(twice). The ether layer was dried and evaporated and the residue distilled to give 1.4 g (83.3%) of compound **8**: bp (0.6 mm) 130–135 °C; NMR ($CDCl_3$) δ 1.70 (s, 3 H), 2.88 (s, 6 H), 3.65 (s, 3 H), 7.13–7.67 (m, 6 H); IR (film) 1721, 1634 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.39; H, 7.79; N, 11.89.

Dimethyl 2-(Dimethylaminomethyleneamino)-2-phenylpentanedioate (9). To a solution of 2.2 g (10 mmol) of amidino ester **2c** in 30 mL of anhydrous MeOH at room temperature under N_2, 300 mg (2.5 mmol) of potassium *tert*-butoxide was added. After 15 min 1.72 g (20 mmol) of methyl acrylate was added and the solution refluxed for 24 h. The solvent was removed in vacuo and the residue dissolved in ether, dried, and filtered through Celite. The oily residue crystallized from ether/hexane to give 2.69 g (87.9%) of compound **9**: mp 61–63 °C; bp (0.7 mm) 166–169 °C; NMR ($CDCl_3$) δ 2.19–2.45 (m, 4 H), 2.89 (s, 6 H), 3.59 (s, 3 H), 3.68 (s, 3 H), 7.19–7.60 (m, 6 H); IR (CH_2Cl_2) 1720, 1633 cm^{-1}.

Anal. Calcd for $C_{16}H_{22}N_2O_4$: C, 62.72; H, 7.24; N, 9.14. Found: C, 63.04; H, 7.38; N, 9.19.

Methyl 2-(Dimethylaminomethyleneamino)-2-methyl-3-phenylpropionate (10). To a solution of 27.5 mmol of LDA in 50 mL of dry THF at −70 °C under N_2 was added dropwise a solution of 5.85 g (25 mmol) of amidino ester **2d** in 50 mL of dry THF. The reaction mixture was warmed to 0 °C and 5.3 g (37.5 mmol) of methyl iodide added neat. After 1 h at room temperature, the reaction mixture was partitioned between ether and basic (NaOH) brine (twice). The ether layer was dried and evaporated. The residue was distilled to give 5.2 g (84%) of compound **10**: bp (0.2 mm) 130 °C; NMR ($CDCl_3$) δ 1.29 (s, 3 H), 2.81 (s, 6 H), 3.08 (s, 2 H), 3.67 (s, 3 H), 7.20 (s, 6 H); IR (film) 1721, 1638 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.66; H, 7.88; N, 11.17.

Methyl 2-Benzyl-2-(dimethylaminomethyleneamino)pentanoate (11). To a solution of 16.5 mmol of LDA in 30 mL of dry THF at −70 °C under N_2 was added a solution of 3.5 g (15 mmol) of amidino ester **2d** in 30 mL of THF. The reaction mixture was warmed to 0 °C and 3.83 g (22.5 mmol) of *n*-propyl iodide added neat. After 6 h at room temperature the reaction mixture was partitioned between ether and basic (NaOH) brine (twice). The ether layer was dried and evaporated and the residue distilled to give 3.32 g (80%) of compound **11**: bp (0.2 mm) 135–140 °C; NMR ($CDCl_3$) δ 0.70–1.95 (m, 7 H), 2.74 (s, 6 H), 3.01–3.11 (m, 2 H), 3.64 (s, 3 H), 6.98 (s, 1 H), 7.11 (s, 5 H); IR (film) 1723, 1638 cm^{-1}.

Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14. Found: C, 69.40; H, 8.62; N, 10.14.

α-Propylphenylalanine (13). A solution of amidino ester **11** (1.38 g, 5 mmol) in 10 mL of concentrated HCl was refluxed for 24 h. On cooling, the hydrochloride salt of **13** crystallized from the solution. Filtration afforded 1.1 g (90.2%), mp 235 °C dec.

Anal. Calcd for $C_{12}H_{17}NO_2$·HCl: C, 59.14; H, 7.44; N, 5.74. Found: C, 59.51; H, 7.67; N, 6.08.

2-Benzyl-2-(dimethylaminomethyleneamino)butyrolactone (12). To a solution of 24 mmol of LDA in 40 mL of dry THF at −70 °C under N_2 was added a solution of 5.04 g (21.6 mmol) of amidino ester **2d** in 20 mL of dry THF. After 1 h at −70 °C the solution was saturated with ethylene oxide, and the bath removed and stirred at room temperature. After 2 days the solvent was removed in vacuo. The residue was dissolved in ether, decolorized with charcoal, dried, and filtered through Celite. The filtrate was evaporated to give 4.18 g of **12** as an oil: NMR ($CDCl_3$) δ 2.03–2.17 (m, 2 H), 2.91 (s, 6 H), 2.96–3.02 (m, 2 H), 3.91–4.13 (m, 2 H), 7.09 (s, 5 H), 7.51 (s, 1 H). This oil was dissolved in acetone and treated with 1 equiv of cyclohexylsulfamic acid to give 5.42 g (60%) of **12**, cyclohexylsulfamate salt: mp 178–180 °C; IR (Nujol) 1768, 1705 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2O_2 \cdot C_6H_{13}NO_3S$: C, 56.46; H, 7.34; N, 9.88. Found: C, 56.31; H, 7.55; N, 9.89.

2-Amino-2-benzylbutyrolactone (14). A solution of 3.63 g (14.7 mmol) of **12** in 25 mL of *p*-dioxane and 25 mL of 5 N HCl was refluxed for 18 h. The reaction mixture was concentrated to one-half volume and extracted with ether (twice). The aqueous layer was further concentrated yielding 950 mg (28.5%) of compound **14** HCl: mp 251–254 °C dec; ir (Nujol) 2010, 1775 cm^{-1}; MS *m/e* 192 ($M^+ + 1$).

Anal. Calcd for $C_{11}H_{13}NO_2$·HCl: C, 58.02; H, 6.20; N, 6.15. Found: C, 58.01; H, 6.43; N, 6.02.

Acknowledgment. We wish to acknowledge the support and encouragement of Dr. Neville Finch, and the analytical work of Ms. Ruth Behnke (NMR), Mrs. Barbara Warren (MS), and Mr. George Robertson (analyses).

Registry No.—**1a,** 56-40-6; **1b,** 59-51-8; **1c,** 2835-06-5; **1d,** 150-30-1; **2a,** 62448-39-9; **2b,** 62448-40-2; **2c,** 62448-41-3; **2d,** 62448-42-4; **4,** 62448-43-5; **4** fumarate, 62448-44-6; **5** isomer a, 62460-38-2; **5** isomer b, 62448-45-7; **6,** 62448-46-8; **7,** 62448-47-9; **7** methanesulfonate, 62448-48-0; **8,** 62448-49-1; **9,** 62448-31-1; **10,** 62448-32-2; **11,** 62448-33-3; **12,** 62448-34-4; **12** cyclohexylsulfamate, 62448-35-5; **13,** 62448-36-6; **14,** 62448-37-7; **15,** 62448-38-8; dimethylformamide dimethyl acetal, 4637-24-5; cinnamyl bromide, 4392-24-9; fumaric acid, 110-17-8; dimethyl-*p*-chlorobenzalmalonate, 52927-44-3; ω-nitrostyrene, 102-96-5; α-*p*-dichlorotoluene, 104-83-6; methanesulfonic acid, 75-75-2; methyl iodide, 74-88-4; methyl acrylate, 96-33-3; *n*-propyl iodide, 107-08-4; ethylene oxide, 75-21-8.

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(11) Most of these compounds can be stored for weeks in a refrigerator or freezer without appreciable deterioration.
(12) The only previously reported α-formamidino esters derived from amino acid esters via treatment with the Vilsmeier reagent are covered by a patent: Japanese Patent 70 34 128; *Chem. Abstr.*, **74**, 54170b (1971).
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Electronic Structure and Nitrogen Hybridization in β-Aminovinylphosphonium Salts by Carbon-13 Nuclear Magnetic Resonance

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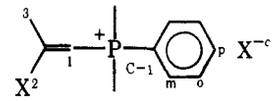
We have previously examined the ^{13}C NMR for a number of β-vinyl substituted phosphonium salts.[1] Current synthetic work in this laboratory has dealt with β-aminovinylphosphonium salts, and thus, a more detailed study of their spectra was undertaken. The following is a report on that study.

Compounds **2–7** were prepared by addition of the corresponding amine to 2-propynyltriphenylphosphonium bromide. The ^{13}C chemical shifts and ^{13}C–^{31}P nuclear couplings of these compounds are listed in Tables I and II, respectively, and their ^1H NMR spectra in Table III. Assignments of the carbons and the stereochemistry of the compounds were made by analogy with previous work.[1] In all cases, the *E* form (as shown) was indicated.

Table I. Carbon-13 Chemical Shifts of β-Substituted Vinylphosphonium Salts[a]



Compd	X	^{13}C chemical shift, ppm									
		1	2	3	4	5	6	C-1	o	m	p
2		80.7	175.8	22.2	28.6			120.3	133.2	130.5	134.7
3		54.3	164.1	17.5	51.5, 52.2	14.6		123.2	132.9	130.1	133.9
4		57.2	162.7	22.1	49.5	25.5, 24.9		123.4	132.9	130.1	133.8
5		59.3	163.7	22.3	48.5	25.5	23.5	123.3	132.9	130.2	134.0
6	$(H_3C)_2N-$	58.4	165.2	21.9	41.4			123.3	132.9	130.1	133.9
7	H_3C-N-	54.1	166.0	21.8	30.1			123.5	132.9	130.0	134.0
8[b]	H_3C-	102.4	172.0	24.8	29.9			119.4	133.2	130.6	134.8
9[b]	H_3C-H_2CO-	76.5	178.9	20.6	66.1	14.0		120.9	133.0	130.0	134.2

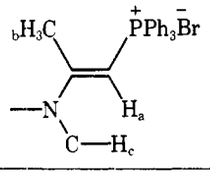
[a] The chemical shifts are referenced to internal Me_4Si. The numbering systems for the propenyl and triphenylphosphonium moieties are shown above Table I; the numbering for the substituent X is shown beside its corresponding number. All samples were run in $CDCl_3$. [b] Reference 1. [c] $X^- = Br^-$ for compounds 2–7 and 9; $X^- = Cl$ for 8.

Table II. $^{31}P-^{13}C$ Coupling Constants for β-Substituted Vinylphosphonium Salts[a]

Compd	$^1J(^{31}P-^{13}C)$, Hz							
	1	2	3	4	C-1	o	m	p
2	106	10.4	3.7		91.6	9.8	12.2	*
3	125.7	13.4	3.7		92.2	10.4	12.8	2.4
4	122.7	14.0	4.9		91.6	10.4	12.8	2.4
5	121.5	14.0	6.7		91.6	10.4	12.8	2.4
6	122.1	14.7	6.1		91.6	10.4	12.8	2.4
7	122.7	13.4	3.7	18.6	91.6	10.4	12.2	2.4
8	89.4	1.2	7.7		89.5	10.6	12.8	2.4
9	96.4	3.0	12.2		92.2	11.0	13.4	3.0

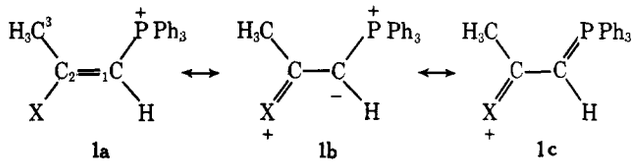
[a] The number system is identical with that used for Table I. The digital resolution was ±0.6 Hz. No coupling from phosphorus was observed beyond the carbons numbered. An asterisk indicates that the coupling was less than the resolution capable.

Table III. Proton Chemical Shifts of β-Substituted Vinylphosphonium Salts



Compd	^1H chemical shift, ppm		
	a	b	c
2	5.31	1.87	2.55
3	3.68	1.70	∿4.40
4	3.73	1.92	∿3.6
5	4.05	1.95	∿3.6
6	3.78	1.90	3.23
7	3.73	1.89	2.98

The preceding work[1] has provided support for the mesomeric structures **1a–c** (X = NHR, OEt, CH_3). Thus, for example, support for mesomer **1b** is seen by the high shielding of carbon 1 when X = NHR or OEt relative to X = CH_3.[1] Likewise, mesomer **1c** is supported by an increased $^1J(^{13}C-^{31}P)$ which may be attributed to a greater electron density on carbon 1.[1]



1a **1b** **1c**

A cursory examination of the present work provides additional support for these proposals. A closer examination, however, discloses an incongruity between the vinylaziridine **2** and the vinylamines **3–7**. In particular, carbon 1 of **2** is deshielded by 21.4–26.6 ppm from **3–7**, and the $^1J(^{13}C-^{31}P)$ is smaller in **2** by 16–20 Hz than that found for **3–7**. Indeed, the data for **2** are curiously closer to those of the vinyl ether **9** than to the other vinylamines.

This large deshielding of carbon 1 in **2** relative to **3–7** was also reflected in the ^1H NMR. Inspection of Table III shows that proton H_a is deshielded in **2** by 1.26–1.63 ppm from those found for **3–7**. Similar effects in NMR spectra of other systems have been reported.[2,4]

Presumably, the variations in carbon and proton chemical shifts and $^{13}C-^{31}P$ coupling in going from **2** to **3–7** arise from differential n–π interaction between the nitrogen lone pair and the olefinic double bond. Since the nitrogen inversion barrier is larger (due to angle strain) in the smaller polymethyleneimines, they are expected to exhibit planar nitrogens less readily[3] and, therefore, poorer π-donating lone pairs in conjugated systems.[8] In addition, calculations and spectroscopic data[5] have indicated that as the C–N–C angle of an amine decreases, the lone pair molecular orbital acquires more s character, becoming a poorer π donor. Similar angle strain arguments have been invoked by Truce and Gorbaty[2] to explain variations in the chemical shifts of β-vinyl protons in various *N*-vinylaziridines.

Assuming similar geometries (aside from ring size) for adducts **2–7**, from the above reasoning one would expect a smooth trend in chemical shifts and coupling. It is apparent from the data in Tables I, II, and III, however, that we are not dealing with a continuous function. A tempting interpretation is that a gross change in ground-state nitrogen geometry from

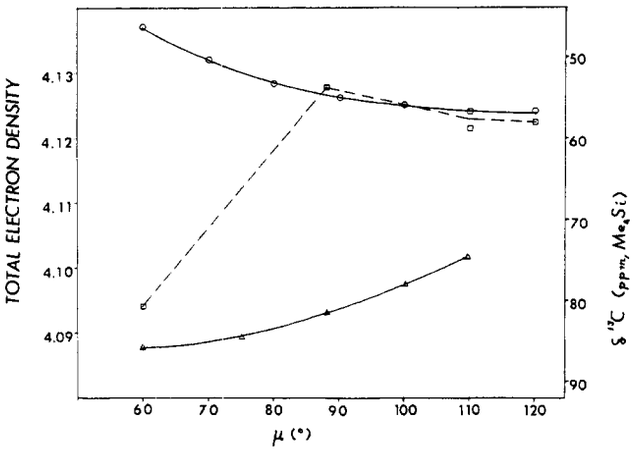


Figure 1. Variance of total electron density on the β carbon of vinylamine as a function of the HNH angle, μ, for ⊙ planar nitrogen, and △ pyramidal nitrogen. The dotted line shows the variance of ^{13}C chemical shift of carbon 1 in **2–6** as a function of μ.

pyramidal (sp^3) in **2** to essentially planar (sp^2) in **3–7** is being observed. Some support for this idea is provided by the work of Kamlet et al.[4] on *N*-(4-nitrophenyl)polymethylenimines. In that system, they found a pattern in the NMR for the ortho protons very similar to that mentioned in this paper, with supporting data from ultraviolet spectra and pK_a values.

In order to give further evidence for this notion, INDO SCF–MO calculations[7] were performed on a model system, vinylamine. Two functions were varied: (1) μ, the HNH angle, reflecting different ring sizes, and (2) θ, the angle between the HNH plane and the plane of the olefinic bond. Since ^{13}C chemical shifts are generally considered to correlate better with total electron density,[6] the latter vaues for the β carbon were plotted against μ for $\theta = 0$ (planar nitrogen) and $\theta = 54.7$ (~tetrahedral nitrogen). The two lines which resulted are shown in Figure 1. Also shown is a plot of the ^{13}C chemical shifts for **2–6** vs. μ (the dotted line).[9] From these data it is apparent that the deshielding of carbon 1 in **2** relative to **3–7** probably stems, in large part, from a pyramidal nitrogen. Deshielding of carbon 1 in **2** may also arise in part from angle strain rehybridization; however, the relative contribution of this effect is difficult to estimate from these calculations.

In conclusion, ^{13}C and ^1H spectra of the β-aminovinylphosphonium salts **3–7**, in conjunction with INDO SCF–MO calculations on vinylamine, seem to indicate structures with considerable enamine conjugation and essentially planar nitrogen atoms. Aziridine **2** appears to have considerably less enamine conjugation than **3–7** (albeit more conjugation than 8) and a pyramidal nitrogen. The nearly planar azetidine nitrogen, though observed previously in other systems,[4] is still quite surprising. The chemistry of these interesting compounds, in particular, derivatives of **2**, is presently under investigation and will be reported in a later publication.

Experimental Section

Carbon-13 spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{13}C data were taken at an operating frequency of 22.63 MHz. The ^{13}C chemical shifts are reported as referenced to Me_4Si. All samples were run in approximately 0.05 M solutions of $CDCl_3$ at 32 °C with broad band ^1H decoupling (except compound **2**, which was run at −5 °C). The proton spectra were obtained on either a Perkin-Elmer R-12 or Varian A-60A spectrometer and were referenced to Me_4Si. Concentrations used for the proton spectra were similar to those used for the ^{13}C spectra. The ^1H spectrum of compound **2** was taken at −10 °C; all others were taken at normal probe temperatures (~30–40 °C).

Acknowledgments. The authors would like to thank Stevan Evans for his help with the INDO SCF–MO calculations and David L. Dalrymple for taking the ^{13}C spectra.

Registry No.—**2,** 62460-44-0; **3,** 62460-45-1; **4,** 62460-46-2; **5,** 62460-47-3; **6,** 62460-48-4; **7,** 62460-49-5; 2-propynyltriphenylphosphonium bromide, 2091-46-5; aziridine, 151-56-4; azetidine, 503-29-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; dimethylamine, 124-40-3; methylamine, 74-89-5.

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An Improved Synthesis of Bicyclo[4.2.1]nonan-2-one

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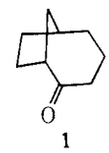
Our interest in the Favorskii rearrangement of bicyclic halo ketones[1] has prompted us to investigate the synthesis of bicyclo[4.2.1]nonan-2-one (**1**). Of the published routes to this



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bicyclic ketone,[2–6] the method of Kraus et al.[6] is the only simple one. This involves treatment of bicyclo[3.2.1]octan-2-one[7] (**2**) with isopropenyl acetate and *p*-toluenesulfonic acid (TsOH) (Scheme I) to give bicyclo[3.2.1]oct-2-en-2-yl acetate (**3**). Dichlorocarbene addition to **3** yields 3,3-dichloro-*exo*-tricyclo[4.2.1.$0^{2,4}$]non-2-yl acetate (**4**), which undergoes re-

Scheme I