

In a similar fashion, 1 was allowed to react to yield 9 (53%), mp 41–44°.

When the dried phosphonium salt 8 was heated in chloroform at 60° for 45 hr, no chloride 9 resulted.

**B. With 2-d.**—A solution of 2-d (1.14 g, 0.01 mol) and triphenylphosphine (2.88 g, 0.011 mol) in 6 ml of carbon tetrachloride was stirred in a dry atmosphere at 60–65° for 3.5 hr. The solvent was removed at 1 mm. By vpc analysis (column C, 100°), the distillate collected by slowly heating the residue to 180° (1 mm) contained a 13.3:86 ratio of 10-d to anti-9-d. Pure samples of anti-9-d and 10-d were collected by vpc (column C, 65°).

Similar reactions of 2 were conducted. Ratios of 10 to 9 varied from 3:97 for residue pyrolyzed at 160° (30 min) to 1.18: for pyrolysis at 60° (6 hr in carbon tetrachloride). The maximum yield for purified 9 and 10 in any run was 19% (30% crude).

**Isomerization Experiment of 10 and 9.**—A solution of 0.1 g of 9 and 10, 0.1 g of triphenylphosphine, and 0.1 g of triphenylphosphine oxide in 0.2 ml of chloroform was heated to 150° during 5 min. The ratios of 10 to 9 measured by vpc (column C, 100°) before and after heating were 1.0:3.0 and 1.0:3.1, respectively.

**Kinetically Followed Decomposition of 8.**—Crude 8 was prepared by stirring a solution of 1 (0.85 g, 7.6 mmol) and triphenylphosphine (2.15 g, 8.2 mmol) in 7 ml of carbon tetrachloride at 65° for 3.5 hr. Solvent was removed *in vacuo* and the residue

was twice shaken up in chloroform and precipitated with anhydrous ether. After being dried *in vacuo* over phosphorus pentoxide, 8 was dissolved in deuteriochloroform (1% TMS) and sealed in two nmr tubes. The tubes were heated at 120 ± 3° and the decomposition of 8 and appearance of 9 were monitored periodically by recording the nmr spectrum and integrating the signals of the 7 proton of 8 (4.82 ppm) and of 9 (3.94 ppm). Experimental plots of log [8] *vs.* time and log ([9]<sub>∞</sub> - [9]) *vs.* time were constructed. Both gave roughly straight-line slopes: for decomposition of 8,  $k \cong 7.7 \times 10^{-6} \text{ sec}^{-1}$ ; for formation of 9,  $k \cong 8.2 \times 10^{-6} \text{ sec}^{-1}$ .

**Registry No.**—Triphenylphosphine, 603-35-0; carbon tetrachloride, 56-23-5; anti-1-d, 23667-07-4; 2-d, 23667-08-5; 9, 765-80-0; anti-9-d, 23667-10-9; syn-9-d, 23754-34-9; 13, 13118-70-2.

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## Vinylogous Imides. II. Ultraviolet Spectra and the Application of Woodward's Rules<sup>1,2</sup>

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The ultraviolet spectra of a variety of  $\beta$ -amino  $\alpha,\beta$ -unsaturated carbonyl compounds and their N-alkyl and N-acyl derivatives were examined with due regard for chromophore stereochemistry. Included in this study were 37 vinylogous amides,  $-\text{NC}=\text{CC}(\text{O})-$ ; 26 vinylogous imides,  $-(\text{O})\text{CNC}=\text{CC}(\text{O})-$ ; 13 vinylogous urethans,  $-\text{NC}=\text{CCOOR}$ ; and 2 vinylogous ureas,  $-\text{NC}=\text{CC}(\text{O})\text{N}-$ . Analysis of the relative locations of the  $\pi \rightarrow \pi^*$  transitions gave substituent increments of +75  $\mu$  for *cis*- $\beta$ -amino, +65  $\mu$  for *trans*- $\beta$ -amino, +10  $\mu$  for  $\beta$ -N-alkyl, -10  $\mu$  for  $\beta$ -N-acetyl, and +6  $\mu$  for  $\beta$ -N-benzoyl. These substituent constants can be used to distinguish between *cis*- and *trans*-vinylogous imides, and also to reinforce stereochemical assignments for vinylogous amides and urethans based upon their molar extinction coefficients.

Empirical rules for correlating the structure of an  $\alpha,\beta$ -unsaturated ketone with the ultraviolet (uv) absorption maximum of its  $\pi \rightarrow \pi^*$  transition were first enunciated by Woodward<sup>4</sup> in 1941. Subsequently these rules were expanded to include the corresponding aldehydes,<sup>5</sup> acids, and esters,<sup>6</sup> and the effect of ring size on band positions for  $\alpha,\beta$ -unsaturated carbonyl compounds in general.<sup>7</sup> Considerable study has also been devoted to the bathochromic effects of various substituents. In 1959 Fieser and Fieser<sup>8</sup> modified slightly the solvent corrections initially applied by Woodward.<sup>4</sup> As spectral information accumulated, the results, including substituent shifts, have been published<sup>8,9</sup> periodically in tabular form to facilitate their application.

The availability of vinylogous amides,  $\beta$ -amino  $\alpha,\beta$ -unsaturated ketones,  $-\text{NC}=\text{CC}(\text{O})-$ , and imides,  $\beta$ -amido  $\alpha,\beta$ -unsaturated ketones,  $-(\text{O})\text{CN}=\text{CC}(\text{O})-$ , of known structure and stereochemistry from a previous project<sup>1</sup> prompted us to investigate their uv spectral properties. Although a substituent increment of +95  $\mu$  for a  $\beta$ -dialkylamino group ( $-\text{NR}_2$ ) of a vinylogous amide was reported<sup>10</sup> in 1946, the compounds included in this study were limited in both number and scope. In addition the relationship of stereochemistry to substituent shift has not been thoroughly investigated for this system. Planar structures I–IV<sup>11</sup> allow maximum resonance stabilization. In the case of form II intramolecular hydrogen bonding of  $-\text{NH}$  to carbonyl oxygen is also possible.

Examination of the literature revealed the existence of spectral data for related compounds such as vinylo-

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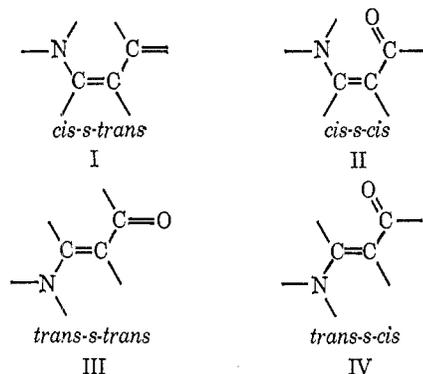
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(11) Stereochemical labels throughout this paper refer to the chromophoric system and not to any specific compound.



gous urethans,  $-\text{NC}=\text{CCOOR}$ ,<sup>10,12-13</sup> N-acyl derivatives,<sup>16</sup> and vinylogous ureas,  $-\text{NC}=\text{CC}(\text{O})\text{N}-$ ,<sup>15,19</sup> and the results are included in the present paper.

### Experimental Section<sup>20</sup>

**Materials.**—Acetyl chloride, benzoyl chloride, and pyridine were all freshly distilled (pyridine from BaO) under a dry atmosphere prior to use. Analytical reagent grade acetic anhydride was used without further purification.

**Spectra.**—Ultraviolet spectra were measured using a Cary Model 14 recording spectrophotometer (Spectrograde solvents) with cells of 1.00-cm path length. The wavelengths were good to  $\pm 1 \text{ m}\mu$ , the extinction to  $\pm 2\%$ . Nmr data were obtained on a Varian A-60 spectrometer with tetramethylsilane as the internal reference.

**Preparation of Compounds.**—The existence of suitable ultraviolet absorption data in the literature obviated the synthesis of many compounds. In addition, the preparation or source of a number of compounds utilized in the present work has been described previously by the author.<sup>1</sup> Samples of 4-methylamino-3-penten-2-one (18)<sup>21</sup> and 4-benzylamino-3-penten-2-one (19)<sup>22</sup> were readily obtained from the appropriate amine and 2,4-pentanedione.

**1-Acetyl-2-aminocyclohexene (1).**—A solution of 14.4 g (0.103 mol) of freshly distilled 2-acetylcyclohexanone, bp 104–106° (16 mm), in 100 ml of absolute methanol was saturated for 2.5 hr with ammonia. Development of a light yellow color was accompanied by slight warming of the solution as the reaction proceeded. After standing at room temperature for 2 hr, the solution was saturated for 2.5 hr again with ammonia. A third and a fourth treatment with ammonia (2 hr each time) on succeeding days resulted in complete conversion into 1 and 5 (tlc).<sup>20</sup> Subsequent removal of solvent gave a slightly wet, yellow solid, which was then dissolved in  $\text{CH}_2\text{Cl}_2$ . After the organic solution had been washed with 100 ml of 5% NaOH and then water, it was dried ( $\text{Na}_2\text{SO}_4$ ) and freed of solvent. The resulting yellow mixture of crystalline 1 and 5 (12.2 g, 85.1%), mp 63–93°, was recrystallized once from cyclohexane and then twice from methanol-water to yield 5.57 g (38.9%) of white 1, mp 99–104°. Removal of solvent from each mother liquor and subsequent chromatography of the individual solid residues gave an additional 2.34 g

(16.3%) of 1 (eluted first with ether), mp 103–104°, and 1.40 g (9.8%) of 5 (eluted with ethyl acetate), mp 112–114°.

Material isolated by chromatography was recrystallized twice from cyclohexane and then vacuum sublimed at 95° (1 mm) to afford an analytically pure sample of 1: mp 104.5–105.4°; nmr ( $\text{CDDl}_3$ )  $\delta$  7.3 (br s, 2,  $\text{NH}_2$ ), 2.38 (m, 4, 2  $\text{CH}_2=\text{C}$ ), 2.07 (s, 3,  $\text{CH}_3\text{CO}$ ), and 1.62 ppm (m, 4).

*Anal.* Calcd for  $\text{C}_8\text{H}_{13}\text{NO}$ : C, 69.03; H, 9.41; N, 10.06. Found: C, 69.13; H, 9.49; N, 10.27.

**2-(1-Aminoethylidene)cyclohexanone (5).**—This compound was a coproduct with 1. Two recrystallizations from cyclohexane followed by vacuum sublimation at 108° (0.5 mm) gave pure 5, mp 112.8–113.5°.

*Anal.* Calcd for  $\text{C}_8\text{H}_{13}\text{NO}$ : C, 69.03; H, 9.41; N, 10.06. Found: C, 69.11; H, 9.54; N, 10.27.

**2-(1-Acetylaminoethylidene)cyclohexanone (6).**—A suspension of 1.00 g (0.00718 mol) of 5 and 5.0 ml of acetic anhydride was heated to reflux under a dry atmosphere, with formation of a yellow color accompanying solution of starting material. After refluxing for 5 min, the solution was allowed to stand overnight. Alcoholysis of excess anhydride by adding 20 ml of methanol and refluxing the resulting solution for 15 min was followed by removal of solvent to give a light yellow, semicrystalline oil. Chromatography (ether) of the crude material yielded 1.10 g (84.5%) of a viscous, colorless oil which crystallized completely in the refrigerator. Two recrystallizations of the product from hexane in a cold room afforded an analytical sample of 6, mp 35–36°.

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{15}\text{NO}_2$ : C, 66.27; H, 8.34; N, 7.73. Found: C, 66.20; H, 8.56; N, 7.88.

**2-(1-Benzoylaminoethylidene)cyclohexanone (7).**—A solution of 1.00 g (0.00719 mol) of benzoyl chloride in 15 ml of dry ether was added dropwise under a dry atmosphere to a stirred suspension of 1.00 g (0.0718 mol) of 5 in 25 ml of dry ether and 0.790 g (0.0100 mol) of pyridine. The expected precipitate of pyridine hydrochloride appeared almost immediately. After stirring overnight, the reaction mixture was transferred to a separatory funnel and washed with two 25-ml portions of 5% HCl, one 25-ml portion of 5%  $\text{NaHCO}_3$ , and finally with water. The organic layer was separated, dried ( $\text{Na}_2\text{SO}_4$ ), and freed of solvent to yield 1.60 g of light yellow crystals. After chromatography (ether) of the crude product and subsequent recrystallization from hexane, there remained 1.46 g (83.5%) of white, crystalline product. Vacuum sublimation at 64° (0.5 mm) for 4 days yielded pure 7, mp 66.0–66.5°.

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_2$ : C, 74.04; H, 7.04; N, 5.76. Found: C, 73.79; H, 7.00; N, 5.86.

The syntheses of 2 and 3 essentially paralleled that of 7, except that larger amounts of reagents were used.

**1-Acetyl-2-acetylaminoethylidene (2).**—From 6.00 g (0.0432 mol) of 1 and 3.38 g (0.0432 mol) of acetyl chloride there resulted 5.90 g of light yellow, liquid product. Fractional distillation of this material under reduced pressure gave 4.55 g (58.3%) of 2, bp 116–118° (0.9 mm). A second distillation afforded an analytical sample of 2, bp 119–121° (1.2 mm).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{15}\text{NO}_2$ : C, 66.27; H, 8.34; N, 7.73. Found: C, 65.99; H, 8.19; N, 7.49.

**1-Acetyl-2-benzoylaminoethylidene (3).**—From 4.00 g (0.0287 mol) of 1 and 3.87 g (0.0276 mol) of benzoyl chloride there was obtained 5.28 g of light yellow, solid product. The crude product was recrystallized from methanol-water; a total of 4.47 g (64.1%) of light yellow 3, mp 73–76°, was obtained when all crops were combined. Chromatography (benzene) of this material removed most of the color, and subsequent vacuum sublimation at 75° (1.0 mm) for 5 days gave an analytical sample of essentially white 3, mp 76.5–77.0°.

*Anal.* Calcd for  $\text{C}_{15}\text{H}_{17}\text{NO}_2$ : C, 74.04; H, 7.04; N, 5.76. Found: C, 73.77; H, 6.91; N, 5.82.

**Ethyl 4-(1-Aminoethylidene)-5-oxohexanoate (21).**—The synthetic procedure outlined previously for compounds 1 and 5 was used to prepare 21 from 8.00 g (0.0400 mol) of ethyl 4-acetyl-5-oxohexanoate.<sup>23</sup> Recrystallization of the crude product (4.58 g) from cyclohexane-ethyl acetate yielded 3.43 g (43.2%) of off-white 21, mp 85–87°. Chromatography (ethyl acetate) of this material followed by one recrystallization from water-ethanol and two from cyclohexane-ethyl acetate produced white platelets. The analytical sample of 21 was then obtained by vacuum sublimation at 83° (0.5 mm): mp 87.0–88.0°; ir

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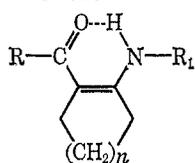
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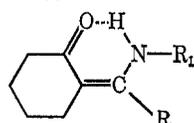
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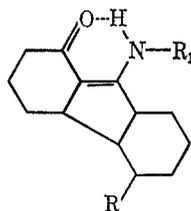
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TABLE I  
 ULTRAVIOLET ABSORPTION DATA FOR ISOCYCLIC AND ACYCLIC *cis-s-cis* COMPOUNDS


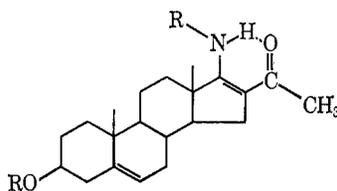
Compd	R	R <sub>1</sub>	n	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
					Calcd	Obsd			
1	CH <sub>3</sub>	H	2	M	312	317	-5	14,100	
2	CH <sub>3</sub>	CH <sub>3</sub> CO	2	M	302	303	-1	13,100	
3	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	2	M	318	321	-3	13,300	
						285 <sup>c</sup>		7630	
						239		11,000	
4	CH <sub>3</sub> O	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	1	95% A	307	297	10	15,800	d



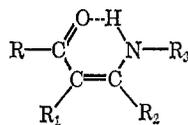
Compd	R	R <sub>1</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
				Calcd	Obsd			
5	CH <sub>3</sub>	H	M	317	320	-3	15,700	
6	CH <sub>3</sub>	CH <sub>3</sub> CO	M	307	313	-6	14,000	
7	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	M	323	331	-8	14,400	
					242		9900	
8	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	A	315	328	-13	26,200	e
9	H	C <sub>6</sub> H <sub>5</sub>	A		357		15,500	e
					295		2080	e
					235		5360	e



Compd	R	R <sub>1</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
				Calcd	Obsd			
10	O=	H	95% A	322	310	12	11,000	f
11	HO	H	95% A	322	320	2	13,200	f
12	O=	CH <sub>3</sub> CO	95% A	312	301	11	9400	f
13	CH <sub>3</sub> CO <sub>2</sub>	CH <sub>3</sub> CO	95% A	312	312	0	10,000	f



Compd	R	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
			Calcd	Obsd			
14	H	95% A	317	314	3	16,500	g
15	CH <sub>3</sub> CO	95% A	307	310	-3	12,600	g



Compd	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		ε	Ref
						Calcd	Obsd		
16	CH <sub>3</sub>	H	H	H	A	290	290	0	h
17	CH <sub>3</sub>	H	CH <sub>3</sub>	H	M	302	299	3	15,500
17	CH <sub>3</sub>	H	CH <sub>3</sub>	H	A		299		h
17	CH <sub>3</sub>	H	CH <sub>3</sub>	H	C		286		13,500
17	CH <sub>3</sub>	H	CH <sub>3</sub>	H	H		285		6120
18	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	M	312	309	3	18,100
18	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	C		302		15,400
19	CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	M	312	311	1	21,300

TABLE I  
(Continued)

Compd	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
						Calcd	Obsd			
19	CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	C		302		17,300	
20	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	M	312	316	-4	15,000	
21	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	H	M	312	313	-1	14,800	
22	C <sub>6</sub> H <sub>5</sub>	H	H	H	A	323 <sup>f</sup>	324	-1	19,000	k
							242		11,000	k
23	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	H	M	331 <sup>i</sup>	329	2	19,400	
							240		8670	
							328		19,700	m
							240		8,670	m
24	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>2</sub> CO	M	292	293	-1	17,000	
25	CH <sub>3</sub>	H	CH <sub>3</sub>	ClCH <sub>2</sub> CO	M	292	292	0	16,300	
25	CH <sub>3</sub>	H	CH <sub>3</sub>	ClCH <sub>2</sub> CO	C		290		16,500	
26	CH <sub>3</sub>	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	M	308	310	-2	15,900	
							286 <sup>c</sup>		10,200	
							239		11,000	
27	CH <sub>3</sub>	H	CH <sub>3</sub>	p-ClC <sub>6</sub> H <sub>4</sub> CO	M	308	311	-3	16,200	
							286 <sup>c</sup>		10,100	
							247		15,200	
28	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> CO	M	302	303	-1	12,400	
28	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> CO	C		307		14,800	
29	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	M	318	322	-4	13,000	
							285 <sup>c</sup>		5190	
							239		10,300	
29	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	E		322		14,200	
							285 <sup>c</sup>		5790	
							238		10,800	
29	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	C		232		14,000	
							286 <sup>c</sup>		5350	
							240		10,200	
30	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	CH <sub>2</sub> CO	M	321 <sup>i</sup>	318	3	22,200	
							260		6490	
31	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CO	M	337 <sup>i</sup>	332	5	23,200	
							249		12,600	
32	CH <sub>3</sub> O	H	H	c-C <sub>6</sub> H <sub>11</sub>	MC	281	281	0	19,000	n
33	C <sub>2</sub> H <sub>5</sub> O	H	CH <sub>3</sub>	H	95% A	282	275	7	18,200	o
34	C <sub>2</sub> H <sub>5</sub> O	H	CH <sub>3</sub>	-CH <sub>2</sub> - <sup>p</sup>	M	292	293	-1	32,100	q
							280		31,100	q
35	C <sub>2</sub> H <sub>5</sub> O	H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	95% A	292	287	5	~23,400	r
36	C <sub>2</sub> H <sub>5</sub> O	H	CH <sub>3</sub>	CH <sub>2</sub> CO	95% A	272	271	1	18,600	o

<sup>a</sup> A = ethanol, C = cyclohexane, E = ether, H = heptane, M = methanol, MC = methylene chloride. <sup>b</sup> Calculated - observed. <sup>c</sup> Shoulder. <sup>d</sup> See ref 12. <sup>e</sup> C. A. Grob and H. J. Wilkens, *Helv. Chim. Acta*, **50**, 725 (1967). <sup>f</sup> E. Wenkert, R. L. Johnson, and L. L. Smith, *J. Org. Chem.*, **32**, 3224 (1967). <sup>g</sup> J. Romo and A. Romo de Vivar, *J. Amer. Chem. Soc.*, **81**, 3446 (1959). <sup>h</sup> P. J. Brignel, U. Eisner, and P. G. Farrell, *J. Chem. Soc., B*, 1083 (1966). <sup>i</sup> N. H. Cromwell and W. R. Watson, *J. Org. Chem.*, **14**, 411, (1949). <sup>j</sup> Based upon a λ<sub>max</sub> of 248 mμ for the parent compound, phenyl vinyl ketone; see ref 10. <sup>k</sup> See ref 10. <sup>l</sup> Based upon a λ<sub>max</sub> of 256 mμ for the parent compound, 1-phenyl-2-buten-1-one: G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, **81**, 1660 (1959). <sup>m</sup> M. M. Robison, W. G. Pierson, L. Dorfman, B. F. Lambert, and R. A. Lucas, *J. Org. Chem.*, **31**, 3206 (1966). <sup>n</sup> See ref 18. <sup>o</sup> See ref 16. <sup>p</sup> Two identical chromophore units are connected by an ethylene bridge. <sup>q</sup> See ref 13. <sup>r</sup> See ref 17.

(CHCl<sub>3</sub>) 3480 (NH), 1715 (ester C=O), 1600 (C=O), and 1570 cm<sup>-1</sup> (C=C).

Anal. Calcd for C<sub>10</sub>H<sub>17</sub>NO<sub>3</sub>: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.46; H, 8.80; N, 7.15.

**5,5-Dimethyl-3-amino-2-cyclohexen-1-one (45).**—This compound was prepared from 5,5-dimethyl-1,3-cyclohexanedione and ammonia according to the procedure of Zymalkowski and Rimek.<sup>24</sup> Yields as high as 90% of pure 45 were obtained, mp 165–166.5° (lit.<sup>24</sup> mp 162–164°).

**5,5-Dimethyl-3-methylamino-2-cyclohexen-1-one (46).**—Substitution of methylamine for ammonia in the above synthesis resulted in an 88% yield of the colorless 46. A sample was recrystallized from acetonitrile for spectral purposes, mp 153–154.5 (lit.<sup>26</sup> mp 156°).

**3-Acetylamino-2-cyclohexen-1-one (49).**—A suspension of 2.50 g (0.0225 mol) of light yellow 3-amino-2-cyclohexen-1-one, mp 120–129° (lit.<sup>24</sup> mp 128–131°), in 15 ml of acetic anhydride

and 4 drops of pyridine was heated just to reflux under a dry atmosphere. When the resulting orange solution was allowed to stand at room temperature for 5 hr, 1.47 g of 49, mp 164–166°, was deposited. Concentration of the mother liquor followed by recrystallization of the solid residue from benzene-methanol afforded an additional 1.00 g of product, mp 162–165°. After the crude product (2.47 g, 71.7%) had been chromatographed (1:2 ethyl acetate-cyclohexane) and then recrystallized from acetonitrile, a sample of 49 was submitted for analysis: mp 166.5–167.5°; nmr (CDCl<sub>3</sub>) δ 8.7 (broad s, 1, NH), 6.82 (s, 1, CH=C), 2.37 (m, 6), and 2.16 ppm (s, 3, CH<sub>3</sub>CO).

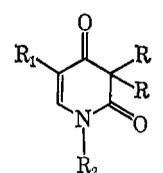
Anal. Calcd for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C, 62.73; H, 7.24; N, 9.15. Found: C, 63.00; H, 7.23; N, 9.21.

**5,5-Dimethyl-3-acetylamino-2-cyclohexen-1-one (50).**—A suspension of 12.93 g (0.0928 mol) of 45 in 60 ml of acetic anhydride and 2.0 ml of pyridine was heated slowly until starting material dissolved, and then refluxed under a dry atmosphere for 1 hr. A semicrystalline residue resulted when the reaction solution was concentrated. Use of acetone as a recrystallizing solvent gave 14.18 g (84.3%) of colorless 50, mp 153–157°, in two crops. Two additional recrystallizations from acetone provided white cubelets of 50: mp 156.3–157.8°; nmr (CDCl<sub>3</sub>) δ 9.15 (s, 1, NH),

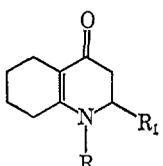
(24) F. Zymalkowski and H. Rimek, *Arch. Pharm. (Weinheim)*, **294**, 759 (1961); *Chem. Abstr.*, **57**, 7228h (1962).

(25) J. Goerdeler and U. Keuser, *Chem. Ber.*, **97**, 2209 (1964).

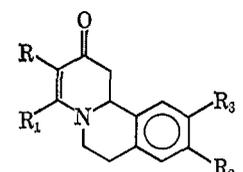
TABLE II  
 ULTRAVIOLET ABSORPTION DATA FOR HETEROCYCLIC *cis-s-trans* COMPOUNDS



Compd	R	R <sub>1</sub>	R <sub>2</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
					Calcd	Obsd			
37	C <sub>2</sub> H <sub>5</sub>	H	H	M	280	303	+23	8240	
38	C <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	M	290	313	-23	8190	
38	C <sub>2</sub> H <sub>5</sub>	H	CH <sub>3</sub>	C		303		7700	
39	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	M	300	(321) <sup>c</sup>	(-21) <sup>e</sup>		
				C		311		9300	d



Compd	R	R <sub>1</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
				Calcd	Obsd			
40	CH <sub>3</sub>	H	A	332	336	-4	14,350	e
41	-(CH <sub>2</sub> ) <sub>4</sub> -		A	332	336	-4	14,000	e



Compd	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
						Calcd	Obsd			
42	H	CH <sub>3</sub>	H	H	95% A	322	319	3	17,200	f
43	-(CH <sub>2</sub> ) <sub>4</sub> -		H	H	95% A	332	333	-1	14,300	f
43	-(CH <sub>2</sub> ) <sub>4</sub> -		H	H	A		336	-4	12,900	g
43	-(CH <sub>2</sub> ) <sub>4</sub> -		H	H	C		312		11,200	g
44	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> O	CH <sub>3</sub> O	95% A	332	335	-3	15,700	f

<sup>a</sup> See Table I, footnote a. <sup>b</sup> See Table I, footnote b. <sup>c</sup> Includes solvent shift measured for compound 38. <sup>d</sup> J. C. Martin, K. C. Brannock, and R. H. Meen, *J. Org. Chem.*, **31**, 2966 (1966). <sup>e</sup> A. I. Meyers, A. H. Reine, J. C. Sicar, K. B. Rao, S. Singh, W. Weidmann, and M. Fitzpatrick, *J. Heterocycl. Chem.*, **5**, 151 (1968). <sup>f</sup> M. von Strandtmann, M. P. Cohen, and J. Shavel, Jr., *J. Org. Chem.*, **31**, 797 (1966). <sup>g</sup> See W. Sobotka, W. N. Beverung, G. G. Munoz, J. C. Sicar, and A. I. Meyers, *ibid.*, **30**, 3667 (1965).

6.88 (s, 1, CH=C), 2.42 (s, 2, CH<sub>2</sub>C=C), 2.25 (s, 2, CH<sub>2</sub>CO), 2.17 (s, 3, CH<sub>3</sub>CO), and 1.10 ppm (s, 6).

*Anal.* Calcd for C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.25; N, 8.56; N, 7.96.

**5,5-Dimethyl-3-benzoylamino-2-cyclohexen-1-one (51).**—A stirred suspension of 4.00 g (0.0287 mol) of **45** in 125 ml of dry<sup>28</sup> 1,2-dimethoxyethane and 2.27 g (0.0287 mol) of pyridine was heated until solution was effected. Heating was discontinued and a solution of 4.03 g (0.0287 mol) of benzoyl chloride in 25 ml of dry<sup>28</sup> 1,2-dimethoxyethane was added dropwise. The addition of the acid chloride was accompanied by the formation of light brown oil droplets. After being stirred overnight at room temperature, the reaction mixture now consisted of a viscous deep red-brown lower layer and a much larger light orange upper layer. Because the lower layer contained no product (tlc)<sup>29</sup> and was essentially water soluble, it was discarded after decantation of the light orange solution. Removal of solvent from the upper layer gave an orange syrup which partially crystallized upon standing. Recrystallization of this material from ethyl acetate gave 1.19 g of yellow crystals, mp 142–146°. A satisfactory second crop could not be obtained; so the mother liquor was diluted with 40 ml of ethyl acetate prior to being washed with 60 ml of 5% HCl. An ethyl acetate (50 ml) extract of the acid wash was combined with the original solution. When the resulting solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and freed of solvent, 2.14 g of a yellow solid was

obtained. This material was reduced to a powder and then triturated with 5% NaHCO<sub>3</sub>. Recrystallization of the solid residue from acetonitrile gave an additional 0.86 g of yellow **51**, mp 146–148°, in several crops. Total yield of product was 2.05 g (29.4%). Chromatography (ethyl acetate) of the yellow product followed by vacuum sublimation at 145° (1 mm) for 2 days yielded colorless material. An analytical sample of **51** was prepared by recrystallization from ethyl acetate: mp 148.5–149°; nmr (CDCl<sub>3</sub>) δ 8.98 (s, 1, NH), 7.85 (m, 2), 7.46 (m, 3), 6.92 (s, 1, CH=C), 2.57 (s, 2, CH<sub>2</sub>C=C), 2.15 (s, 3, CH<sub>3</sub>CO), and 1.06 ppm (s, 6).

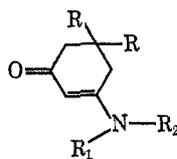
*Anal.* Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>2</sub>: C, 74.04; H, 7.04; N, 5.76. Found: C, 74.28; H, 7.14; N, 5.92.

## Results and Discussion

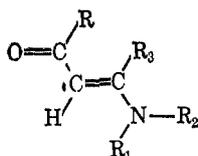
Spectral data, including a comparison of calculated and observed values for λ<sub>max</sub>, is included in Tables I–IV. Arrangement of the various compounds is governed by the stereochemistry of the conjugated system<sup>11</sup> and location of the nitrogen atom, although later discussion will focus on functionality.

Designation of the absorption bands as π → π\* transitions is supported both by the locations and intensities of the various maxima. The π-p conjugate interaction of the parent α,β-unsaturated carbonyl system with the β nitrogen's unshared electron pair

(26) The solvent was distilled directly from lithium aluminum hydride into the reaction vessel and dropping funnel.

TABLE III  
 ULTRAVIOLET ABSORPTION DATA FOR ISOCYCLIC AND ACYCLIC *trans-s-trans* COMPOUNDS


Compd	R	R <sub>1</sub>	R <sub>2</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
					Calcd	Obsd			
45	CH <sub>3</sub>	H	H	M	292	287	5	28,000	
45	CH <sub>3</sub>	H	H	E		270		23,400	
46	CH <sub>3</sub>	H	CH <sub>3</sub>	M	302	288	14	30,000	
47	CH <sub>3</sub>	H	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	A	302	293	9	32,000	<i>c</i>
48	CH <sub>3</sub>	CH <sub>3</sub>	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	A	312	303	9	32,500	<i>c</i>
49	H	H	CH <sub>3</sub> CO	M	282	278	4	19,300	
50	CH <sub>3</sub>	H	CH <sub>3</sub> CO	M	282	280	2	18,400	
51	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub> CO	M	298	291	7	21,200	
						233		8140	
51	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub> CO	E		279		19,500	
						231		9440	



Compd	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Solvent <sup>a</sup>	λ <sub>max</sub> , mμ		Δλ <sub>max</sub> <sup>b</sup>	ε	Ref
						Calcd	Obsd			
52	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	A	300	307	-7	28,000	<i>d</i>
53	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	-(CH <sub>2</sub> ) <sub>5</sub> -		H	A	300	308	-8	28,000	<i>e</i>
54	CH <sub>3</sub>	-(CH <sub>2</sub> ) <sub>4</sub> -		CH <sub>3</sub>	A	312	312	0	32,000	<i>c</i>
55	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	HOCH <sub>2</sub> CH <sub>2</sub>	H	A	333 <sup>f</sup>	344	-11	23,300	<i>g</i>
							243		11,300	<i>g</i>
56	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	A	333 <sup>f</sup>	343	-10	26,000	<i>d</i>
							243		12,000	<i>d</i>
57	CH <sub>3</sub> O	H	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	H	MC	271	270	1	23,400	<i>h</i>
58	CH <sub>3</sub> O	-(CH <sub>2</sub> ) <sub>4</sub> -		H	A	282	283	-1	30,200	<i>h</i>
							228		1990	<i>h</i>
59	CH <sub>3</sub> O	-(CH <sub>2</sub> ) <sub>5</sub> -		H	A	282	282	0	32,200	<i>h</i>
59	CH <sub>3</sub> O	-(CH <sub>2</sub> ) <sub>5</sub> -			E		273		26,500	<i>i</i>
60	CH <sub>3</sub> O	(CH <sub>3</sub> ) <sub>2</sub> CH	(CH <sub>3</sub> ) <sub>2</sub> CH	H	A	282	283	-1	30,200	<i>h</i>
61	C <sub>2</sub> H <sub>5</sub> O	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	95% A	282	276	6	≈28,800	<i>j</i>
62	C <sub>2</sub> H <sub>5</sub> O	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	A	292	288	4	31,000	<i>d</i>
63	C <sub>2</sub> H <sub>5</sub> O	H	CH <sub>3</sub> CO	CH <sub>3</sub>	95% A	262	265	-3	18,600	<i>k</i>

<sup>a</sup> See Table I, footnote *a*. <sup>b</sup> See Table I, footnote *b*. <sup>c</sup> G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **30**, 1407 (1965). <sup>d</sup> See ref 10. <sup>e</sup> K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946). <sup>f</sup> See footnote *j*, Table I. <sup>g</sup> G. N. Walker, *J. Org. Chem.*, **27**, 4227 (1962). <sup>h</sup> See ref 18. <sup>i</sup> E. Winterfeldt and H. Preuss, *Chem. Ber.*, **99**, 450 (1966). <sup>j</sup> See ref 17. <sup>k</sup> See ref 16.

would be expected<sup>9c,10,27</sup> to produce the bathochromic and hyperchromic effects which are observed. Measurement of solvent effects also provides additional confirmatory evidence, although considerable variation in the relationship between absorption maxima and solvent polarity exists in the present work. A solvent correction, relative to ethanol or methanol, of +11 mμ has been proposed<sup>8</sup> for the π → π\* bands of α,β-unsaturated ketones in hexane solution. This compares with extreme values in cyclohexane of +24 mμ for the *cis-s-trans*-vinyllogous amide, 1,2,3,4,7,11b-hexahydro-6H-dibenzo[*a,f*]quinolizin-13(12H)-one (43),<sup>28</sup> and -4 mμ for the chelated *cis-s-cis* vinyllogous imide, 4-acetylamino-3-methyl-3-penten-2-one (28). Comments on this apparent discrepancy will be postponed until specific compound categories are examined.

Many of the compounds chosen as examples for the present study exist as stable stereoisomers, owing to

partial or complete incorporation of the conjugated system into a cyclic ring. In the case of acyclic representatives, stereochemical classification was based largely on nmr and infrared studies in chloroform and/or less polar solvents.<sup>29</sup> However, solvent-dependent interconversions of *cis* and *trans* isomers<sup>11</sup> have recently been observed for acyclic vinyllogous amides [-NHC=CC(O)-]<sup>30,31</sup> and vinyllogous urethans (-NHC=CCO-OR)<sup>16,17,30-33</sup> derived from primary amines. Relative isomer stability in solution would depend upon several factors, including steric effects, intramolecular or intermolecular hydrogen bonding of solute molecules, and solute-solvent interactions. Unless there is sufficient steric resistance to formation of the six-membered chelate ring, the intramolecularly hydrogen-bonded

(29) For details, see the appropriate references for specific compounds.

(30) G. O. Dudek and G. P. Volpp, *J. Amer. Chem. Soc.*, **85**, 2897 (1963).

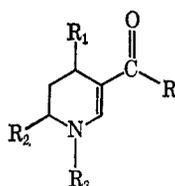
(31) C. H. McMullen and C. J. M. Stirling, *J. Chem. Soc., B*, 1217 (1966).

(32) K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, **99**, 2546 (1966).

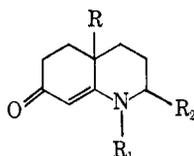
(33) W. E. Truce and D. G. Brady, *J. Org. Chem.*, **31**, 3543 (1966).

(27) W. R. Benson and A. E. Pohland, *J. Org. Chem.*, **29**, 385 (1964).

(28) See Table II., footnote *g*.

TABLE IV  
 ULTRAVIOLET ABSORPTION DATA FOR HETEROCYCLIC *trans-s-trans* COMPOUNDS


Compd	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Solvent <sup>a</sup>	$\lambda_{\max}$ , m $\mu$		$\Delta\lambda_{\max}^b$	$\epsilon$	Ref
						Calcd	Obsd			
64	CH <sub>3</sub>	H	H	H	A	300	301	-1	21,150	c
65	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub>	H	H	H	95% A	300	302	-2	26,000	d
66	CH <sub>3</sub>	H	H	CH <sub>3</sub>	A	310	315	-5	31,300	e
67	CH <sub>3</sub>	H	H	HOCH <sub>2</sub> CH <sub>2</sub>	A	310	311	-1	29,000	e
68	CH <sub>3</sub>	N≡C	H	CH <sub>3</sub>	A	310	298	12	30,000	f
69	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	H	M	333 <sup>g</sup>	305	28	24,000	h
							227		10,400	h
70	CH <sub>3</sub>	H	O=	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	A	290	294	-4	16,600	i
71	C <sub>2</sub> H <sub>5</sub> O	H	H	H	95% A	282	286	-4	21,000	d
72	CH <sub>3</sub> O	H	H	CH <sub>3</sub>	A	292	295	-3	23,600	f
73	NH <sub>2</sub>	H	H	H	95% A	282	287	-5	19,500	d
74	NH <sub>2</sub>	H	H	CH <sub>3</sub>	A	292	297	-5	27,600	e
75 <sup>i</sup>	NH <sub>2</sub>	H	H	CH <sub>3</sub> CO	M	272	271	1	19,400	



Compd	R	R <sub>1</sub>	R <sub>2</sub>	Solvent <sup>a</sup>	$\lambda_{\max}$ , m $\mu$		$\Delta\lambda_{\max}^b$	$\epsilon$	Ref
					Calcd	Obsd			
76	H	H	H	A	302 <sup>k</sup>	298	4	30,800	l
77	H	C <sub>2</sub> H <sub>5</sub>	H	A	312 <sup>k</sup>	304	8	31,600	l
78	H	H	O=	M	282 <sup>k</sup>	278	4	30,200	
79	H	CH <sub>3</sub>	O=	M	292 <sup>k</sup>	279	13	27,400	
79	H	CH <sub>3</sub>	O=	E		272		30,500	
79	H	CH <sub>3</sub>	O=	C		271		29,600	
80	C <sub>6</sub> H <sub>5</sub>	H	O=	M	282 <sup>k</sup>	280	2	27,300	
81	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	O=	M	292 <sup>k</sup>	281	11	27,200	

<sup>a</sup> See Table I, footnote a. <sup>b</sup> See Table I, footnote b. <sup>c</sup> M. Freifelder, *J. Org. Chem.*, **29**, 2895 (1964). <sup>d</sup> See ref 15. <sup>e</sup> See ref 19. <sup>f</sup> See ref 14. <sup>g</sup> See footnote j, Table I. <sup>h</sup> See R. E. Lyle and D. A. Nelson, *J. Org. Chem.*, **28**, 169 (1963). <sup>i</sup> A. G. Anderson, Jr., and G. Berkelhammer, *J. Amer. Chem. Soc.*, **80**, 992 (1958). <sup>j</sup> This compound was kindly supplied by Professor L. D. Quin of Duke University; see ref 15. <sup>k</sup> No allowance is made for the location of the carbon-carbon double bond. <sup>l</sup> See footnote e, Table I.

*cis-s-cis* structure II is distinctly,<sup>32,33</sup> and in many cases completely,<sup>17,30,34</sup> favored in dilute solution in nonpolar solvents such as C<sub>6</sub>H<sub>6</sub> and CCl<sub>4</sub>. Increase in solution concentration and/or use of polar solvents, particularly those which form strong hydrogen bonds, should enhance intermolecular bonding and so displace the equilibrium in favor of the extended *trans* isomer III or IV. This conclusion has been amply verified in the literature.<sup>17,30,31,35</sup>

The above statements regarding isomer stability can also be applied to other classes of acyclic compounds in this paper. Strengthening of the intramolecular hydrogen bond *via* N-acylation should enhance the relative stability of the *cis-s-cis* structure II, and our results for chelatable vinylogous imides, -(O)C<sub>N</sub>H<sub>C</sub>=

CC(O)-, support this prediction. Conversely, acyclic compounds derived from secondary amines (see Table III) can not undergo chelation, and here the *trans* isomer III or IV should be favored, unless opposing steric effects exist.

Assignment of substituent constants to  $\beta$ -amino,  $\beta$ -N-alkylamino, and  $\beta$ -N-acylamino groups of various  $\alpha,\beta$ -unsaturated carbonyl derivatives is a main objective of the present investigation. To facilitate understanding of Tables I-IV by the reader, these values are presented in Table V, along with essential ones from the literature. Their justification will become explicit as particular classes of compounds are now discussed.

**Vinylogous Amides.**—It is generally agreed that the absorption intensities of the  $\pi \rightarrow \pi^*$  transitions of *trans* isomers are greater than those for the *cis* isomers of a conjugated system.<sup>36</sup> Consistent agreement with this guideline exists for fixed *cis* compounds 1, 10, 11, 14, and 40-44, and fixed *trans* compounds 45-48, 64-69, 76, and 77. Molar extinction coefficients (in methanol or ethanol) range in value from 11,000 (10) to 17,200 (42) for *cis* isomers and from 21,150 (64) to 32,500 (48)

(34) G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 2099 (1961); **84**, 2692 (1962).

(35) For example, Schadt<sup>17</sup> found that in CCl<sub>4</sub> at 20° the *trans* isomer (61) of ethyl 3-benzylaminocrotonate completely isomerizes to the *cis* form (35) within 30 min. In ethanol at 20° an equilibrium ratio of the two isomers (35 to 61) of ca. 3 is attained in 70 hr. It should be noted that whenever comparisons are possible, *i.e.*, identical concentrations in the same solvent and analogous structures, the chelated *cis-s-cis* form II of a vinylogous amide is more stable relative to the *trans* form than is the case with the corresponding urethan and its weaker intramolecular hydrogen bond.<sup>30,31,34</sup>

(36) Reference 9d, p 20.

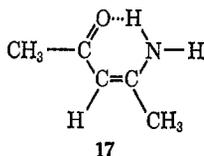
TABLE V  
CONSTANTS FOR CALCULATION OF ABSORPTION MAXIMA  
OF  $\alpha,\beta$ -UNSATURATED CARBONYL DERIVATIVES IN ETHANOL

Parent system <sup>a</sup>	Ketone, 215 m $\mu$	Ester, 197 m $\mu$
$\alpha$ -Alkyl <sup>a</sup>	+10	+10
$\beta$ -Alkyl <sup>a</sup>	+12	+10
Exocyclic double bond <sup>a</sup>	+5	+5
Endocyclic double bond <sup>a</sup> (five-membered ring)	+5	+5
<i>cis</i> - $\beta$ -Amino	+75	+75
<i>trans</i> - $\beta$ -Amino	+65	+65
$\beta$ -N-Alkyl <sup>b</sup>	+10	+10
$\beta$ -N-Acetyl <sup>b</sup>	-10	-10
$\beta$ -N-Benzoyl <sup>b</sup>	+6	...

<sup>a</sup> Literature values from ref 9c, pp 218, 219. <sup>b</sup> To be added to constants for *cis*- or *trans*- $\beta$ -amino.

for the *trans* forms. Extension of this criterion to acyclic examples provides confirmatory evidence for previous stereochemical assignments resulting from nmr and infrared studies,<sup>29</sup> and also substantiates provisional judgments based upon structural analogy.

An initial value of the substituent constant for the chelated *cis*- $\beta$ -amino group ( $-\text{NH}_2$ ) can be derived from the observed  $\lambda_{\text{max}}$  of 4-amino-3-penten-2-one (17) in methanol solution. Dudek and Holm<sup>34</sup> have deter-



mined the nmr spectrum of 17 in deuteriochloroform and were able to detect only the chelated *cis-s-cis*-structure. The relative stability of this form could only increase in very dilute cyclohexane solution. Therefore, the close correlation of the molar extinction coefficients<sup>37</sup> of 17 in methanol ( $\epsilon$  15,500) and cyclohexane ( $\epsilon$  13,500) indicates that no substantial change in stereochemistry has occurred in the polar, strongly hydrogen-bonding solvent methanol.<sup>38</sup> Subtraction of constant values of 215 and 12 m $\mu$  for parent enone and  $\beta$ -alkyl, respectively, from the observed  $\lambda_{\text{max}}$  of 299 m $\mu$  for 17 yields a provisional value of +72 m $\mu$  for the chelated *cis*- $\beta$ -amino group.

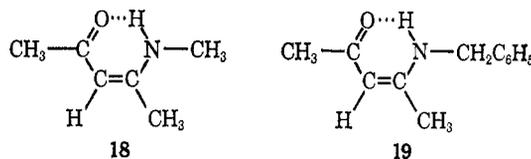
Compounds 5, 20, and 21 also possess the indicated stereochemistry in view of the close similarity in structure and absorption intensity between them and 17. Cross conjugation of a phenyl group with the vinylogous amide chromophore, as in 3-amino-1-phenyl-2-propen-1-one (22) and 3-amino-1-phenyl-2-buten-1-one (23), results in a hyperchromic effect of sufficient magnitude so as to blur the distinction between *cis* and *trans* isomers. Consequently, assignment of a chelated structure to 22 and 23 is not absolute.<sup>39</sup> N-Alkylation, as

(37) Although the position of  $\lambda_{\text{max}}$  for  $\pi \rightarrow \pi^*$  transitions is usually affected by solvent polarity, it is not accompanied by a marked change in absorption intensity.<sup>9c</sup>

(38) If significant isomerization of *cis*-17 to the *trans* form had taken place in methanol solution, one should observe an  $\epsilon_{\text{max}}$  much closer to the measured value of 28,000 for 5,5-dimethyl-3-amino-2-cyclohexen-1-one (46), a cyclic *trans-s-trans* compound which duplicates the skeletal features of 17. A more subtle change in stereochemistry to the nonchelated *cis-s-trans* conformer owing to substantial solvation of carbonyl and amino groups by methanol would result in an increase in nonbonded interactions, as exemplified in studies of 1-acetylcyclohexene and 2-methyl-1-acetylcyclohexene: R. L. Erskine and F. S. Waight, *J. Chem. Soc.*, 3425 (1960).

(39) Two isomers were isolated in the synthesis of 22, and the spectral values in Table I represent a compromise.<sup>10</sup>

in the cases of 8 and 19, is also accompanied by a hyperchromic effect, particularly when the alkyl group is benzyl.<sup>40</sup> However, both 19 and its N-methyl analog



18 yield nmr data<sup>34</sup> (deuteriochloroform as solvent) consistent only with the chelated form. Even in a solvent as polar as pyridine or acetone, 19 retains its stereochemical integrity.<sup>34</sup> Comparison of the observed  $\lambda_{\text{max}}$  values of 17 and 18 in methanol permits a direct calculation of the bathochromic effect of N-alkylation, *i.e.*, +10 m $\mu$ .

A final substituent constant of +75 m $\mu$  for the chelated *cis*- $\beta$ -amino group is obtained when calculated  $\lambda_{\text{max}}$  values are adjusted to agree within  $\pm 5$  m $\mu$  of the observed values for 12 of the 14 model compounds in Table I. The small differences for 22 and 23 are probably fortuitous in view of the large deviation between calculated and observed  $\lambda_{\text{max}}$  values for similar *trans* compounds 55 and 56 (*vide infra*). Significant deviations exist for compounds 8-10. Apparently, the conjugation extends to the aromatic ring in both 8 and 9. An explanation for the low band position observed for 10 is not readily apparent, since 10 is structurally quite similar to the "normal" compound 11.

Application of substituent constants calculated for chelated *cis* vinylogous amides to *cis-s-trans* compounds 40-44 (Table II) is quite successful. Evidently, the absence of intramolecular hydrogen bonding in these compounds does not result in the expected hypsochromic shift,<sup>41</sup> and the nomenclature in Table V reflects this observation.

As noted earlier in this section, molar extinction coefficients are relatively large for *trans* vinylogous amides, and an  $\epsilon_{\text{max}}$  of 30,000 or more is not unusual for the examples shown in Tables III and IV. For many of these compounds stereochemical mobility, particularly *s-cis*  $\rightleftharpoons$  *s-trans*, cannot be arbitrarily excluded. In most of the cases, however,  $\beta$  hydrogen is *cis* to the carbonyl group and the stable conformations of compounds 52, 53, and 64-67 are presumably *s-trans*, the arrangement generally favored with  $\alpha,\beta$ -unsaturated ketones.<sup>42</sup> The steric properties of the  $\beta$ -methyl group<sup>42</sup> in 54 and of the 1-phenyl group<sup>43</sup> in 55 and 56 would result in an *s-cis* conformation for these molecules if chromophore planarity is retained. Substitution at the 4 position of the ring in 68 and 69 produces a hypsochromic effect, which can be examined more fruitfully as substituent constants are now discussed.

The relatively close agreement between calculated and observed values for *cis* vinylogous amides unfortunately does not extend to the  $\lambda_{\text{max}}$  values of the *trans* isomers. An increment of +10 m $\mu$  is retained for a  $\beta$ -N-alkyl substituent, although its apparent batho-

(40) This may be due to homoconjugation of the aromatic ring with the vinylogous amide chromophore: E. Santos, J. Padilla, and P. Crabbé, *Can. J. Chem.*, **45**, 2275 (1967).

(41) L. K. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, p 528.

(42) Reference 9c, p 421.

(43) S. Searles, Jr., R. A. Sanchez, R. L. Soulen, and D. G. Kundiger, *J. Org. Chem.*, **32**, 2655 (1967).

chromic effect varies from +1 (46 vs. 45) to +14  $m\mu$  (66 vs. 64). Assignment of a substituent constant of +65  $m\mu$  to *trans*- $\beta$ -amino appears to give a reasonable correspondence both in the frequency and absolute magnitudes of positive and negative deviations from the calculated  $\lambda_{\max}$  values.

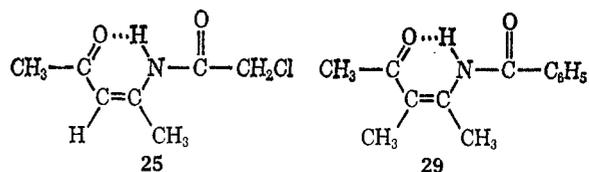
Inspection of Tables III and IV indicates that values of  $\Delta\lambda_{\max}$  are acceptable for those *trans* vinylogous amides where steric hindrance to conjugation is minimal, *i.e.*, for compounds 45, 64-67, and 76. In contrast,  $\Delta\lambda_{\max}$  for N,N-dialkyl compounds 48 and 52-56 varies from +9 (48) to -11  $m\mu$  (55). Qualitative examination of their molecular models does indicate that an increase in nonbonded interactions between an N-alkyl group and the *cis*  $\alpha$  hydrogen accompanies rehybridization of the nitrogen atom from  $sp^3$  to  $sp^2$ . However, the anticipated hypochromic effect owing to loss of chromophore planarity does not materialize. Because of the large variation observed in  $\Delta\lambda_{\max}$ , extreme caution must be exercised when assignment of a *trans* configuration to a vinylogous amide is based solely upon the location of the absorption band. The comparatively low-wavelength absorptions of both 3-acetyl-4-cyano-1-methyl-1,4,5,6-tetrahydropyridine (68)<sup>14</sup> and 3-benzoyl-4-phenyl-1,4,5,6-tetrahydropyridine (69)<sup>44</sup> are in accord with the studies of Hofmann, Kosower, and Wallenfels<sup>45</sup> concerning the "methyl effect" in the uv spectra of the 1,4-dihydropyridines.

The existence of a pronounced solvent effect for non-chelated *cis* and *trans* vinylogous amides has been noted in the literature,<sup>28</sup> and the large shift of -17  $m\mu$  relative to methanol in  $\lambda_{\max}$  for the *trans-s-trans* compound 45 in ether<sup>46</sup> is as expected. In contrast, the chelated *cis-s-cis* vinylogous amides 17-19 in cyclohexane show "normal"<sup>28</sup> shifts of -13, -7, and -9  $m\mu$ , respectively, again relative to methanol. Evidently, chelation provides important stabilization of the excited state in a nonpolar solvent.

Given the magnitude of substituent constants for the *cis*- $\beta$ -amino and *trans*- $\beta$ -amino groups, it would appear that the vinylogous amide chromophore can be successfully detected by the uv spectroscopy relative to alternative arrangements of the nitrogen atom and the two multiple bonds. Assignment of stereochemistry can then be made on the basis of the molar extinction coefficients in alcohol solution, if conjugation involving an aromatic ring is absent. For vinylogous amides lacking the benzoyl group and/or an N-benzyl substituent, values of  $\epsilon_{\max}$  range from 11,000 (10) to 18,100 (18) for *cis* and from 21,150 (64) to 32,500 (48) for *trans* isomers. Use of substituent constants to confirm these results would be possible for *cis* compounds, and, with care, for *trans* compounds as well.

**Vinylogous Imides.**—Previous arguments regarding the stereochemical integrity of vinylogous amides are also applicable in the present context. In the case of acyclic vinylogous imides the spectral consequences of solvent variation are of considerable importance. No significant dependence of either  $\lambda_{\max}$  or  $\epsilon_{\max}$  upon solvent polarity was observed for three model compounds, 4-chloroacetyl-amino-3-penten-2-one (25), 4-acetyl-amino-

3-methyl-3-penten-2-one (28), and 4-benzoylamino-3-methyl-3-penten-2-one (29). Evidently, the chelated



*cis* isomer enjoys unique stability in solution owing to strong intramolecular hydrogen bonding.<sup>47</sup> The absence of a solvent-induced shift in band position indicates that chelation also provides substantial stabilization of ground and excited states in a polar (methanol) as well as a nonpolar (cyclohexane) solvent.

The introduction of an electron-withdrawing acyl group at the nitrogen atom of a vinylogous amide should give a compound absorbing at shorter wavelength and with reduced intensity. However, no consistent pattern emerges when reduced intensity. However, no consistent pattern emerges when one examines the molar extinction coefficients of model vinylogous imides in Tables I-IV. A small hypochromic effect accompanies N-acylation in most cases, and *trans* isomers generally show higher absorption intensities than *cis* ones.

Comparison of observed  $\lambda_{\max}$  values demonstrates that N-acetylation of a vinylogous amide results in a hypsochromic shift in band position. Numerical values for this effect range from -4 (15 vs. 14) to -14  $m\mu$  (2 vs. 1). If previously calculated substituent constants for  $\beta$ -amino (*cis* or *trans*) and  $\beta$ -N-alkyl are retained and a substituent increment of -10  $m\mu$  is assigned to  $\beta$ -N-acetyl, then  $\Delta\lambda_{\max}$  for 11 model N-acetyl compounds exceeds  $\pm 4 m\mu$  in only two examples, chelated *cis-s-cis* compounds 6 and 12. However, comparison on an individual basis of 6 with 5 and of 12 with 10 yields constants of -7 and -9  $m\mu$  respectively, for  $\beta$ -N-acetyl.

Additional support is provided by spectral data for heterocyclic *trans-s-trans* vinylogous imides 70 and 78-81. Each of these compounds can be envisioned as resulting from the replacement of a methylene group (-CH<sub>2</sub>-) in the vinylogous amide by a carbonyl group (C=O). Based upon substituent constants of +10  $m\mu$  for  $\beta$ -N-alkyl and -10  $m\mu$  for  $\beta$ -N-acetyl, a hypsochromic shift of -20  $m\mu$  should manifest itself in the observed  $\lambda_{\max}$ . Experimentally, the results are as follows: 69 vs. 66, -21; 78 vs. 76, -20; 79 vs. 77, -25; 80 vs. 76, -18; 81 vs. 77, -23  $m\mu$ . Calculated values of  $\lambda_{\max}$  for the N-methyl compounds 79 and 81 are quite high, and presumably are due to steric interaction of the methyl group with the  $\alpha$  vinylic hydrogen, a phenomenon discussed earlier for related *trans* vinylogous amides.

Three heterocyclic *cis-s-cis* vinylogous imides, 37-39, were investigated, and the data contrast strongly with the results presented above. There appears to be a normal spectral response to alkyl substitution and solvent polarity. Explanation of the observed band intensities and positions requires additional information, and these compounds must be regarded as exceptional for the time being.

A moderate bathochromic shift in the observed  $\lambda_{\max}$ , ranging from +3 (31 vs. 23) to +11  $m\mu$  (26 vs. 17),

(44) See Table IV, footnote h.

(45) D. Hofmann, E. Kosower, and K. Wallenfels, *J. Amer. Chem. Soc.*, **83**, 3314 (1961).

(46) Compound 45 and related ones are essentially insoluble in cyclohexane.

(47) This conclusion is supported by nmr data.<sup>1</sup>

accompanies N-benzoylation and indicates that the aromatic ring is not completely insulated from the original vinylogous amide chromophore. The final substituent constant of  $+6 \text{ m}\mu$  for  $\beta$ -N-benzoyl is obtained in the manner outlined previously for  $\beta$ -N-acetyl.

Use of substituent increments to distinguish between *cis* or *trans* vinylogous imides appears quite feasible. For 15 out of the 18 *cis* compounds studied,  $\Delta\lambda_{\text{max}} \leq 0 \text{ m}\mu$ . Only one exception, compound 12, remains if the two examples with 1-phenyl substituents (30 and 31) are excluded. The relative insensitivity of the band position of a chelated *cis-s-cis* compound to solvent polarity further characterizes this isomer. A total of eight *trans-s-trans* compounds were examined, and the calculated  $\lambda_{\text{max}}$  exceeds the observed value for all compounds except 1-benzyl-5-acetyl-3,4-dihydro-2-pyridone (70). The (theoretical) assignment of a *cis* configuration to 70 would yield a  $\Delta\lambda_{\text{max}}$  of  $+6 \text{ m}\mu$ , clearly an unacceptable value. Comparison of the molar absorptivity of a new vinylogous imide with those of structural analogs in Tables I-IV would likely provide additional proof of configuration.

**Vinylogous Urethans.**—Although our primary goal was the investigation of vinylogous amides and imides, we were naturally interested in applying the results to other related systems. The preparation of a number of  $\beta$ -amino  $\alpha,\beta$ -unsaturated esters (vinylogous urethans), together with uv data, was recently reported by Huisgen, Herbig, Siegl, and Huber,<sup>18</sup> and the stereochemistry of these compounds was firmly established through nmr and infrared measurements. Inclusion of several isolated examples from the literature provided a total of five *cis* and eight *trans* model compounds.

It appears that stereochemical assignments can be given to vinylogous urethans on the same basis previously advanced for the corresponding amides. Omitting N-benzyl compounds 35 and 61, molar extinction coefficients vary from 15,800 (4) to 19,000 (32) for *cis-s-cis* structures and from 21,000 (71) to 32,500 (59) for *trans* compounds in polar solvents. An  $\epsilon_{\text{max}}$  of 32,100 for diethyl 3,3'-(ethyldiimino)dicrotonate (34) reflects the presence of two identical vinylogous urethan chromophore units in the same molecule.

Apparently, the newly obtained substituent constants for  $\beta$ -amino and  $\beta$ -N-alkyl can effectively supplement intensity measurements for *trans* vinylogous urethans.<sup>48</sup> Only in the case of ethyl 3-benzylaminocrotonate (61) does  $\Delta\lambda_{\text{max}}$  for *trans* isomer exceed the limits of  $\pm 4 \text{ m}\mu$ . Similar calculations for the *cis-s-cis* compounds

4 and 32-35, found in Table I, show no correspondingly useful trend.

Grob<sup>18</sup> reinvestigated the acetylation of ethyl 3-aminocrotonate and isolated both geometric isomers (36 and 63) of ethyl 3-acetylaminocrotonate, an N-acyl vinylogous urethan. Although their  $\epsilon_{\text{max}}$  values are identical, band positions are as expected for 36 and 63.

**Vinylogous Ureas.**—A parent value for the  $\pi \rightarrow \pi^*$  band position of an  $\alpha,\beta$ -unsaturated amide apparently has not been reported in the literature. The  $\lambda_{\text{max}}$  values calculated for 1,4,5,6-tetrahydropyridinamide (73)<sup>14</sup> and its N-methyl and N-acetyl derivatives 74<sup>19</sup> and 75,<sup>14</sup> respectively, are based upon a constant of 197  $\text{m}\mu$  for the related  $\alpha,\beta$ -unsaturated ester chromophore. Before the apparent consistency in  $\Delta\lambda_{\text{max}}$  found here can be confirmed, additional spectral data for other vinylogous ureas (and parent  $\alpha,\beta$ -unsaturated amides) is obviously needed.

**Registry No.**—1, 23645-69-4; 2, 23645-70-7; 3, 23674-49-9; 4, 10472-19-2; 5, 23652-78-0; 6, 23652-79-1; 7, 23652-80-4; 8, 23652-81-5; 9, 23652-82-6; 10, 13369-48-7; 11, 13369-51-2; 12, 13369-50-1; 13, 13369-52-3; 14, 5297-31-4; 15, 5088-57-3; 16, 2802-09-7; 17, 23652-84-8; 18, 23652-85-9; 19, 23652-86-0; 20, 23652-87-1; 21, 23652-88-2; 22, 23652-89-3; 23, 23652-90-6; 24, 23652-91-7; 25, 23754-49-6; 26, 23112-27-8; 27, 23112-29-0; 28, 23652-94-0; 29, 23652-95-1; 30, 23652-96-2; 31, 23652-52-0; 32, 7542-81-6; 33, 626-34-6; 34, 23652-55-3; 35, 21759-74-0; 36, 23652-56-4; 37, 77-04-3; 38, 1130-18-3; 39, 13382-19-9; 40, 1127-58-8; 41, 14099-74-2; 42, 5114-60-3; 43, 4155-70-8; 44, 5114-65-8; 45, 873-95-0; 46, 701-58-6; 47, 1500-76-1; 48, 23645-82-1; 49, 23674-56-8; 50, 23645-83-2; 51, 23674-57-9; 52, 23652-57-5; 53, 23652-58-6; 54, 23652-59-7; 55, 23652-60-0; 56, 23674-58-0; 57, 7542-80-5; 58, 7542-90-7; 59, 7542-91-8; 60, 5229-31-2; 61, 21731-13-5; 62, 21731-16-8; 63, 23652-67-7; 64, 7032-12-4; 65, 7032-09-9; 66, 14996-96-4; 67, 14996-94-2; 68, 3284-34-2; 69, 3335-03-3; 70, 23645-88-7; 71, 3335-05-5; 72, 3284-32-0; 73, 7032-11-3; 74, 14996-98-6; 75, 7032-13-5; 76, 1971-15-9; 77, 16236-60-5; 78, 1128-75-2; 79, 1130-77-4; 80, 1216-47-3; 81, 1149-82-2.

(48) Bowden, Braude, and Jones<sup>10</sup> have proposed a substituent increment of  $+81 \text{ m}\mu$  for a  $\beta$ -dialkylamino group ( $-\text{NR}_2$ ). Only one model compound of unknown configuration, ethyl 3-diethylaminocrotonate (62), was involved. Our assignment of a *trans* structure to 62 is based upon analogy to later work<sup>18</sup> and its relatively large molar absorptivity.