near the end-point. The accepted value was the average of three analyses in which the maximum deviation between analytical results for any concentration was less than 0.07%.

Molal concentrations were then obtained and molar concentrations were calculated with the use of densities.

A saturated solution was prepared by allowing a warm concentrated copper sulfamate solution to cool to 25°, then permitting it to come to equilibrium with the solid phase which separated. Weighed samples of the supernatant liquid were analyzed as before. The solubility was found to be 74.73 (±0.05) g. per 100 g. of water.

Treatment of Results.—The apparent molal volumes were calculated from the observed densities by means of the equation proposed by Gucker[1]

$$\phi(V_2) = 1000/c - 1/d_1[1000d/c - M_2] \qquad (1)$$

where $\phi(V_2)$ is the apparent molal volume, M_2 is the molecular weight of the copper sulfamate, d_1 and d are the densities of the solvent and solution, respectively, and c is the concentration (moles of solute per liter of solution). The absolute density of water was used as 0.99707 g./ml. The densities and the corresponding values of concentration and apparent and partial molal volumes are shown in Table I.

TABLE I

Density	Concentration Molal	Concentration Molar	$\overline{V}_2$	$\phi(V_2)$	$d\phi(V_2)$
1.01340	0.08348	0.08283	59.86	58.77	−0.30
1.02316	.13394	.13250	60.40	59.00	− .10
1.10238	.56471	.54394	65.33	62.31	+ .02
1.18428	1.0484	.97910	68.86	64.72	+ .18
1.22814	1.3315	1.2199	71.14	66.51	− .27
1.28484	1.7130	1.5304	73.09	67.90	− .13
1.36007	2.2627	1.9495	75.54	69.74	− .05
1.44351	2.9221	2.4140	77.36	71.01	+ .38

From the data a second order equation expressing $\phi(V_2)$ as a function of c was found. The value of the coefficients was obtained by the method of averages[2]

$$\phi(V_2) = 56.08 + 7.07c^{1/2} + 1.92c \qquad (2)$$

In Column 6 are shown the deviations, $d\phi(V_2)$, of the observed values from those calculated from the equation.

Partial molal volumes were obtained using concentrations and calculated apparent molal volumes by the relation proposed by Gucker[1]

$$\overline{V}_2 = \phi(V_2) + c^{1/2}\left[\frac{1000 - c\,\phi(V_2)}{2000 + c^{3/2}\dfrac{\partial\phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\phi(V_2)}{\partial c^{1/2}} \qquad (3)$$

where $\phi(V_2)$ is the apparent molal volume and

$$\partial\phi(V_2)/\partial c^{1/2} = 7.07 + 3.84c^{1/2} \qquad (4)$$

as obtained from equation (2).

The partial molal volume of copper sulfamate at zero concentration was determined as 56.08 ml. per gram molecular weight by the evaluation of the first constant in equation (2).

Summary

1. Densities at 25 ± 0.02° of copper sulfamate solutions ranging from 0.08 to 2.4 molar have been determined.

2. The solubility of copper sulfamate at 25° was determined: 74.73 g. per 100 g. of solvent.

3. The apparent and partial molal volumes of the solute have been calculated.

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[1] Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

[2] Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, Inc., New York, N. Y., 1921, pp. 126, 145.

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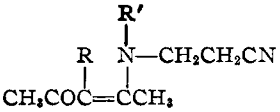
[JOINT CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Spectra of Amino-substituted α,β-Unsaturated Ketones

BY NORMAN H. CROMWELL, FOIL A. MILLER,[1] AGATHA R. JOHNSON, ROBERT L. FRANK AND DAVID J. WALLACE

A recent study of some cyclizations involved the preparation of 4-(2′-cyanoethyl)-amino-3-penten-2-one (I), 4-(2′-cyanoethyl)-amino-3-methyl-3-penten-2-one (II) and 4-N-(2′-cyanoethyl)-methylamino-3-penten-2-one (III) and the possibility of their ring closure by the aldol condensation. The properties of these substances



$$CH_3COC(R)=C(CH_3)N(R')CH_2CH_2CN$$

I, R = R′ = H
II, R = CH_3, R′ = H
III, R = H, R′ = CH_3

have proved to be unusual and have prompted us to undertake a study of their infrared absorption spectra and those of a number of previously reported related compounds.

Preparation and Properties

Compounds I, II and III were readily prepared by condensation of the appropriate β-aminopropionitrile with acetylacetone or 3-methylacetylacetone. Assignment of the double bond in these structures to the position α,β to the carbonyl rather than β,γ between the carbon and nitrogen atoms, is based on their ultraviolet absorption maxima in the region characteristic of α,β-unsaturated carbonyl compounds and on a comparison of their infrared spectra with those of compounds VII through IX of known structure.

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[1] Present address: Mellon Institute, Pittsburgh, Pennsylvania.

It is of interest that ammonia and β-aminopropionitrile fail to condense with 3,3-dimethylacetylacetone, a case in which the double bond of the product cannot take the position α,β to the carbonyl group.[2]

These amino ketones are structurally vinylogs of amides, and have been found to behave chemically more like amides than ketones. Our experiments performed mostly on 4-(2′-cyanoethyl)-amino-3-penten-2-one (I), show, for example, that they do not form phenylhydrazones; they fail to give a positive haloform reaction under the usual conditions; they fail to cyclize under conditions favorable for aldol condensation. Hydrolysis occurs in aqueous acid but not readily in water or aqueous alkali. Reaction with picric acid occurs only accompanied by cleavage to yield the picrate of the β-aminopropionitrile.

The preparation and properties of compounds IV,[2] V,[3] VI,[4] VII,[5] VIII,[5] IX,[5] X,[4] XI,[6,8,9] XII,[6,8,9] XIII,[5] XIV[7] and XV[9] have been described previously as indicated by the references.

Experimental

β-Aminopropionitrile.—The method of Ford, Buc and Greiner[10] was employed using 106 g. (2.00 moles) of acrylonitrile and 1 l. of 28% ammonium hydroxide. The yield was 81 g. (63%), b. p. 66–69° (5 mm.); $n^{20}\mathrm{D}$ 1.4400. Its picrate had m. p. 178° (lit.,[11] 178°).

β-Methylaminopropionitrile.—The method of Whitmore and co-workers[11] for β-ethylaminopropionitrile was applied using 106 g. (2.00 moles) of acrylonitrile and 300 ml. of 35% aqueous methylamine (3.00 moles of amine), and gave 117.5 g. (70%) of product, b. p. 90° (30 mm.); $n^{20}\mathrm{D}$ 1.4318.

4-(2′-Cyanoethyl)-amino-3-penten-2-one (I).—Addition of 13.5 g. (0.19 mole) of β-aminopropionitrile to 20.0 g. (0.20 mole) of acetylacetone resulted in an exothermic reaction. The product solidified on cooling to give a quantitative yield, 28.8 g.; m. p. 88°. An analytical sample was prepared by two recrystallizations from benzene–petroleum ether (3:1) to form white needles, m. p. 89.5–90°. These gave a purple color with ethanolic ferric chloride.

Anal.[12] Calcd. for $C_8H_{12}N_2O$: C, 63.16; H, 7.89. Found: C, 63.35; H, 7.68.

An alternative preparation involved the solution of 200 g. (2.00 moles) of acetylacetone in 150 ml. of 28% ammonium hydroxide, followed by addition of 106 g. (2.00 moles) of acrylonitrile. The mixture was refluxed for four hours and the excess water then removed under reduced pressure to yield several crops of crystals totaling 76 g. (25%), m. p. 88°.

The ultraviolet absorption spectrum was determined by Mrs. Calvin Brantley with a Beckman Model D spectrophotometer. A maximum occurs at 308 mμ with log ϵ = 4.265, where ϵ, the molecular extinction coefficient, is given by log $I_0/I = \epsilon \times c$ (moles/l.) $\times$ d(cm.). The solution employed contained 0.0006 g./l. in 95% ethanol.

Experiments designed to cyclize this compound to a dihydropyridine involved refluxing ethanolic solutions with piperidine, piperidine carbonate, sodium hydroxide, and sodium ethoxide; heating it with zinc chloride; heating it alone at temperatures up to 240°; and allowing it to stand with hydrochloric acid, acetic anhydride, and acetyl chloride. None of these attempts yielded a cyclized product. In most cases the starting material was recovered, although refluxing with 4% hydrochloric acid caused hydrolysis to β-aminopropionitrile hydrochloride.

Reaction with phenylhydrazine and with sodium hypoiodite according to the directions of Shriner and Fuson[13a,b] gave negative results. Reaction with picric acid[13c] gave the picrate of β-aminopropionitrile, m. p. 178° (lit.,[11] 178°).

4-(2′-Cyanoethyl)-amino-3-methyl-3-penten-2-one (II).—Mixing of 7.0 g. (0.060 mole) of 3-methylacetylacetone and 4.0 g. (0.057 mole) of β-aminopropionitrile and cooling of the hot reaction mixture gave the solid product. Recrystallization from benzene gave 9.0 g. (92%) of colorless needles, m. p. 109–110°. The compound forms a red color with ethanolic ferric chloride.

Anal. Calcd. for $C_8H_{14}N_2O$: C, 65.03; H, 8.43. Found: C, 65.25; H, 8.36.

The ultraviolet absorption spectrum, measured as reported for the preceding compound, had a peak of 327 mμ (log ϵ = 4.048; concentration 0.0092 g./l. in 95% ethanol).

4-N-(2′-Cyanoethyl)-methylamino-3-penten-2-one (III).—Twenty grams (0.20 mole) of acetylacetone and 17.0 g. (0.20 mole) of β-methylaminopropionitrile were mixed and heated on a steam cone for one half-hour. White needles (32.5 g., 98%) formed on cooling, m. p. 69–70°. These gave a purple color with ethanolic ferric chloride.

Anal. Calcd. for $C_8H_{14}N_2O$: C, 65.03; H, 8.43. Found: C, 64.85; H, 8.61.

The ultraviolet absorption spectrum, measured as described for the preceding compounds, had a maximum at 306 mμ (log ϵ = 4.357; concentration 0.0006 g./l. in 95% ethanol).

Infrared Absorption Spectra

The infrared spectra of compounds I-XV were measured from 650 to 3800 cm.$^{-1}$ with a Perkin–Elmer model 12B recording infrared spectrometer employing a sodium chloride prism. Table I summarizes the results. The samples were in the form of Nujol mulls, so the strong bands of Nujol at 1378, 1458 and about 2920 cm.$^{-1}$ appear in all the spectra. Since these bands are due to aliphatic C–H bending and stretching vibrations,[14] they would doubtless be present in the spectra of the compounds alone. They have therefore been included in the table and marked with an asterisk. Nujol also has a weak band at 720 cm.$^{-1}$ which probably would not be exhibited by the compounds. This has been observed in some of the spectra, and is also marked in the table. The accuracy of the wave length measurement is estimated to be ± 1 cm.$^{-1}$ at 1000 cm.$^{-1}$, ± 4 cm.$^{-1}$ at 1500 cm.$^{-1}$ $\pm$ 7 cm.$^{-1}$ at 2000 cm.$^{-1}$, and ± 17 cm.$^{-1}$ at 3000 cm.$^{-1}$.

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(2) Combes and Combes, *Bull. soc. chim.*, [3] **7**, 779 (1892).

(3) Cromwell and Witt, This Journal, **65**, 308 (1943).

(4) Cromwell, *ibid.*, **62**, 2897 (1940).

(5) Cromwell, Babson and Harris, *ibid.*, **65**, 312 (1943).

(6) Cromwell and Hoeksema, *ibid.*, **71**, 708 (1949).

(7) Raiford and Peterson, *J. Org. Chem.*, **1**, 544 (1937).

(8) Cromwell and Wankel, This Journal, **71**, 711 (1949).

(9) Cromwell and Hoeksema, *ibid.*, **71**, 716 (1949).

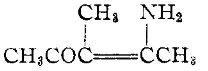
(10) Ford, Buc and Greiner, *ibid.*, **69**, 844 (1947).

(11) Whitmore, Mosher, Adams, Taylor, Chapin, Weisel and Yanko, *ibid.*, **66**, 725 (1944).

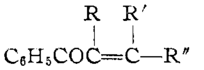
(12) Microanalyses were carried out by Misses Emily Davis and Theta Spoor.

(13) (a) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, 1948, p. 116; (b) p. 138; (c) p. 180.

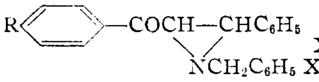
(14) Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

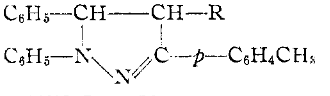

$CH_3COC(CH_3){=}C(NH_2)CH_3$

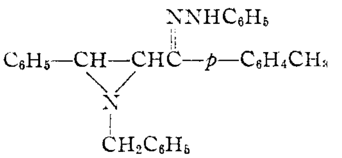
IV


$C_6H_5COC(R){=}C(R')-R''$

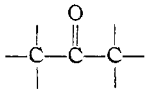
V, R = $N(CH_3)CH_2C_6H_5$, R′ = H, R″ = C_6H_5
VI, R = morpholino, R′ = H, R″ = C_6H_5
VII, R = H, R′ = $NHCH_2C_6H_5$, R″ = C_6H_5
VIII, R = H, R′ = cyclohexylamino, R″ = C_6H_5
IX, R = H, R′ = $NHCH_2C_6H_5$, R″ = CH_3
X, R = H, R′ = morpholino, R″ = C_6H_5


XI, R = CH_3, *trans* form
XII, R = CH_3, *cis* form
XIII, R = H

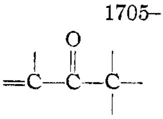

XIV, R = H
XV, R = $NHCH_2C_6H_5$


XVI

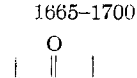
Compounds I-X.—We shall consider first the 1500–1700 cm.$^{-1}$ region of the spectra of compounds I-X. Here one expects to find bands due to the phenyl group, the carbonyl group, to C=C bonds, and to the N–H bending of amines. The phenyl bands occur very nearly at 1500 and 1600 cm.$^{-1}$.[15] They are characteristic and are rather easily identified by their intensity and shape. The carbonyl stretching vibration in ketones is found quite consistently at the following wave numbers

(a) Unconjugated ketones,[15a] 
$-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}-$

1705–1720[16,17,18,19]

(b) α,β-Unsaturated ketones, (including aryl ketones) 
$=\overset{|}{C}-\overset{O}{\overset{\|}{C}}-\overset{|}{\underset{|}{C}}-$

1665–1700[16,17,18,19]

(c) α,β,α′,β′-Unsaturated ketones, (including diaryl ketones) 
$=\overset{|}{C}-\overset{O}{\overset{\|}{C}}-\overset{|}{C}=$

1650–1670[16,17,18]

It is noteworthy that further extension of the conjugation to the γ,δ bond (O=C—C=C—C=C—) has little additional effect on the carbonyl frequency. The C=C band is to be expected at 1600–1625 cm.$^{-1}$ in these compounds since it is in every case conjugated with the carbonyl group, and in some cases is also conjugated with a phenyl group.[15] The intensity of this band is known to vary greatly from one compound to another. Primary amines exhibit an N–H bending absorption at 1580–1640 (usually only one band is observed).[15] Little information seems to be available on secondary amines. Finally one often observes "extra" bands in this region which are due to combination tones and overtones. Their intensity may be enhanced by Fermi resonance so that they occasionally appear to be moderately intense.

Since our compounds I-X contain both keto and amino groups, it is convenient for discussion to classify them in several categories

	Examples
(1) α-Amino-α,β,α′,β′-unsaturated ketones	
(a) N-Disubstituted	V, VI
(2) β-Amino-α,β-unsaturated ketones	
(a) N-Unsubstituted	IV
(b) N-Monosubstituted	I, II
(c) N-Disubstituted	III
(3) β-Amino-α-β,α′,β′-unsaturated ketones	
(a) N-Monosubstituted	VII, VIII, IX
(b) N-Disubstituted	X

We now consider the bands which are observed experimentally in the double bond region. These are reproduced in Fig. 1 in the form of a line chart. The height of a line is a measure of the band intensity. The cross-hatched areas indicate the regions in which the carbonyl bands are expected to appear.

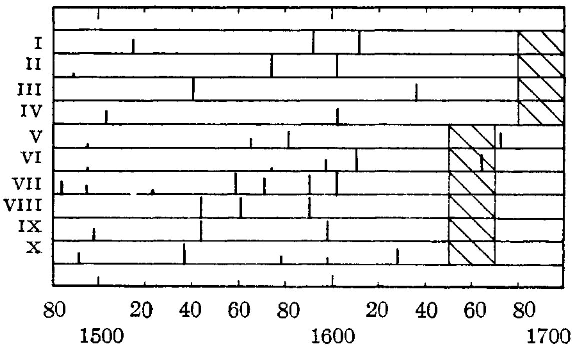


Fig. 1.—Infrared absorption spectra.

Only the two α-amino-α,β,α′,β′-unsaturated ketones (V and VI) have carbonyl bands in the expected range. The phenyl bands are rather

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[15] Barnes, Gore, Stafford and Williams, *Anal. Chem.*, **20**, 402 (1948).

[15a] The upper limit of this range should be increased to 1760 cm.$^{-1}$ if the carbonyl group is in a strained ring, such as a four- or five-membered one. See: (a) reference 19a; (b) Whiffen and Thompson, *J. Chem. Soc.*, 1005 (1946).

[16] Barnes, Gore, Liddel and Williams, "Infrared Spectroscopy," Reinhold Publishing Corporation, New York, N. Y., 1944, p. 21.

[17] Thompson and Torkington, *J. Chem. Soc.*, 640 (1945).

[18] Unpublished research of Agatha R. Johnson and Foil A. Miller.

[19] (a) Jones, Williams, Whalen and Dobriner, THIS JOURNAL, **70**, 2024 (1948); (b) Jones, Humphries and Dobriner, *ibid.*, **71**, 241 (1949); (c) Rasmussen, Tunnicliff and Brattain, *ibid.*, **71**, 1068 (1949); (d) Hartwell, Richards and Thompson, *J. Chem. Soc.*, 1436 (1948).

TABLE I

INFRARED ABSORPTION SPECTRA

vw = very weak. w = weak. m = medium. s = strong. vs = very strong.

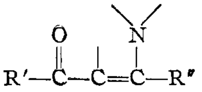
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I	cm.$^{-1}$ I
739 vw	694 vw	762 w	878 w	681 vw	685 w	670 vw	683 vw	677 vw	674 vw	688 w	695 s	652 vw	678 vw	687 vw
760 s	770 w	769 vw	974 vs	692 m	691 m	680 vw	692 s	690 m	691 s	695 s	699 s	685 s	689 m	694 w
796 vw	813 m	808 s	1005 w	697 w	705 m	692 s	706 s	696 s	706 s	700 s	729 vs	697 vs	693 m	704 w
833 m	855 vw	904 vw	1011 vw	702 m	734 w	704 s	745 s	707 m	735 m	719* m	753 s	708 s	712 vw	717* vw
874 vw	920 vw	953 s	1092 vw	725 m	753 m	733 s	768 vw	731 s	770 s	729 s	778 w	738 s	743 s	746 m
905 vw	932 vw	998 m	1224 s	744 m	777 vw	748 s	777 m	751 s	783 s	751 s	795 w	748 vs	757 m	750 m
934 vw	975 s	1021 vs	1274 s	800 m	824 vw	764 m	794 vw	793 s	798 vw	757 w	813 m	763 w	790 vw	759 w
976 w	988 w	1050 s	1352 s	849 vw	848 vw	775 w	811 w	808 s	809 vw	795 w	821 w	775 m	819 s	819 w
999 vw	1009 vw	1133 s	1373* s	894 vw	876 m	795 w	842 vw	833 w	823 w	802 w	848 w	819 vw	841 vw	823 vw
1011 w	1046 w	1181 vs	1460* m	902 w	889 m	805 vw	891 m	849 vw	840 vw	821 m	854 vw	849 vw	868 vw	828 vw
1021 vw	1077 m	1216 w	1470 s	908 vw	894 w	845 vw	921 w	878 vw	847 vw	849 vw	871 vw	857 w	873 m	842 vw
1049 vw	1088 m	1250 w	1503 vs	912 vw	909 w	852 vw	924 w	897 vw	862 vw	858 vw	882 m	867 vw	876 w	869 vw
1109 w	1145 m	1278 w	1602 vs	956 m	935 m	894 vw	969 vw	925 vw	870 m	865 m	901 w	906 w	906 vw	876 vw
1206 m	1223 m	1355 s	2920*	971 vw	980 s	926 vw	977 w	974 m	898 m	871 vw	924 w	914 m	944 vw	944 vw
1211 m	1267 vs	1377* vs	3120 s	991 m	1000 m	931 vw	1000 w	983 vw	923 vs	903 w	957 vw	920 m	955 vw	959 vw
1242 w	1298 s	1388 s	3265 vs	1003 w	1025 vw	963 m	1025 m	1002 vw	937 m	911 vw	988 w	936 m	996 w	968 vw
1274 m	1359 s	1419 vs		1026 vw	1050 vw	970 vw	1050 w	1016 vw	972 vw	926 w	1007 vw	950 vw	1002 vw	976 vw
1298 s	1376* m	1459* vs		1071 vw	1066 vw	973 vw	1060 m	1028 m	1001 w	957 w	1018 m	971 vw	1014 vw	991 vw
1356 m	1429 m	1541 vs		1078 vw	1076 vw	987 vw	1070 w	1066 m	1019 s	967 vw	1027 s	980 vw	1021 vw	1016 vw
1377* m	1459* s	1636 s		1103 vw	1120 vs	1005 vw	1085 m	1090 w	1034 s	981 vw	1038 m	993 vw	1026 vw	1029 vw
1435 m	1471 s	2255 w		1110 vw	1164 m	1025 m	1145 m	1105 vw	1061 m	1001 vw	1074 w	1001 vw	1030 vw	1034 vw
1461* s	1489 vw	2920*		1153 vw	1198 s	1030 m	1152 w	1112 vw	1068 w	1008 w	1099 vw	1024 m	1040 vw	1076 w
1515 s	1574 vs			1173 m	1216 m	1061 s	1176 vw	1155 vw	1115 m	1018 w	1123 vw	1030 m	1071 vw	1081 vw
1592 vs	1602 vs			1187 m	1222 m	1078 vw	1186 vw	1177 vw	1126 s	1032 m	1156 vw	1052 s	1078 vw	1111 vw
1612 vs	2255 w			1195 w	1243 s	1087 vw	1225 m	1227 vw	1150 vw	1057 s	1184 s	1059 vs	1103 vw	1138 m
2250 w	2920*			1207 w	1270 s	1147 m	1250 m	1247 vw	1174 vw	1067 s	1204 w	1073 w	1111 vw	1160 vw
2920*				1229 m	1289 vw	1157 w	1277 vw	1276 m	1187 vw	1092 m	1215 vw	1087 w	1134 s	1177 vw
3090 w				1258 m	1303 vw	1177 vw	1294 w	1290 s	1210 vs	1096 m	1224 vw	1095 vw	1148 vw	1195 vw
3145 w				1289 vw	1315 vw	1183 vw	1306 vw	1310 vs	1227 s	1113 w	1241 s	1153 vw	1182 vw	1220 vw
3410 w				1312 w	1338 vw	1195 vw	1335 vs	1322 s	1256 s	1180 s	1273 vw	1174 m	1201 vw	1256 vw
				1358 w	1345 vw	1228 m	1378* m	1372* s	1271 m	1212 m	1280 vw	1182 w	1240 vw	1273 vw
				1367 m	1378* m	1251 m	1459* s	1439 s	1305 vw	1230 s	1301 vw	1213 w	1270 vw	1300 vw
				1376* w	1401 w	1270 m	1473 s	1454* vs	1339 m	1235 s	1311 vw	1224 vs	1279 vw	1327 w
				1414 m	1449 s	1286 m	1544 vs	1497 m	1361 m	1248 vw	1346 s	1232 s	1300 vw	1345 vw
				1424 m	1459* s	1311 m	1561 vs	1544 vs	1379* s	1263 w	1362 vw	1251 vw	1304 vw	1378* w
				1457* s	1495 vw	1338 s	1590 vs	1598 vs	1412 s	1285 w	1378* m	1300 w	1327 s	1394 s
				1470 m	1574 vw	1365 m	1945 vw	2920*	1443 s	1307 w	1393 w	1311 w	1336 vw	1458* s
				1495 w	1597 s	1379* w	2920*	3025 vw	1459* s	1313 vw	1413 vw	1357 m	1345 vw	1500 s
				1565 m	1610 s	1439 s	3025 vw	3060 vw	1491 s	1358 m	1457* s	1380* m	1378* w	1574 w
				1581 vs	1664 vs	1453* s	3045 vw	3190 vw	1536 vs	1378* m	1496 m	1418 w	1395 s	1597 m
				1672 s	2920*	1459 s			1578 s	1407 vw	1608 s	1452 s	1413 w	2920*
				2920*	3055 vw	1484 s			1598 m	1419 w	1651 s	1459* s	1458* s	3020 vw
				3010 vw		1495 m			1628 vs	1449 m	2920*	1497 m	1502 vs	3050 vw
				3050 vw		1523 w			2920*	1456* s	3015 w	1578 vw	1554 vw	
						1559 vs			3055 w	1465 m	3040 w	1599 m	1575 vw	
						1571 vs			3490 w	1498 m		1685 vs	1599 s	
						1590 vs				1605 s		2920*	1666 vw	
						1602 vs				1678 vs		3020 w	2920*	
						2920*				2920*		3050 w	3020 vw	
						3040 w				3020 w			3060 vw	
										3055 w				

easily located in these two compounds, and the 1610 band in VI may well be due to the C═C vibration. The only puzzling questions are the explanation of 1565 cm.$^{-1}$ in V and the whereabouts of the C═C band in V.

In all the remaining compounds (I-IV and VII-X) the highest band in the 1500–1700 cm.$^{-1}$ region, which is presumably the C═O band, is lower than expected by from 20 to 80 cm.$^{-1}$. It is well known[19d] that hydrogen bonding will lower a carbonyl frequency. This effect can not be operative in III or X, however (nor in V or VI), because they are tertiary amines. One must therefore conclude that the substitution of an amino group in the beta position of these α,β-unsaturated ketones lowers the carbonyl frequency. This is particularly striking when one compares VI and X, since these compounds are identical except for the position of substitution.

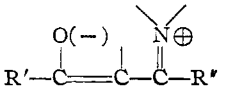
Compound III should possess a C═C band. The only band in the double bond region besides the carbonyl band is an intense one at 1541, which is 60 cm.$^{-1}$ lower than expected. It can scarcely be due to a combination tone because of its marked intensity. In X one finds an analogous band in nearly the same position, 1537 cm.$^{-1}$. There are in addition phenyl bands at 1491 and 1598, and an unexplained band at 1578.

Let us now consider why in compounds III and X the carbonyl band is low, why the C═C band is missing, and what may be the origin of the band near 1540. One possibility is that the high band is not really due to the C=O group, but that it is due to C=C and that the C=O band is missing. This is unlikely because (a) the carbonyl band is almost invariably a strong band, and (b) the 1540 band must still be explained. Another possibility is that with the amino group substituted on the β carbon atom, the ionic resonance form (b) can contribute appreciably to the ground state.



$R'-\overset{\overset{O}{\|}}{C}-\overset{|}{C}=\overset{\overset{N}{|}}{C}-R''$

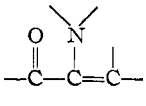
a



$R'-\overset{\overset{O(-)}{|}}{C}=\overset{|}{C}-\overset{\overset{N\oplus}{\|}}{C}-R''$

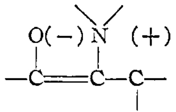
b

This would have the effect of lowering the C=O frequency, lowering the C=C frequency, and raising the C—N frequency. Thus it does qualitatively fit the observed results. The 1540 band would then be explained as either the lowered C=C or the enhanced C—N frequency—probably the former. This explanation also makes it understandable that the α-amino ketones (V and VI) do not exhibit these anomalies, since the ionic resonance structures that one can write in this case (d and e) would be expected to contribute much less to the actual ground state of the molecule.[20]



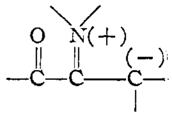
$-\overset{\overset{O}{\|}}{C}-\overset{\overset{N}{|}}{C}=\overset{|}{C}-$

c



$-\overset{\overset{O(-)}{|}}{C}=\overset{\overset{N}{|}}{C}-\underset{|}{\overset{(+)}{C}}-$

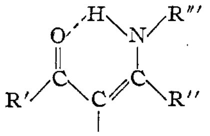
d



$-\overset{\overset{O}{\|}}{C}-\overset{\overset{N(+)}{\|}}{C}-\underset{|}{\overset{(-)}{C}}-$

e

The remaining compounds (I, II, IV, VII, VIII and IX) are further complicated by hydrogen bonding. It has been shown[21] that hydrogen bonding will lower a carbonyl frequency, and it has already been mentioned that this bonding cannot occur in compounds III, V, VI, nor X because they are tertiary amines. Now it is precisely in compounds III and X that the anomalous lowering of the carbonyl frequency is smallest. In the other β-amino ketones the effect of hydrogen bonding is apparently superimposed on this first effect. This is supported by the fact that no N–H stretching frequency is observed in the usual region around 3300 cm.$^{-1}$. The N–H band has probably been broadened and lowered to around 3000 cm.$^{-1}$ where it is hidden by the C–H bands. The spectrum of II was measured in chloroform solution and no shift to higher frequencies was observed. The hydrogen bonding must therefore be largely intramolecular. It will be noted that these compounds offer favorable opportunities for chelation.



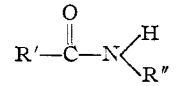
In general the spectra of these remaining β-amino ketones show the same features as those of III and X except for having lower carbonyl bands. The phenyl bands can usually be found readily, and the C=C not at all if one assigns the highest frequency to C=O. Extra bands appear in many cases which may be due to the N–H bending vibration. And finally there is in nearly every case a strong band somewhere in the range 1500–1560 whose explanation is puzzling. We can think of no explanation for this other than the one already advanced.

When the spectra of compounds I-IV and VII-X were first measured, the compounds were suspected of being monosubstituted amides because of this strong band around 1540 cm.$^{-1}$. Richards and Thompson[22] give some general results for amides in the solid state

	Band "B"	C=O
R—CO—NH$_2$	1630	1655
R—CO—NHR	1530–1570	1640–1680
R—CO—NR$_1$R$_2$	....	1650

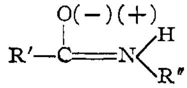
Band "B" near 1540 cm.$^{-1}$ is so characteristic of monosubstituted amides that it, in conjunction with an N–H stretching band near 3270 cm.$^{-1}$, serves as an excellent test for this class of compounds. We have already pointed out, however, that our compounds I-IV and VII-X are not amides but are vinylogs of amides.

The question now arises as to whether this 1540 cm.$^{-1}$ band might not have the same explanation in the monosubstituted amides and in the vinylogs. The origin of band "B" in amides is not settled. Richards and Thompson[22] discuss four possible explanations and conclude that it is due to the N–H bending motion. This is supported by its absence in disubstituted amides. These authors have pointed out that deuterization experiments should provide a critical test of this explanation. Should it be disproved, a possible alternative is to explain band "B" as the C-N stretching frequency enhanced by a large contribution from the ionic form g



$R'-\overset{\overset{O}{\|}}{C}-N{<}^{H}_{R''}$

f



$R'-\overset{\overset{O(-)(+)}{|}}{C}=N{<}^{H}_{R''}$

g

The analogy to the vinylogs (structures a and b) is evident, and affords some support for this idea. Nevertheless there are certain difficulties with this explanation. In the first place the ionic form must make a very important contribution

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[20] Additional ionic resonance forms besides d and e are of course possible in the cases having phenyl groups attached to this system.

[21] The work of Thompson, *et al.*, reference 19d indicates that simple hydrogen bonding can lower the carbonyl frequency in some cases. Rasmussen, *et al.*, reference 19c, have found that intramolecular hydrogen bonding as in diacetone alcohol has almost no effect on the carbonyl vibrational frequency. On the other hand these latter authors state that "conjugated chelation" as in enolyzed beta-diketones produces a major shift of the carbonyl infrared band to about 1613 cm.$^{-1}$ with a considerable increase in intensity. The analogy between the structures of β-secondary or primary amino α,β-unsaturated ketones and the enols of β-diketones is obvious.

[22] Richards and Thompson, *J. Chem. Soc.*, 1248 (1947).

to the final ground state if the C–N stretching frequency is to be as high as 1540 cm.$^{-1}$. This should at the same time lower the carbonyl frequency markedly, since it acquires a large amount of single bond character. This frequency is indeed lower in amides than in aldehydes and unconjugated ketones, but by nowhere nearly the amount expected. Secondly one wonders why the 1540 cm.$^{-1}$ band is found only in monosubstituted amides, whereas with the vinylogs the 1500–1560 band appears regardless of whether the amine group is unsubstituted, monosubstituted, or disubstituted. We are therefore inclined to feel that the origin of the 1540 band is fundamentally different in the amides and in their vinylogs. Conversely if the origin is actually different, several of our unsaturated ketones might be expected to exhibit *two* bands between 1500 and 1600 cm.$^{-1}$ (in addition to any phenyl bands) ... namely the characteristic band at 1500–1560 cm.$^{-1}$ due to the resonance effect already described, and a second band due to the N–H bending in a secondary amine. Two bands are found in compounds I, VII and VIII, although there is only one in II and IX.

Compounds XI–XV.—Compounds XI and XII have been indicated to be the *trans* and *cis* modifications, respectively, of 1-benzyl-2-phenyl-3-*p*-toluylethyleneimine,[6,8,9] and it is of interest that while the *trans* form (XI) exhibits a carbonyl band in the normal region for α,β-unsaturated carbonyls (including aromatic unsaturation), the *cis* form (XII) has a band about 25 cm.$^{-1}$ below this region. These spectra help settle the relationship of the configuration of structure XIII to that of XI, inasmuch as its band in the α,β-unsaturated carbonyl region, 1680–1700 cm.$^{-1}$, resembles that of XI rather than XII.

Compound XV is the structure shown for the reaction product of phenylhydrazine with the ethyleneimine XII,[9] but the possibility was considered that the correct structure might instead be represented by XVI. A comparison of its infrared spectrum with that of the other four compounds (XI–XIV) confirms the previous conclusion that it has the pyrazoline structure (XV) rather than the ethyleneimine form (XVI). Thus for example it has the moderately strong bands at 1138 and 1394 cm.$^{-1}$ which have counterparts in XIV but not in XI, XII, nor XIII. Moreover it does not exhibit the strong bands at 1020–1060, 1175–1185, 1220–1240 and 1325–1360 cm.$^{-1}$ shown by each of XI, XII and XIII.

Summary

1. Certain β-amino α,β-unsaturated ketones have been shown to behave chemically more like amides, of which they are vinylogs, than like ketones or vinyl amines.

2. Infrared spectra of fifteen unsaturated amino ketones or derivatives thereof have been studied and their peculiarities discussed. The presence of an amino group (either substituted or unsubstituted) on the beta carbon atom of an α,β-unsaturated ketone lowers the carbonyl band by 20–80 cm.$^{-1}$.

URBANA, ILLINOIS
LINCOLN, NEBRASKA

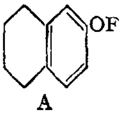
RECEIVED JANUARY 7, 1949

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

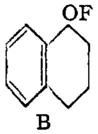
The Catalytic Dehydrogenation of 2-Substituted Tetrahydronaphthalene Derivatives

BY MELVIN S. NEWMAN AND J. ROGER MANGHAM[1]

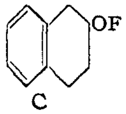
The following report describes a continuation of studies designed to obtain more information about the liquid phase dehydrogenation over palladium-on-charcoal of oxygenated hydroaromatic compounds. The previous reports,[2,3] respectively, dealt with 6-substituted 1,2,3,4-tetrahydronaphthalenes, A, and 1-substituted 1,2,3,4-tetrahydronaphthalenes, B, where OF indicates the oxygenated function. Since the oxygenated functions of A and B differed both in their positions with respect to the point of ring fusion and in their relative positions with respect to the hydrogen to be removed, it is necessary to study compounds of type C and D before a complete discussion can be attempted. In this paper we describe the behavior of 2-substituted-1,2,3,4-tetrahydronaphthalenes, C, under the above conditions.



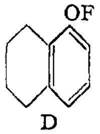
A



B



C



D

In the discussion R will be used to designate the 1,2,3,4-tetrahydro-2-naphthyl radical and R′, the 2-naphthyl radical. In Table I are summarized the results with the following compounds: $\mathrm{RCOOCH_3}$, I; $\mathrm{RCH_2OH}$, II; $\mathrm{RCH_2OCOCH_3}$, III; RCHO, IV; $\mathrm{R\overline{CHOCH_2CH_2O}}$, V; $\mathrm{RCOCH_3}$, VI; $\mathrm{RCH_2COCH_3}$, VII; and $\mathrm{RCH_2CH_2COCH_3}$, VIII.

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[1] This work was taken from the dissertation submitted by J. R. Mangham to The Ohio State University in partial fulfilment of the requirements for the Ph.D. degree, December, 1948.

[2] Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

[3] Newman and O'Leary, *ibid.*, **68**, 258 (1946).