., April, 1959. Supported in part under Contract No. 36-039-SC72410, U. S. Army Signal Corps.

[2] C. C. Price and L. E. St. Pierre, THIS JOURNAL, **78**, 3432 (1956); C. C. Price and M. Osgan, *ibid.*, **78**, 4787 (1956).

[3] P. Karrer, P. Portmann and M. Suter, *Helv. Chim. Acta*, **31**, 1617 (1948).