is strongly reduced,[17] but let us concede for the moment that the reduction here is due to an inductive effect. This hypothesis is immediately contradicted by the results for Py(CH$_2$)$_2$Py: here, k_2 is again 70% of k_1 and the change from three to two methylenes would call for a much greater reduction in k_2 if the reduction were due solely to an effect transmitted intramolecularly along the methylene chain. Furthermore the effect of the first quaternization in ArCH$_2$Ar seems too large when compared with the (almost identical) observed effect in PyCH=CHPy, where the charge is *in* the ring which is conjugated with the second ring *via* the ethylene linkage. Structural models show that the N–N distance in Py(CH$_2$)$_3$Py is only slightly greater than in Py(CH$_2$)$_2$Py and that this distance is less for ArCH$_2$Ar. Taken together, these results argue that an electrostatic field effect is operating: the positive charge on the nitrogen first quaternized would attract an approaching BuBr molecule (dipole) and thereby decrease its probability of reaching the uncharged nitrogen and hence decrease the probability of forming the intermediate complex necessary for SN2 reaction at that site. The activation energy for the second quaternization is slightly higher than that for the first; this could well correspond to the extra energy needed for the BuBr molecule to make a successful contact with the uncharged nitrogen in the field of the first charged one. An alternative electrostatic effect cannot be excluded; indeed both may be active. The reaction medium is highly polar; therefore electrostriction on a molecular scale might so increase the local density around a once quaternized diamine that the diffusion rate of the BuBr molecules to the reaction site would be decreased.

Comparison of the results for PyCH$_2$CH$_2$Py and PyCH=CHPy also argues against an intramolecular effect as the sole cause of the decrease in k_2 with respect to k_1: in the ethane, the two rings are joined by the essentially insulating methylene groups, while in the ethylene, they are joined by an excellent electronic conductor; hence any intramolecular effect due to the first quaternization should be enormously enhanced in the ethylene. Experiment shows only a slightly greater effect. The absolute magnitude of k_1 for the ethylene is about the same as the rate constant for pyridine; this may well be a consequence of the conjugative coupling which leads to the same electron density in PyCH=CHPy as in pyridine: push and pull just balance.

NEW HAVEN, CONNECTICUT

[17] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, N. Y., 1953, p. 737, Table 46-6.

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Syntheses and Infrared Spectra of α,β-Unsaturated-β-ketoamines and their Copper Chelates[1]

BY HENRY F. HOLTZCLAW, JR., JAMES P. COLLMAN AND RICHARD M. ALIRE

RECEIVED AUGUST 14, 1957

Syntheses and infrared spectra are described for several α,β-unsaturated-β-ketoamines and their copper chelates. The spectra are discussed and comparisons are made with spectra for other compounds with which analogies can logically be expected.

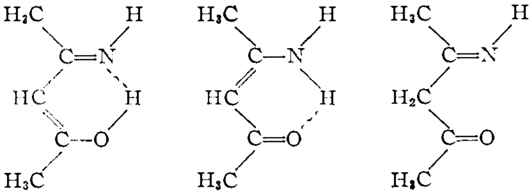
Introduction

In a previous paper from this Laboratory,[2] the infrared spectra for various 1,3-diketones and their metal chelates were discussed. The present paper discusses syntheses and infrared spectra of several α,β-unsaturated-β-ketoamines and their copper chelates.

Although a few α,β-unsaturated-β-ketoamines have been prepared previously, the literature reveals very little work with metal chelates of these compounds. Combes and Combes[3] reported the formation of a crystalline material in an alcoholic solution of 4-amino-3-pentene-2-one and copper(II) acetate. No attempt to characterize the substance was reported. Ueno and Martell[4] have recently reported the preparation and spectra of the ligand molecules and several corresponding metal chelates for bisacetylacetoneethylenediimine and related compounds.

Results and Discussion

Three forms, A, B and C, are possible for the α,β-unsaturated-β-ketoamines.



A B C

Ueno and Martell[4] concluded that a tautomeric equilibrium exists between the forms corresponding to A and B for bisacetylacetoneethylenediimine and related substances. Inasmuch as no absorption was obtained in the region around 1700 cm.$^{-1}$, the free carbonyl group, and hence structure C, was ruled out for that type of compound. Cromwell, *et al.*,[5] in an infrared study of various amino-sub-

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[1] Abstracted from the M.S. Theses of James P. Collman, June, 1956, and Richard M. Alire, June, 1956, University of Nebraska.

[2] H. F. Holtzclaw, Jr., and J. P. Collman, THIS JOURNAL, **79**, 3318 (1957).

[3] A. Combes and C. Combes, *Bull. soc. chim. France*, [3] **7**, 778 (1892).

[4] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **61**, 257 (1957).

[5] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337 (1949).

TABLE I

INFRARED ABSORPTION BANDS, CM.$^{-1}$, OF α,β-UNSATURATED-β-KETOAMINES AND THEIR COPPER(II) CHELATES

$\mathrm{I_{lig}}$[a]	$\mathrm{I_{che}}$	$\mathrm{II_{lig}}$	$\mathrm{II_{che}}$	$\mathrm{III_{lig}}$	$\mathrm{III_{che}}$	$\mathrm{IV_{lig}}$	$\mathrm{IV_{che}}$	Assignment
3380s	....	3200w,b	3320w	...	....	3280m	3290m	N–H or O–H
....	3250s	....	3250w	...	....	....	....	N–H or O–H
3210s	....	....	....	...	....	3140m	....	
3050sh	....	....	....	...	....	....	....	
1700s	....	....	....	...	....	....	....	C=O
1625s	....	1628s	....	1612s	....	1625s,b	....	Enol-chelate
....	....	....	....	1588s	1595sh	1593s	1590s	Phenyl
1585w	1585s	1595s	1584s	1569s	1575s	1568s,b	1570s	C=C (or perturbed carbonyl in chelate)
....	....	....	1534s	...	....	....	....	
1540s	1530s	1528m	1514sh	1502m	1515s	1533s	1515s	C=C (or C=N)
....	....	....	....	1490m	1488m	....	1488s	Phenyl
....	....	....	....	...	1406s	1407w	1417s	
1360s	1347sh	1358s	1350s	1352m	1368sh	1324s	1341s	
....	....	1308s	1300sh	1310m	....	1306m	....	
1290s,b	....	1287s	1270s	1270s	1272m	1285m,b	1245m,b	
1260sh	....	....	....	...	....	....	....	
1232w,sh	1227m	....	1227w	....	1245m	....	....	
....	1216m	1201w	1215w	1218w	....	....	....	
1197s	1180s	1188w,b	1189w	1185m	1195m	1177w	1185m	
....	....	....	1177w	...	....	....	1170m	
....	1165s	....	1163s	...	....	....	....	
1108m,b	....	....	....	...	....	1124m	1102m	
....	....	1080m	....	1080w	1070w	1068w	1070m	
1020s	1017s	1018m	1018s	1022m	1014m	1030m	1028m	
990s	....	....	....	...	....	....	....	
930m	932s	970m	935s	920m	938m	995m	958m	
....	....	....	....	...	....	937w	....	
....	....	....	....	905m	907m	....	....	
897s	....	....	....	...	....	....	....	
....	....	835m	....	840m	840m	849s	855m	
....	810s	....	....	818m	....	806m	800m	
....	792s	772w	770s	768m	765m	755s	773s	
743s	758s	....	....	750s	752s	....	758s	
....	720w	734s	718w	...	....	708s	700s	
....	....	....	....	694s	695s	685w	695s	Phenyl
675sh	685w	....	675w,sh	670m	685s	670m	....	

[a] Spectrum of the pure liquid. Infrared intensity abbreviations: s, strong; m, medium; w, weak; b, broad; sh, shoulder. Bands in the Nujol region are not listed.

stituted-α,β-unsaturated ketones presented convincing evidence for structure B.

For the metal chelates of α,β-unsaturated-β-ketoamines, structures corresponding to chelates of A and B (plus the additional forms possible if *cis*- and *trans*-isomers exist) may be written. In this regard, it is interesting to note that *cis*- and *trans*-isomers across copper square planar dsp^2 bonds have never been established.

Table I lists the frequencies of absorption bands for the following ligands and their copper chelates: I, 4-amino-3-pentene-2-one; II, 4-methylamino-3-pentene-2-one; III, 4-anilino-3-pentene-2-one; IV, 1-phenyl-3-amino-2-butene-1-one.

4000-1650 cm.$^{-1}$ Region.—Bands found above 3000 cm.$^{-1}$ may be assigned to N–H or O–H stretching vibrations. The exact origin of these bands, some of which seem to disappear upon chelation, is not clear. Bands found above 3000 cm.$^{-1}$ for metal chelates of I and IV might be assigned to N–H bonds. This interpretation, however, cannot be applied to the chelate of ligand II, which absorbs above 3000 cm.$^{-1}$ even though the nitrogen is completely substituted. Establishment of the possibility of an equilibrium between A and B is very difficult, and the N–H and O–H stretching frequencies cannot be distinguished with any degree of certainty. Previous work does not clarify this situation. Ueno and Martell[4] favor an O–H assignment for bands above 3000 cm.$^{-1}$ for the bisacetylacetoneethylenediimine type compounds. Cromwell, *et al.*,[5] state that N–H bands would be expected in this region but may be lowered by hydrogen bonding and lie masked under the C–H absorption. Svatos, Curran and Quagliano[6] point out that coördination with metals by molecules containing H–N bonds may be expected to lower the frequency more than hydrogen bonding. The apparent disappearance of the band with chelation may, therefore, actually be a decrease into the Nujol range where the band is obscured.

All ligands and chelates listed in Table I show normal C–H absorptions, which are masked by Nujol in those spectra run in Nujol mull.

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[6] G. F. Svatos, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 6159 (1955).

Ligand I shows a carbonyl absorption at 1700 cm.$^{-1}$, indicating some of the keto form to be present. No such normal ketone absorption was reported for the compounds studied by Cromwell, *et al.*,[5] or by Ueno and Martell.[4] The other molecules listed in Table I show no other absorptions between 1650 and 2900 cm.$^{-1}$.

1650-1500 cm.$^{-1}$ Region.—As is true for the 1,3-diketones and their metal chelates,[2] this is the most significant region of the spectra. Characteristic absorptions of the free ligand as well as of the chelated ligand appear here. Each free ligand gives rise to an enol–chelate (hydrogen-bonded carbonyl) band in this region. Completely analogous to 1,3-diketones, the enol chelate band in the α,β-unsaturated-β-ketoamines is centered between 1630 and 1610 cm.$^{-1}$ and disappears upon chelation. It seems to arise from vibrations characteristic of a hydrogen-bonded, conjugated carbonyl in the quasi six-membered ring.

The first strong band found in the chelates of α,β-unsaturated-β-ketoamines is in the same general position as a strong band found in the free ligand and centered in the 1590 to 1570 cm.$^{-1}$ region. A second band is found in the lower 1500 region in the spectra of all the ligands and their copper chelates. For the bisacetylacetoneethylenediimine type of compounds, Ueno and Martell[4] have assigned two corresponding bands to C=C and C=N stretching vibrations, respectively. If the ligand is present entirely in the amine form, the C=N absorption would not be expected. Both upper and lower bands might then be assigned to C=C absorptions. Alternatively, in analogy to chelates of the 1,3-diketones,[2] the upper band may arise in the chelate from a perturbed (chelated) carbonyl and the lower band from the carbon–carbon double bond. It should be noted, however, that in the pseudo aromatic chelate ring, both the C–O and the C–N bonds would be expected to have partial double bond character, and absorptions may logically arise for either in the 1500 cm.$^{-1}$ region. Sarma and Bailar,[7] in this connection, report that the C=N band for a Schiff base is very little changed by coördination.

Factors such as conjugation, ring structures and hydrogen bonding have not been extensively studied in the spectra of C=N bonds but may have an effect upon the C=N stretching frequency. Moreover, the conjugated, hydrogen-bonded carbonyl, the C=C, and the C=N vibrations might all be expected in the lower 1600 cm.$^{-1}$ region. Therefore, the authors feel that assignments of bands within this region should be considered as tentative in the light of present evidence.

Other bands in the region can be attributed to vibrations of functional groups such as phenyl rings.

1400-650 cm.$^{-1}$ Region.—Bands were found in the 1280 cm.$^{-1}$ region for each ligand, which might be assigned to an N–H or O–H band in the hydrogen-bonded enol ring of the ligand. The band which Ueno and Martell reported at 1150 cm.$^{-1}$ for their compounds and assigned to a chelated carbon–oxygen single bond, was not found in the α,β-unsaturated-β-ketoamines nor their copper chelates. The strong absorptions found in the upper 700 cm.$^{-1}$ region appear to be analogous to those reported for the bisacetylacetoneethylenediimine type compounds[4] and for several 1,3-diketones and their metal chelates.[2] In view of the findings for the 1,3-diketones and their metal chelates, however, some doubt is cast upon assignment to out-of-plane hydrogen deformation, as postulated for the bisacetylacetoneethylenediimine type compounds. Several 1,3-diketones which are substituted at the methylene carbon and have no hydrogen on the carbon–carbon double bond in either the ligand or the chelate nevertheless show bands in the 700 cm.$^{-1}$ region which cannot be attributed to a hydrogen out-of-plane deformation vibration.[2]

Phenyl absorptions were found around 700 cm.$^{-1}$ in the spectra of those compounds containing phenyl groups. No bands were detected between 650–700 cm.$^{-1}$ which could be assigned to metal-donor vibrations. Such bands probably occur below 650 cm.$^{-1}$

Experimental

Spectra.—All spectra were determined in the frequency range 4000–650 cm.$^{-1}$ with a Perkin–Elmer Model 21 recording spectrophotometer, using sodium chloride optics. Compounds were usually examined as solids in Nujol mulls. A few samples, as indicated in the table, were studied as pure liquid films.

Preparation of Compounds. (1) Preparation of Ligand Molecules. (a) **4-Amino-3-pentene-2-one.**—This compound was prepared by the method of Combes.[3] The melting point, after recrystallization from cold diethyl ether, was 42–43°; literature[3] 43°.

(b) **4-Methylamino-3-pentene-2-one.**—A method was developed which is analogous to that used for 4-amino-3-pentene-2-one. A sample of 2,4-pentanedione was fractionally distilled, collecting the fraction boiling at 135–137°. After cooling the purified 2,4-pentanedione in an ice-bath, a 40% methylamine–water solution was added slowly. The crystalline material which formed immediately was recrystallized from diethyl ether; m.p. 40–41°.

(c) **4-Anilino-3-pentene-2-one.**—The method of Roberts and Turner[8] was used. The melting point, after recrystallization of the long, needle-like crystals, was 47°; literature[3] 48°.

(d) **1-Phenyl-3-amino-2-butene-1-one.**—Concentrated ammonium hydroxide was refluxed with 1-phenyl-2,4-butanedione for three hours. The precipitate which formed upon cooling the mixture was removed by filtration; m.p. 143°; literature[9] 143°.

(2) Preparation of Copper Chelates. (a) **Bis-(4-amino-3-pentene-2-one)-copper(II).**—A solution of two grams of 4-amino-3-pentene-2-one in 25 ml. of 95% ethanol was added to a 4% solution (by weight) of copper(II) acetate in dilute ammonium hydroxide. The grey precipitate which immediately formed was allowed to stand overnight and was then filtered and recrystallized from 95% ethanol; yield 60%. *Anal.* Calcd.: Cu, 24.80; N, 10.8. Found: Cu, 24.95; N, 11.2.

(b) **Bis-(4-methylamino-3-pentene-2-one)-copper(II).**—An ammoniacal solution of copper(II) nitrate was mixed with two g. of 4-methylamino-3-pentene-2-one dissolved in 15 ml. of 95% ethanol. When the mixture was heated on the steam-bath, a grey solid formed which was filtered off and sublimed under vacuum at 2 mm. and 120°; yield before sublimation, 70%. *Anal.* Calcd.: Cu, 22.4; N, 9.72. Found: Cu, 22.7; N, 9.81.

(c) **Bis-(4-anilino-3-pentene-2-one)-copper(II).**—A solution of four g. of 4-anilino-3-pentene-2-one in 25 ml. of acetone was added to a 4% solution of copper(II) acetate in

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[7] B. D. Sarma and J. C. Bailar, Jr., THIS JOURNAL, **77**, 5476 (1955).

[8] E. Roberts and E. E. Turner, *J. Chem. Soc.*, 1832 (1927).

[9] E. Fischer and C. Bülow, *Ber.*, **18**, 2131 (1885).

dilute ammonium hydroxide. A solution of approximately 0.1 *M* sodium hydroxide was added slowly with stirring until a black precipitate formed which was filtered and recrystallized from 95% ethanol; yield 70%. *Anal.* Calcd.: Cu, 15.4; N, 6.8. Found: Cu, 15.2; N, 7.0.

(d) Bis-(1-phenyl-3-amino-2-butene-1-one)-copper(II).—A solution of ammoniacal copper(II) nitrate was added to a solution of 1.5 g. of 1-phenyl-3-amino-2-butene-1-one dissolved in 95% ethanol. The green solid which formed was recrystallized from acetone. *Anal.* Calcd.: Cu, 17.5; N, 7.3. Found: Cu, 16.8; N, 7.3.

Methods of Analysis.—Analysis for copper was made by decomposition with sulfuric acid followed by a potassium iodide–sodium thiosulfate titration to a starch indicator end-point. Nitrogen analysis was made by the Kjeldahl method.

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LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Haloboranes with Organocyclosiloxanes. I. Boron Chloride with Methyl and Ethyl Trimer and Tetramer[1,2]

BY PATRICK A. MCCUSKER AND THOMAS OSTDICK, O.S.B.

RECEIVED SEPTEMBER 30, 1957

The reaction of boron chloride with hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane produces initially dialkylchlorosiloxydichloroboranes. These are thermally unstable and disproportionate rapidly to tris-(dialkylchlorosiloxy)-boranes and boron chloride on attempted distillation even at low pressures. Tris-(dialkylchlorosiloxy)-boranes on short refluxing at atmospheric pressure followed by fractional distillation disproportionate to *sym*-tetraalkyldichlorodisiloxanes and boric oxide. *sym*-Tetraalkyldichlorodisiloxanes are more stable to disproportionation than the siloxyboranes but on long heating and slow fractional distillation at atmospheric pressure they can be made to disproportionate completely into dialkyldichlorosilanes and hexaalkylcyclotrisiloxanes. No linear or higher cyclosiloxanes are formed in this disproportionation reaction. The rate of the initial boron chloride–cyclosiloxane reaction is affected strongly by a steric factor involving the availability of the oxygen atoms of the cyclosiloxanes.

The reaction of boron chloride with trialkylboroxines has been shown by work in these laboratories[3] to yield alkyldichloroboranes along with a semi-solid residue which on hydrolysis gave boric acid and alkylboronic acid. No products intermediate to the starting materials and the final products were observed in the boroxine reaction. The analogous reaction of boron chloride with alkylcyclosiloxanes has now been investigated and found to be similar to the boroxine reaction except that with the alkylcyclosiloxanes a number of intermediate products have been isolated. The results of this study are reported in the present paper. A similar reaction between boron halides and linear trialkylsiloxanes has been reported by Wiberg and Krüerke[4] and the related reaction of aluminum chloride with organocyclosiloxanes has been reported by Hyde.[5]

Experimental

Reagents.—Boron chloride was obtained in technical grade from the Matheson Company. A practical grade of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane as well as diethyldichlorosilane were obtained from the Anderson Laboratories, Inc., Weston, Michigan. The methyl trimer was recrystallized three times from ethyl ether before use and the methyl tetramer was purified by fractional distillation, b.p. 175.5–176° at 750 mm., n^{20}_{D} 1.3962, d^{20} 0.9563. Hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane[6] were prepared by the hydrolysis of diethyldichlorosilane according to the methods reported by Hyde and DeLong[7] and Patnode and Wilcock[8] for the methyl compounds. Ethyl trimer: b.p. 88.7–89.0° at 1.9 mm., n^{20}_{D} 1.4305, d^{20} 0.9567; ethyl tetramer: b.p. 139.5–140.5° at 3 mm., n^{20}_{D} 1.4340, d^{20} 0.9590.

Reaction Apparatus.—The apparatus consisted of a 3-necked 300-ml. flask fitted with a thermometer, a reflux condenser and a glass tube drawn out to a capillary tip to facilitate bubbling the boron chloride into the cyclosiloxanes. Boron chloride was bubbled through mercury and then passed through a mercury safety release at the beginning of the reaction set-up. The condenser was connected to sulfuric acid bubbling bottles to which a stopcock was attached.

Purification and Characterization of Products.—The products were purified by fractional distillation either through a 12 × 500 mm. Vigreux column or through a 12 × 1500 mm. total reflux, partial take-off glass-helix packed column. Solid carbon dioxide–acetone and liquid nitrogen traps were provided.

Analysis for chlorine was made by titration of aqueous suspensions of the products under an ether layer with standard base using methyl orange as indicator. The same aqueous suspensions were analyzed for boron by adding mannitol and phenolphthalein and continuing the titration with standard base. Densities were determined with calibrated 0.5-ml. or 5.0-ml. Lipkin pycnometers and refractive indices were measured with an Abbe refractometer at 20.0 ± 0.1°. Molar refractions were calculated from the data for silicon compounds given by Warrick.[9] A value of 1.67 for the boron–oxygen bond refraction was calculated from Otto's data[10] on *n*-butyl and *n*-amyl borate. A value of 6.98 for the boron–chlorine bond refraction was derived from the data on *n*-amyl- and *n*-hexyldichloroborane given by McCusker, Ashby and Makowski.[3] Molecular weights were obtained from cryoscopic measurements in benzene.

Reaction of Boron Chloride with Methyl Trimer.—Boron chloride was passed into 18.5 g. (0.083 mole) of solid methyl trimer at room temperature. Boron chloride was absorbed and the solid partially liquefied. After 10 minutes the

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[1] Presented at the New York Meeting of the American Chemical Society, September, 1957.

[2] Work supported under AEC Contract AT (11-1)-38, Radiation Project of the University of Notre Dame.

[3] P. A. McCusker, E. C. Ashby and H. S. Makowski, THIS JOURNAL, **79**, 5182 (1957).

[4] E. Wiberg and U. Krüerke, *Z. Naturforschg.*, **8b**, 608 (1953).

[5] J. F. Hyde, U. S. Patent 2,645,654 (July 14, 1953); *C. A.*, **48**, 7050a (1954). British Patent 685,183 (Dec. 31, 1952); *C. A.*, **48**, 2761b (1954).

[6] Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane will be referred to as the methyl trimer, methyl tetramer, ethyl trimer and ethyl tetramer, respectively.

[7] J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1941).

[8] W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

[9] E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[10] M. M. Otto, *ibid.*, **57**, 1476 (1935).