Vinylogous Imides. I. Nuclear Magnetic Resonance Spectra[1a]

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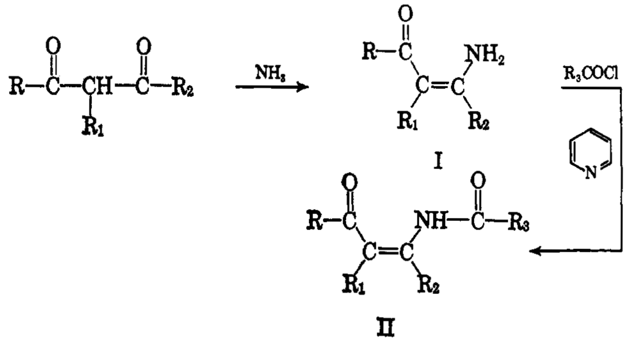
The proton resonance spectra of a number of compounds purported to be vinylogous imides have been examined for the presence of other tautomers. In no case is reassignment of structure necessary. Preference for a six-membered chelate ring, when possible, is noted. Evaluation of the *cis* NH-CH spin-spin coupling constant is permitted in one compound.

The transmission of electronic effects of functional groups through a conjugated system has been correlated by the empirical generalization known as the principle of vinylogy.[2] Numerous examples of vinylogs of simple amides,[3-7] amidines,[8] urethans,[9,10] cyanamides,[11] and acids[12] exist in the chemical literature. As expected, marked changes in chemical and spectral properties result from the π-p conjugate interaction accompanying extension of a functional group through insertion of one or more vinylene links.

In view of the considerable experimental interest in vinylogous systems, it was decided to investigate the properties of the corresponding imides. This paper and succeeding ones will deal with those compounds which contain one vinylene link, *i.e.*, β-amido α,β-unsaturated ketones, —(O)C—N—C=C—C(O)—, although higher homologs are known.[13]

Several methods have arisen whereby β-amido α,β-unsaturated ketones have been synthesized. Perhaps the most obvious and direct approach is that of Benary and his collaborators.[14] The first step involves condensation of the appropriate β-diketone with ammonia or a primary amine to give a vinylogous amide (I); subsequent acylation of I gives the desired acyclic vinylogous imide (II) in good yield.[15] Model compounds[16] utilized in the present work are shown in Chart I.

CHART I



I

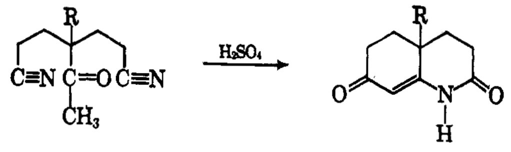
II

	R	R₁	R₂	R₃
IIa	CH_3	H	CH_3	CH_3
b	CH_3	H	CH_3	$ClCH_2$
c	CH_3	H	CH_3	C_6H_5
d	CH_3	H	CH_3	*p*-ClC_6H_5
e	CH_3	CH_3	CH_3	CH_3
f	CH_3	CH_3	CH_3	C_6H_5
g	C_6H_5	H	CH_3	CH_3
h	C_6H_5	H	CH_3	C_6H_5

Acylation of vinylogous amides derived from primary amines (—(O)C—C=C—NH—R) has been reported in two instances.[14b,17] The limited number of examples do not allow one to generalize, although attack at nitrogen seems to predominate.[18]

Formation of Δ^8-octahydro-2,7-quinolinediones (IV), cyclic vinylogous imides, by the action of sulfuric acid on γ-acetylpimelonitriles (III), has been observed by Koelsch and Walker.[19] Their results are summarized in Chart II.

CHART II



IIIa, R = C_6H_5
b, R = CH_3
c, R = $CH_2CH_2C\equiv N$
d, R = $CO_2C_2H_5$

IVa, R = C_6H_5
b, R = CH_3
c, R = $CH_2CH_2CO_2H$
d, R = H

Additional reactions leading to vinylogous imides include the base-catalyzed ring closure of δ-amino-β-keto γ,δ-unsaturated esters,[20] the Beckmann rearrangement of the acetoxime of an α,β-unsaturated ketone,[21]

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[1] (a) Support of this work by a Frederick Gardner Cottrell Grant from the Research Corporation is gratefully acknowledged. (b) Address for the 1964-1965 academic year: College of Science, Mosul, Iraq.

[2] R. C. Fuson, *Chem. Rev.*, **16**, 1 (1935).

[3] E. Benary, *Ber.*, **63**, 1573 (1930), and earlier papers.

[4] S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1016 (1945).

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

[6] N. F. Albertson, *ibid.*, **74**, 249 (1952).

[7] G. N. Walker, *J. Org. Chem.*, **27**, 4227 (1962).

[8] G. N. Walker and M. A. Moore, *ibid.*, **26**, 432 (1961), and references cited therein.

[9] N. A. Nelson and R. S. P. Hsi, *ibid.*, **26**, 3086 (1961); N. A. Nelson, K. O. Gelotte, Y. Tamura, H. B. Sinclair, J. M. Schuck, V. J. Bauer, and R. W. White, *ibid.*, **26**, 2599 (1961).

[10] G. N. Walker and R. N. Beaver, *ibid.*, **26**, 4441 (1961).

[11] S. Baldwin, *ibid.*, **26**, 3288 (1961).

[12] The enol tautomer of an enolizable β-diketone constitutes the most common example of a vinylogous acid. A classical case of some interest is provided by tropolone.

[13] E. Benary and H. Psille, *Ber.*, **57B**, 828 (1924); E. Benary, *ibid.*, **59B**, 2198 (1926).

[14] (a) E. Benary, *ibid.*, **24**, 3912 (1909); (b) E. Benary, *ibid.*, **60**, 1826 (1927); (c) E. Benary, F. Reiter, and H. Soenderop, *ibid.*, **50**, 65 (1917).

[15] Inasmuch as compound I is an enamino ketone, one might expect to obtain products derived from C- and/or O-acylation [J. A. West, *J. Chem. Educ.*, **40**, 199 (1963); G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkoviz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 215 (1963); G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **29**, 798 (1964); S. Hunig, E. Benzing, and E. Lucke, *Ber.*, **90**, 2833 (1957)] as well as N-acylation. Indeed IIb was originally[14a] considered to be the C-acylated product, 4-amino-3-chloroacetyl-3-penten-2-one, a conclusion which was revised on the basis of later experiments.[14b] Structure assignments made by Benary followed from the elemental analysis and chemical properties, particularly hydrolysis, *e.g.*, IIc and h giving benzamide as well as other expected products.

[16] Compounds IIb, c, g, and h were prepared by Benary[14]; the others are new.

[17] R. E. Lyle and D. A. Nelson, *J. Org. Chem.*, **28**, 169 (1963).

[18] Attempts to prepare the N-benzoyl and N-acetyl derivatives of the secondary vinylogous amide 4-methylamino-3-penten-2-one through acylation have resulted in uncharacterized oils which decompose upon vacuum distillation: unpublished results of M. M. McClelland and D. L. Ostercamp.

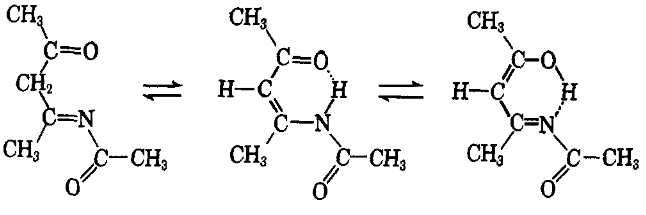
[19] C. F. Koelsch and H. M. Walker, *J. Am. Chem. Soc.*, **72**, 346 (1950).

[20] F. Hoffmann-La Roche and Co., German Patent 634,284 (1937); *Chem. Abstr.*, **31**, 219 (1937).

[21] J. Romo and A. Romo de Vivar, *J. Am. Chem. Soc.*, **81**, 3447 (1959)

and the oxidation of a suitable hydroxy compound.[22] Only in the case of the cyclization has the synthetic utility of these reactions been investigated.

Although the skeletal features of the vinylogous imides seem well established, structural ambiguities exist. Unanswered questions include the position of equilibrium for possible tautomers as well as for geometrical isomers, and also the character of any chelation effects. Using 4-acetylamino-3-penten-2-one (IIa) as an example, the forms V–VII may be present



V VI VII

in tautomeric equilibrium as shown.[23] Both VI and VII may also exist as extended geometrical isomers where chelation is not possible.

It was felt that n.m.r. measurements would reveal the relative contributions of forms V–VII to the structure of vinylogous imides. No previous proton resonance studies of such compounds seem to have been attempted, although proton chemical shifts and coupling constants have been reported[7,24] recently for the closely related Schiff bases formed from amines and aliphatic β-diketones or α-hydroxymethylene ketones. Available evidence indicates that these Schiff bases exist predominately as vinylogous amides, the relative abundance of *cis* and *trans* geometrical isomers being determined by structural factors and solvent effects.

Experimental

Spectra.—Proton magnetic resonance (p.m.r.) spectra were obtained on the Varian A-60 high resolution n.m.r. spectrometer (precalibrated chart) at normal probe temperature (35 ± 3°). Chemical shift values are reported in p.p.m. downfield from tetramethylsilane as the internal zero of reference. Line positions are accurate to ±0.02 p.p.m., unless band width precluded such accuracy. Solution concentrations were approximately 2 *M*.

Preparation of Compounds.—The compounds shown in Table I were prepared according to directions in the literature. The following compounds were prepared for the first time in this work.

1-Methyl-Δ^8-octahydro-2,7-quinolinedione.[26]—To a stirred suspension of 10.00 g. (0.0606 mole) of powdered Δ^8-octahydro-2,7-quinolinedione, m.p. 237–240° (lit.[19] m.p. 225–233°), in 80 ml. of methanol and 22.0 ml. (29.2 g., 0.232 mole) of freshly distilled dimethyl sulfate, b.p. 73–75° (10 mm.), saturated methanolic potassium hydroxide was added dropwise at such a rate that the mixture refluxed mildly. When the reaction mixture remained basic for 5 min., it was cooled to 33° and the salt was removed by filtration. The methanol was distilled and the gummy product was dried on a steam bath under reduced pressure. This gum was extracted with 200 ml. of boiling ethyl acetate, leaving a residue of potassium sulfate. Distillation of the ester solvent gave a light yellow sirup which was distilled under reduced pressure. Upon cooling, the distillate solidified to give 8.26 g. (0.0461 mole, 76%) of 1-methyl-Δ^8-octahydro-2,7-quinolinedione, b.p. 165° (0.6 mm.), m.p. 88–90°. An analytical sample, m.p. 89.5–91.0°, was obtained upon sublimation of the initial product. The dione can be recrystallized readily from ethyl acetate–petroleum ether "B" (b.p. 60–68°).

TABLE I

Compd.	M.p., °C.	Ref.	Lit. m.p., °C.
4-Amino-3-penten-2-one	39–41	*a*	43
4-Amino-3-methyl-3-penten-2-one	109–110	*a*	105
3-Amino-1-phenyl-2-buten-1-one	141–143	*b*	143
4-Chloroacetylamino-3-penten-2-one	71.5–72.0	*c*	71
4-Benzoylamino-3-penten-2-one	81.0–82.5	*d*	82
3-Acetylamino-1-phenyl-2-buten-1-one	96.5–97.4	*e*	101
3-Benzoylamino-1-phenyl-2-buten-1-one	110–111	*e*	114
Δ^8-Octahydro-2,7-quinolinedione	237–240	*f*	225–233
4α-Phenyl-Δ^8-octahydro-2,7-quinolinedione	235–238	*f*	237–239
1-Methyl-4α-phenyl-Δ^8-octahydro-2,7-quinolinedione	171–172	*f*	169–170
3,3-Diethyl-2,4-dioxotetrahydropyridine[g]	90.5–91.8	*h*	98–99
1-Methyl-3,3-diethyl-2,4-dioxotetrahydropyridine	74.9–76.2	*i*	74–75

[a] Ref. 27. [b] E. Fischer and C. Bulow, *Ber.*, **18**, 2131 (1885). [c] Ref. 14a. [d] Ref. 14c. [e] Ref. 14b. [f] Ref. 19. [g] This compound was obtained as a generous gift from Hoffmann-La Roche, Inc , Skokie, Ill. [h] Ref. 20. [i] F. Hoffmann-La Roche and Co., German Patent 637,385 (1937); *Chem. Abstr.*, **31**, 817 (1937).

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.52; H, 7.26; N, 7.88.

4-Acetylamino-3-penten-2-one.—A solution of 15.94 g. (0.203 mole) of acetyl chloride (Eastman White Label P334) in 25 ml. of dry ether was added dropwise under a dry atmosphere to a stirred solution of 20.10 g. (0.203 mole) of 4-amino-3-penten-2-one, m.p. 39–41° (lit.[27] m.p. 43°), and 24.10 g. (0.305 mole) of pyridine (Mallinckrodt analytical reagent 7180) in 200 ml. of dry ether. The expected precipitate of pyridine hydrochloride appeared almost immediately. After stirring overnight, the reaction mixture was filtered to remove the precipitated salt; the ethereal solution was then washed with two 50-ml. portions of 10% hydrochloric acid, one 50-ml. portion of 10% sodium hydrogen carbonate, and finally with water. After being dried over sodium sulfate, the organic solution was fractionally distilled to yield 21.43 g. (0.152 mole, 74.9%) of crude 4-acetylamino-3-penten-2-one, b.p. 69–73° (4.0 mm.), which did not solidify completely at room temperature. Recrystallization of the crude product gave 19.89 g. (0.141 mole, 69.4%) of material, m.p. 41.0–44.0°. After an additional distillation under reduced pressure and several recrystallizations from cyclohexane, an analytical sample, m.p. 43.0–44.5°, was obtained.

Anal. Calcd. for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.29; H, 7.86; N. 10.01.

Essentially the same experimental procedure and molar ratio 2:2:3 of aminoalkenone–acyl chloride–pyridine was employed to prepare the three remaining compounds.

4-*p*-Chlorobenzoylamino-3-penten-2-one.—From 6.80 g. (0.687 mole) of 4-amino-3-penten-2-one,[27] m.p. 39–41°, and 11.90 g. (0.0680 mole) of *p*-chlorobenzoyl chloride (Eastman White Label 3332) there was obtained 12.95 g. (0.0545 mole, 80.2%) of 4-*p*-chlorobenzoylamino-3-penten-2-one, m.p. 82–83°. One recrystallization from methanol–water and two from cyclohexane gave the analytical sample, m.p. 83.0–83.8°.

Anal. Calcd. for $C_{12}H_{12}ClNO_2$: C, 60.64; H, 5.09; N, 5.89. Found: C, 60.47; H, 4.92; N, 5.94.

4-Acetylamino-3-methyl-3-penten-2-one.—The reaction of 10.00 g. (0.0885 mole) of 4-amino-3-methyl-3-penten-2-one, m.p. 109–110° (lit.[27] m.p. 105°), with 7.02 g. (0.0894 mole) of acetyl chloride (Eastman White Label P334) yielded 10.22 g. (0.0659 mole, 74.4%) of crude product, b.p. 124–126° (18 mm.). Upon recrystallization from cyclohexane, 8.99 g. (0.0579 mole, 65.5%) of

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(22) A. G. Anderson, Jr., and G. Berkelhammer, *J. Am. Chem. Soc.*, **80**, 992 (1958).

(23) A fourth tautomer involving enolization of the amide carbonyl of VI is unlikely: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 203.

(24) G. O. Dudek and G. P. Volpp, *J. Am. Chem. Soc.*, **85**, 2697 (1963), and preceding papers of the series.

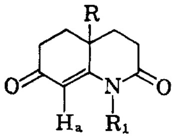
(25) Melting points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(26) D. L. Ostercamp, Ph.D. Thesis, University of Minnesota, 1959.

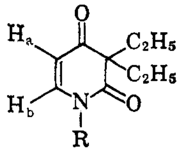
(27) A. Combes and C. Combes, *Bull. soc. chim. France*, [3] **7**, 778 (1892).

Table II

Proton Resonance Data for Cyclic Compounds[a]



R	R_1	Ring methylenes	H_a (J, c.p.s.)[b]	N-Methyl	NH	Aromatic protons
C_6H_5	H	2.20[c]	5.82		10.43	7.38
C_6H_5	CH_3	2.27[c]	5.83	3.32		7.31[d]
H[e]	H	2.10[c]	5.26 (1.8)		10.35	
H	CH_3	2.27[c]	5.53 (1.9)	3.17		



R	Methyl (J, c.p.s.)[b]	Methylene (J, c.p.s.)[b]	H_a (J, c.p.s.)[b]	H_b (J, c.p.s.)[b]	NH	N-Methyl
H	0.85 (7.5)[f]	1.98 (7.5)[g]	$5.64\left\{\begin{matrix}8.0\\1.3\end{matrix}\right\}^{g}$	$7.30\left\{\begin{matrix}8.0\\6.0\end{matrix}\right\}^{g}$	9.55	
CH_3	0.77 (7.8)[f]	1.94 (7.6)[g]	5.58 (8.3)	7.28 (8.1)		3.30

[a] In p.p.m. relative to tetramethylsilane; dissolved in $CDCl_3$, unless otherwise specified. [b] Coupling in c.p.s. [c] Broad with many peaks. [d] Multiplet. [e] Dissolved in CD_3SOCD_3. [f] Triplet. [g] Quartet.

4-acetylamino-3-methyl-3-penten-2-one, m.p. 46.0–47.5°, was obtained. An analytical sample, m.p. 46.5–47.8°, was obtained after distillation under reduced pressure and two subsequent recrystallizations from cyclohexane.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.93; H, 8.53; N, 8.87.

4-Benzoylamino-3-methyl-3-penten-2-one.—The reaction of 7.00 g. (0.0619 mole) of 4-amino-3-methyl-3-penten-2-one,[27] m.p. 109–110°, with 8.68 g. (0.0615 mole) of benzoyl chloride (Eastman White Label 293) yielded 10.75 g. (0.0495 mole, 80.5%) of the desired compound, m.p. 63.5–65.0°, when the crude product (not distilled) was recrystallized from methanol–water. After two recrystallizations from cyclohexane, two from methanol-water, and two from cyclohexane again, a sample, m.p. 64.2–64.9°, was submitted for analysis.

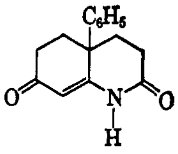
Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.10; H, 7.02; N, 6.41.

A suspension of 2.00 g. (0.00930 mole) of the compound in 8.00 g. of 6 *N* sulfuric acid was heated until solution was effected. When 10 ml. of water was added to the cooled solution, an off-white precipitate (0.71 g., m.p. 121–123°) formed and was filtered off. Powdered calcium carbonate was added to the mother liquor until the pH of the mixture was about 4. Precipitated calcium sulfate was removed by filtration, and the filtrate was extracted with ether. Evaporation of the solvent from the dried ether solution gave an additional amount (0.15 g., m.p. 126.5–128.5°) of white product. Melting points of mixtures with an authentic sample indicated that the product (0.86 g., 0.0071 mole, 76%) was benzamide.

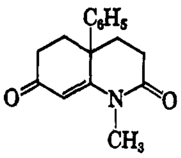
Results and Discussion

Cyclic Compounds.—Proton resonance data for the cyclic compounds examined in this work are listed in Table II. These compounds are of particular interest in that both geometrical isomerism and intramolecular hydrogen bonding (chelation) can be ruled out. The n.m.r. results, together with preliminary infrared and ultraviolet spectral measurements (*vide infra*), appear to be compatible with a single stable tautomer, the vinylogous imide.

The spectrum of 4α-phenyl-Δ⁸-octahydro-2,7-quinolinedione (IVa, R = C_6H_5; R_1 = H) in deuteriochloroform solution is shown in Figure 1. A highly unshielded proton at δ 10.43 (broad singlet) is provisionally assigned as the imido hydrogen.[28] Additional singlets are observed at δ 7.38 (C_6H_5) and 5.82 (—CO—N—C=CH—CO—), with a broad multiplet centered at δ 2.20 (ring CH_2 groups).[29] An impurity peak at δ 3.14 (singlet) is most likely due to water. N-methylation (VIII, R = C_6H_5; R_1 = CH_3) produces the expected changes in the n.m.r. spectrum. A new singlet appears at δ 3.32 (N–CH_3) with concomitant loss of the low-field NH signal. The vinylic proton (δ 5.83), alicyclic methylene protons (δ 2.27), and aromatic proton (δ 7.31) peaks persist, although the aromatic signal is now a fairly sharp multiplet.



IVa



VIII

It should be emphasized that *only the vinylogous imide structure* accounts satisfactorily for the observed chemical properties of 1-methyl-4α-phenyl-Δ⁸-octahydro-2,7-quinolinedione (VIII), *e.g.*, the reduction[30] to 1-methyl-4α-phenyldecahydroquinoline, and reaction[30] with phenylmagnesium bromide to give 1,4-diphenyl-3-oxo-4-(β-benzoylethyl)cyclohexene. Although tautomeric forms analogous to V, VI, and VII (see beginning) are possible for the parent compound IVa, the experimental evidence indicates that the vinylogous imide is also the most stable form here. Such a conclusion is dictated by (1) the chemical properties[19,30] of IVa, in particular ozonolysis[19] to give 3-phenyl-2,6-piperidinedione-3-propionic acid; (2) an n.m.r. spectrum closely related to that of VIII; and

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(28) This assignment is supported by the work of H. Hart and F. Freeman, [*J. Am. Chem. Soc.*, **85**, 1161 (1963); *J. Org. Chem.*, **28**, 2063 (1963)], who have measured the proton chemical shifts of simple imides such as phthalimide and succinimide, as well as substituted succinimides. The imido proton consistently appears as a singlet at δ 11.00 ± 0.20. A slight diamagnetic shift observed in the present work can be attributed to a decrease in the electron-withdrawing power of one of the carbonyls upon insertion of the vinylene link.

(29) Peak areas in all n.m.r. spectra agree closely with the expected number of protons.

(30) C. F. Koelsch and D. L. Ostercamp, *J. Org. Chem.*, **26**, 1104 (1961).

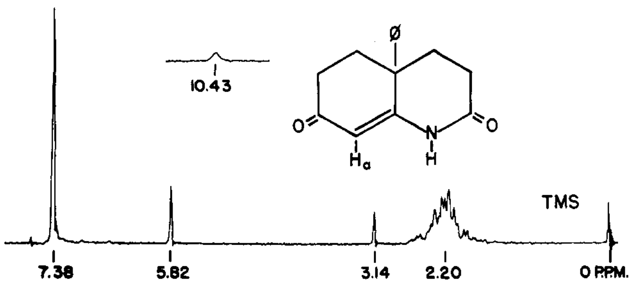


Figure 1.—The n.m.r. spectrum of 4α-phenyl-Δ^8-octahydro-2,7-quinolinedione in $CDCl_3$ at 60.00 Mc.

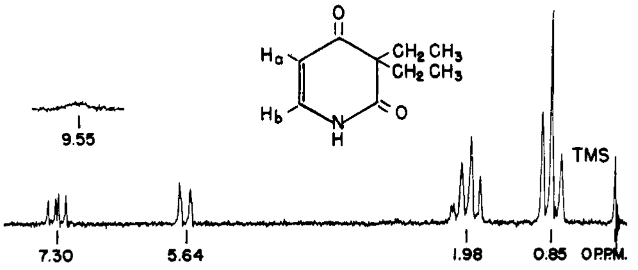


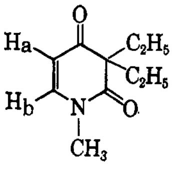
Figure 2.—The n.m.r. spectrum of 3,3-diethyl-2,4-dioxotetrahydropyridine in $CDCl_3$ at 60.00 Mc.

(3) comparison of the infrared and ultraviolet absorption spectra of IVa and VIII—IVa: $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 280 mμ (ϵ 27,300); $\nu_{\max}^{\text{Nujol}}$ 3140 (broad), 1696, 1622, 1602 (sh), 1586 cm.$^{-1}$; VIII: $\lambda_{\max}^{\text{CH}_3\text{OH}}$ 281 mμ (ϵ 27,200); $\nu_{\max}^{\text{CHCl}_3}$ 1690, 1650, 1581 cm.$^{-1}$.[31]

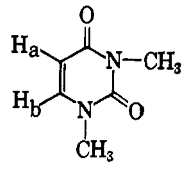
Analysis of the spectra of the unsubstituted Δ^8-octahydro-2,7-quinolinedione (IVd, R = H; R_1 = H) and its N-methyl derivative (R = H; R_1 = CH_3) indicates that the proposed structures are indeed correct. The highly unshielded imido proton of the parent compound (in hexadeuteriodimethyl sulfoxide solution) appears as a broad singlet at δ 10.35; as expected, the vinylic proton at δ 5.26 is split into a doublet by the allylic 4α-hydrogen, with the coupling constant of 1.8 c.p.s. comparing favorably with the literature[32] value of 0.5–2.0 c.p.s. for such systems; a broad multiplet centered at δ 2.10 can be attributed to nine alicyclic protons. Absorption peaks for the N-methyl compound are observed as follows: a singlet at δ 3.17 (N–CH_3), a doublet at 5.53 (vinylic proton) with J = 1.9 c.p.s., and a broad multiplet centered at 2.27 (ring protons).

An interesting example of spin–spin coupling between the imido hydrogen and the vinylic protons appears in the spectrum (see Figure 2) of the monocyclic compound 3,3-diethyl-2,4-dioxotetrahydropyridine. The ethyl groups are observed as the familiar set of two multiplet signals, one a triplet at δ 0.85 (CH_3) and the other a quartet at 1.98 (CH_2) with both J values = 7.5 c.p.s. A poorly resolved quartet at δ 5.64, by analogy with the preceding bicyclic compounds, is from H_a, with a *cis* double-bond hydrogen spin–spin coupling of 8.0 c.p.s. and a *trans* CH=C—NH– spin–spin coupling of 1.3 c.p.s.[33] A second quartet at δ 7.30 is due to the terminal vinylic (H_b) proton with $J_{H_aH_b}$ = 8.0 c.p.s. and a *cis* NH–CH spin–spin coupling of 6.0 c.p.s.[34] The broad NH signal is at δ 9.55.

Examination of the n.m.r. results for 1-methyl-3,3-diethyl-2,4-dioxotetrahydropyridine (IX, R = CH_3) reinforces the spin–spin coupling assignments made for the NH compound. The two vinylic proton signals now appear as distinct doublets at δ 5.58 (H_a, J = 8.3 c.p.s.) and 7.28 (H_b, J = 8.1 c.p.s.). Additional peaks include a singlet at δ 3.30 (N–CH_3), a quartet at δ 1.94 (CH_2, J = 7.6 c.p.s.), and a triplet at δ 0.77 (CH_3, J = 7.8 c.p.s.). A closely related compound, 1,3-dimethyluracil (X), possesses a spectrum[35] (in deuteriochloroform solution) comparable to IX. Doublets at δ 5.73 ($J \sim 8$ c.p.s.) and 7.20 ($J \sim 8$ c.p.s.) are from H_a and H_b, respectively.



IX



X

Acyclic Compounds.—Spectra of the three vinylogous amides which were parent compounds in the present work were measured for purposes of comparison; these results are recorded in Tables III and IV. One of the compounds, 4-amino-3-penten-2-one, has been studied previously,[36] and good agreement for methyl and vinylic proton chemical shifts exists. However, perplexingly broad NH resonance lines were observed in each of the three compounds examined by us, an effect which may be due primarily to ^{14}N-quadrupole relaxation.[37]

Although the questionable positions of the NH resonances for 4-amino-3-methyl-3-penten-2-one and 3-amino-1-phenyl-2-buten-1-one neither prove nor disprove the preponderance of a single geometrical isomer (a conclusion also indicated upon a rough evaluation of steric effects using Fisher–Taylor–Hirschfelder models), it is suggested that, analogous to 4-amino-3-penten-2-one, these compounds also exist in the six-membered chelate ring vinylogous amide tautomer. A paramagnetic shift of 0.71 p.p.m. observed for the vinylic proton in 3-amino-1-phenyl-2-buten-1-one compared to 4-amino-3-penten-2-one is attributable to long-range deshielding by the benzene ring.[38]

The spectrum of 4-chloroacetylamino-3-penten-2-one (IIb) in deuteriochloroform solution is shown in Figure 3, and the exact band positions are listed in Table III. Singlets at δ 2.17 and 2.38 are ascribed to the acetomethyl and allylic methyl (CH_{3b}) groups re-

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[31] The three major bands observed in the 1700–1580-cm.$^{-1}$ regions of the infrared spectra of both IVa and VIII show a regular increase in intensity as the absorption frequency decreases. Consistent similarities in the infrared and ultraviolet spectra have also been observed for other compounds described as vinylogous imides in this article; a detailed discussion of these results will constitute part II of this series.

[32] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, p. 85.

[33] This value for J is quite comparable to that observed with the analogous hydrocarbon system.[32]

[34] A *trans* NH–CH coupling constant of 12.8 c.p.s. has been observed for appropriate vinylogous amides.[24]

[35] N. S. Shacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, spectrum no. 460.

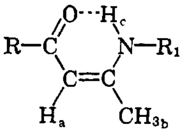
[36] G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1963).

[37] J. D. Roberts, "Nuclear Magnetic Resonance Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 80.

[38] See ref. 32, p. 115.

Table III

Proton Resonance Data for Acyclic Compounds[a]

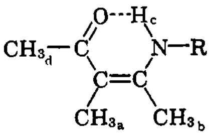


R	R_1	Methyls			Hydrogens			
		R	$R_1(CH_3CO-)$	b	a	c	R_1	Aromatic protons
CH_3	H	1.92		2.03	5.02	9.7[b]	5.9[b]	
C_6H_5	H			2.02	5.73	*c*	*c*	7.39, 7.88[d]
CH_3	CH_3CO	2.13	2.13	2.37	5.33	12.33		
CH_3	$ClCH_2CO$	2.17	4.10[e]	2.38	5.46	12.88		
CH_3	C_6H_5CO	2.15		2.50	5.43	13.38		7.48, 8.03[d]
CH_3	*p*-ClC_6H_4CO	2.21		2.53	5.48	13.48		7.49, 7.99[f]
C_6H_5	CH_3CO		2.23	2.52	6.05	12.85		7.43, 7.93[d]
C_6H_5	C_6H_5CO			2.68	6.17	13.83		7.52, 8.04[d]

[a] In p.p.m. relative to tetramethylsilane; dissolved in $CDCl_3$. [b] Very broad. [c] Ambiguous. [d] Multiplets. [e] For $ClCH_2$. [f] Doublets, $J = 8.6$ c.p.s.

Table IV

Proton Resonance Data for 4-Acylamino-3-methyl-3-penten-2-ones[a]



R	Solvent	Methyls				Hydrogens		
		a	b	d	$R(CH_3CO-)$	R	c	Aromatic protons
H[b]	$CDCl_3$	1.84	2.14	1.97		7.7[c]	?[d]	
CH_3CO	$CDCl_3$	1.94	2.43	2.27	2.13		12.96	
	CCl_4	1.92	2.37	2.20	2.06		12.86	
	Pyridine	1.75	2.38	2.20	2.05		12.97	
	C_6H_6	1.92	1.80	2.30	1.46		13.02	
C_6H_5CO	$CDCl_3$	1.75	2.52	2.23			13.87	7.45, 8.02[e]

[a] In p.p.m. relative to tetramethylsilane. [b] 4-Amino-3-methyl-3-penten-2-one. [c] Poorly defined. [d] Not observed. [e] Multiplets.

spectively; these assignments are consistent with chemical shifts recorded in Tables III and IV for other similar compounds. The methylene protons of the chloroacetyl group are observed at δ 4.10, a shift comparable to the experimental[39] value of δ 4.17 reported for $ClCH_2CON(R)_2$. Evidence that the compound exists in a six-membered chelate ring analogous to VI or VII is afforded by appearance of additional signals at δ 5.46, corresponding to the vinylic proton H_a (see Table II also), and at 12.88 (very broad), ascribable to the imido proton shifted ~2.5 p.p.m. downfield through intramolecular hydrogen bonding.

The remaining compounds in Table III and IV have the anticipated spectra. The presence of benzene rings in particular compounds is reflected in the small differences observed in band positions for a given proton or set of protons. Comparison of results for N-benzoyl and N-acetyl compounds indicates that paramagnetic shifts of ~1.0 p.p.m. for NH and 0.10–0.15 p.p.m. for allylic methyl (CH_{3b}) are due to long-range deshielding by the aromatic ring,[38] the vinylic proton H_a being essentially unaffected. Pronounced deshielding of H_a does occur in the 4-acylamino-1-phenyl-2-buten-1-ones (last two compounds in Table III), the phenyl group causing downfield shifts of 0.72 and 0.74 p.p.m.[40] in the N-acetyl and N-benzoy compounds, respectively.

Sensitivity of band positions to solvents of varying polarity and basicity was investigated for 4-acetylamino-3-methyl-3-penten-2-one (IIe) and the results are included in Table IV. Dilution studies were not attempted. Except for solvent shifts, the spectra resemble closely those of related compounds in Tables III and IV. Surprisingly the broad signal due to the highly unshielded (and presumably moderately acidic) imido proton, characteristic of the chelated ring tautomer, is essentially unshifted, even in the presence of the base, pyridine. Methyl assignments, made by analogy with the results in Table III, are tentative. If one accepts the peak assignments made in the other three solvents though, then the methyl shifts observed in benzene can be rationalized. Hydrogen bonding of an aromatic proton to the ketonic carbonyl would focus the aromatic diamagnetic ring current upon the terminal methyl CH_{3b} and the acetamido methyl, thus producing the observed shifts upfield of 0.57 and 0.60 p.p.m. (relative to CCl_4 solution), respectively.[41]

Definitive evidence for the location of the low-field proton in the above acyclic compounds is not provided

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[39] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 88.

[40] A paramagnetic shift of 0.72 p.p.m. for the vinylic proton in bis(benzoylacetone)ethylenediimine compared to bis(acetylacetone)ethylenediimine has been reported.[38]

[41] This explanation has been advanced previously to account for analogous shifts observed in bis(acetylacetone)ethylenediimine.[38]

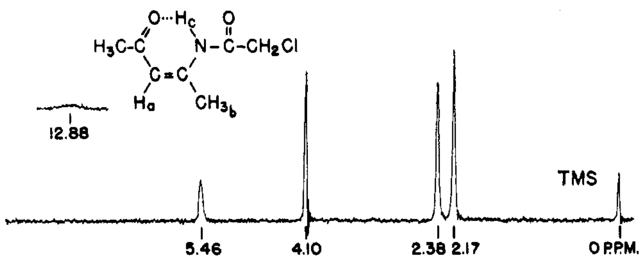
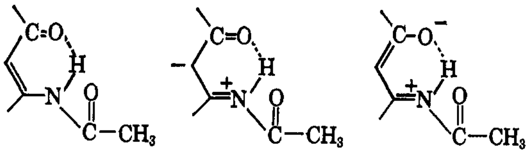


Figure 3.—The n.m.r. spectrum of 4-chloroacetylamino-3-penten-2-one in $CDCl_3$ at 60.00 Mc.

by the n.m.r. results.[42] Unfortunately, replacement (indirect) of the imido proton by a methyl group in the 4-acylamino-3-penten-2-ones for purposes of spectra comparison was not successful.[18] It has been noted[36] that the enolic proton in acetylacetone is shifted 0.9 p.p.m. downfield when benzene replaces carbon tetrachloride as the solvent. Thus the corresponding shift of only 0.16 p.p.m. observed for 4-acetylamino-3-methyl-3-penten-2-one (IIe) lends support to the vinylogous imide as the predominant tautomer for appropriate compounds in Tables III and IV. This conclusion is strongly reinforced by infrared and ultraviolet spectral measurements.[31] For example, the following absorption peaks observed for 4-acetylamino-3-penten-2-one (IIa) are quite comparable to those noted in the prior discussion of cyclic compounds—IIa: $\lambda_{\max}^{CH_3OH}$ 293 mμ (ϵ 17,000); $\nu_{\max}^{CCl_4}$ 1723, 1645, and 1597 cm.$^{-1}$ The absence of a distinct NH stretching band coupled with a normal ketone band at 1723 cm.$^{-1}$ in the infrared spectrum of IIa can only be interpreted satisfactorily on the basis of the chelated vinylogous imide structure.

From the above evidence, it is concluded that the introduction of an electron-withdrawing acyl group at the nitrogen atom of a vinylogous amide is not accompanied by a tautomeric shift; rather, a stable vinylogous imide results. This is in agreement with previous studies[36] which have shown simple vinylogous amides maintain their structural integrity with a variety of nitrogen substituents ranging from ethyl to β,β,β-trifluoroethyl. It seems likely from the infrared results that the presence of an additional carbonyl group decreases the contributions of such polar forms as the following structures to the resonance stabilization of the vinylogous imide.



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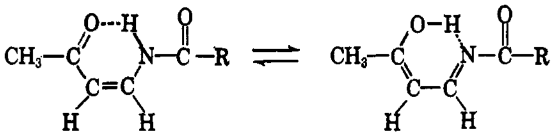
(42) Proton resonance data should suffice in the case of the 4-acylamino-3-buten-2-ones. Coupling between the NH and adjacent CH in the vinylogous imide should occur, with a *trans* NH–CH spin–spin coupling of ~13.0 c.p.s.[24] Such compounds will be studied.



Equilibrium and Kinetic Studies of the Meerwein–Ponndorf–Verley–Oppenauer (MPVO) Reaction[1]

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Equilibrium constants have been measured in toluene at 45° for the Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reduction of nine methyl ketones, $RCOCH_3$, with 9-fluorenol and aluminum *t*-butoxide. The equilibrium constants have been successfully correlated with substituent constants by the equation, $\log K = 0.456 + 1.13\sigma^* - 0.08156\#$, $R = 0.992$, $s = 0.082$. By the "swamping" technique, the reaction was found to be first order with respect to aluminum *t*-butoxide, 9-fluorenol, and $RCOCH_3$. Both the reaction between 9-fluorenol and aluminum *t*-butoxide and the hydride ion transfer are slow steps in the over-all reaction. Infrared spectra indicate the presence of a small amount of *t*-butyl alcohol in an equilibrated mixture of 9-fluorenol and aluminum *t*-butoxide. This supports the first step of the generally accepted mechanism.

Wilds[2] has reviewed the Meerwein-Ponndorf-Verley reduction of aldehydes and ketones and Djerassi[3] has reviewed the Oppenauer oxidation of primary and secondary alcohols. Each of these reactions is reversible and the mechanism is probably similar for both reactions.[3] The stoichiometry for either reaction is $RR'C{=}O + R''R'''CHOH \rightleftharpoons RR'CHOH + R''R'''C{=}O$, with an aluminum alkoxide as catalyst. If the primary interest is in the reduction of $RR'C{=}O$ to $RR'CHOH$, then this reaction is the Meerwein–Ponndorf–Verley reduction and is usually carried out with isopropyl alcohol as reducing agent and aluminum isopropoxide as catalyst. On the other hand, if the principal concern is in the oxidation of $R''R'''CHOH$ to $R''R'''C{=}O$, then the same reaction is referred to as the Oppenauer oxidation with, usually, acetone as oxidizing agent and aluminum *t*-butoxide as catalyst. Consequently, it may be more appropriate to refer to the over-all oxidation–reduction as the Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction.

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(1) Abstracted in part from the Ph.D. Dissertation of B. J. Yager, Texas A & M University, Aug. 1962.

(2) A. L. Wilds, *Org. Reactions*, **2**, 178 (1944).

(3) C. Djerassi, *ibid.*, **6**, 207 (1951).