the filter cake was washed with hexane. The solvent was removed *in vacuo*, yielding a liquid weighing 35.2 g. Vacuum distillation afforded 30.0 g of product ( $\sim 85\%$ ): bp 49–50° (0.3 mm); ir (CHCl<sub>3</sub>) 1805 (C=O) and 1608 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$  2.70 (m, 2 H, -CH<sub>2</sub>-), 4.10 (m, 2 H, bridgehead), 5.90 (m, 2 H, CH=CH).

Anal. Calcd for C<sub>7</sub>H<sub>6</sub>Cl<sub>2</sub>O: C, 47.47; H, 3.42; Cl, 40.06. Found: C, 47.33; H, 3.48; Cl, 40.16.

Bicyclo[3.2.0]hept-2-en-6-one (2).—To a vigorously stirred suspension of 11.0 g (0.169 g-atom) of zinc dust in 15 ml of glacial acetic acid at room temperature was added dropwise 5.00 g (0.028 mol) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one in 5 ml of glacial acetic acid. After addition was complete, the temperature was raised to and maintained at 70° for 40 min. Tlc analysis (pentane-I<sub>2</sub>) after 40 min indicated no starting material remaining. The reaction mixture was cooled and treated with ether, and the zinc residue was filtered. The ethereal layer was washed with a saturated solution of Na<sub>2</sub>CO<sub>3</sub> to remove the acetic acid and dried (MgSO<sub>4</sub>). The solvent was removed on a rotary evaporator at *ca*. 10° and the product (2.89 g, 95%, homogeneous by tlc) was isolated by distillation: bp 60° (~15 mm); ir (CHCl<sub>3</sub>) 1778 (C==O) and 1605 cm<sup>-1</sup> (C==C); nmr (CCl<sub>4</sub>)  $\delta$  2.4–2.9 (3 H, m), 3.0–3.6 (2 H, m), 3.6–4.0 (1 H, m), 5.80 (2 H, broad singlet).

Lactone of cis-2-Hydroxycyclopent-4-ene-1-acetic Acid (3).— To a solution of 3.24 g (30 mmol) of bicyclo[3.2.0]hept-2-en-6-one in 85 ml of 90% aqueous acetic acid cooled to 0° was added 8.15 g of 30% hydrogen peroxide in 70 ml of 90% aqueous acetic acid. The reaction was stirred at 0° for 24 hr (overnight). The product was extracted with ether and washed with 10% aqueous sodium sulfite and saturated sodium bicarbonate. The ether layer was dried over MgSO<sub>4</sub> and the solvent was removed *in vacuo*. Distillation afforded 3.35 g (90%) of lactone 3: bp 70–71° (0.2 mm); ir (CHCl<sub>8</sub>) 1760 (C=O) and 1605 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$ 2.0–3.0 (4 H, m), 3.45 (1 H, m), 5.05 (1 H, m), 5.65 (2 H, m); mass spectrum m/e 124.

Anal. Calcd for  $C_7H_8O_2$ : C, 67.73; H, 6.49. Found: C, 67.83; H, 6.40.

Reduction of 3 to Hemiacetal 4.-Diisobutylaluminum hydride (6.39 g, 45 mmol) was added dropwise with stirring to a solution of pure lactone 3 (3.72 g, 30 mmol) in 200 ml of dry toluene cooled to  $-78^{\circ}$ . The reaction mixture was stirred under nitrogen at  $-78^{\circ}$  for 2 hr. The reaction was quenched by the addition of methanol (1.0 ml until gas evolution ceased) and was warmed to room temperature. After it was stirred for an additional 15 min, the reaction mixture was diluted with 100 ml of ether and 100 ml of 50% brine solution. The resulting emulsion was destroyed by the addition of 100 ml of an aqueous solution containing 5 ml of concentrated hydrochloric acid. An additional 150 ml of ether organic extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent in vacuo afforded 3.68 g (99%) of a clear liquid, bp 44-45° (0.01 mm), which was homogeneous by tlc (methylene chloride-methanol, 19:1,  $R_f$  0.58): ir (CHCl<sub>3</sub>) 3598, 3395 (OH), and 1605 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$  1.50-2.20 (2 H, m), 2.40–2.70 (2 H, m), 3.30 (1 H, m), 4.50–4.95 (2 H, m), 5.25-5.65 (3 H, m); mass spectrum m/e 108 (M - 18).

Anal. Caled for  $C_7H_{10}O_2$ : C, 66.64; H, 7.99. Found: C, 66.75; H, 7.86.

2-(cis-2-Pentenyl)cyclopent-3-en-1-ol (5).—*n*-Propyltriphenylphosphonium bromide (17.71 g, 46 mmol), dried for 1 hr at 75° (0.2 mm), was dissolved in 90 ml of freshly distilled dimethyl sulfoxide (DMSO, distilled from CaH<sub>2</sub>). To this solution at room temperature under nitrogen was added sodium methylsulfinylmethide, which yielded a red-orange solution. The anion of DMSO was prepared as follows: 2.90 g (69 mmol) of 57% sodium hydride dispersion was washed with dry pentane to remove the mineral oil. Dry DMSO (50 ml) was added and the mixture was stirred at 75° for ca. 1.5 hr.

Pure hemiacetal 4 (2.90 g, 23 mmol) in dry DMSO (10 ml) was added after 5 min. The reaction was stirred at room temperature for 2.5 hr, at which time tle analysis (CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 99:1) indicated no starting material remaining. The reaction was quenched by the addition of ice water and the mixture was extracted with hexane. The organic layer was washed with saturated sodium chloride solution, dried (MgSO<sub>4</sub>), and evaporated to afford 3.35 g of crude product. Distillation of the product afforded 2.45 g (70%) of pure product, by 48° (0.01 mm), homogeneous by tle (CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 99:1,  $R_f$  0.60): ir (CHCl<sub>3</sub>) 3600, 3460 (OH), and 1605 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$  1.00 (3 H, t), 1.80–2.80 (8 H, m), 4.30 (1H, m), 5.30–5.70 (4 H, m); mass spectrum m/e 152, 135 (M – 18).

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O: C, 78.89; H, 10.60. Found: C, 79.02; H, 10.64.

2-(cis-2-Pentenyl)-2-cyclopentenone (7).—A solution of 200 mg (1.32 mmol) of alcohol 5 in 10 ml of acetone was cooled to 0° and was treated dropwise with 1 equiv of standard Jones reagent (~0.4 ml). After 5 min, 0.2 ml of isopropyl alcohol was added and the mixture was extracted with pentane. The organic layer was subsequently washed with 10% NaHCO<sub>3</sub> and water, dried (MgSO<sub>4</sub>), and evaporated *in vacuo* to afford 190 mg of crude  $\Delta^{8}$ -cyclopentenone 6, homogeneous by tlc (methylene chloride,  $R_{t}$  0.75): ir (CHCl<sub>3</sub>) 1749 cm<sup>-1</sup> (C=O); nmr (CCl<sub>4</sub>)  $\delta$  0.98 (3 H, t), 1.70–2.60 (5 H, m), 2.60–3.00 (2 H, m), 5.35 (2 H, m), 6.05 (2 H, broad singlet).

The crude ketone 6 was treated with 8.0 ml of aqueous 2% NaOH solution under nitrogen at  $\sim$ 70°. Isomerization to the more stable  $\alpha,\beta$ -unsaturated ketone 7 was essentially complete after *ca*. 1 hr. The mixture was cooled, extracted with pentane, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, affording 166 mg of dienone 7, bp 67-68° (0.05 mm), which was homogeneous by tlc (methylene chloride,  $R_i$  0.53): ir (CHCl<sub>8</sub>) 1690 (C=O) and 1630 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$  0.98 (3 H, t), 1.80-3.00 (8 H, m), 5.40 (2 H, m), 7.18 (1 H, broad singlet).

(C=0) and 1050 cm<sup>-1</sup> (C=0), min (CC14) 5 0.58 (3.11, t), 1.50<sup>-2</sup> 3.00 (8 H, m), 5.40 (2 H, m), 7.18 (1 H, broad singlet). *cis*-Jasmone (9).—To a solution of 140 mg (0.93 mmol) of ketone 7 in 3 ml of anhydrous ether cooled to 0° was added 1.2 ml (2.0 mmol) of 1.66 *M* methyllithium in ether. After 15 min at room temperature the mixture was quenched with cold water. The product was extracted with pentane, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated *in vacuo* to afford 149 mg of alcohol 8, ir (CHCl<sub>3</sub>) 3610, 3430 cm<sup>-1</sup>.

The crude carbinol was dissolved in 3 ml of ether, cooled to 0°, and treated dropwise with a solution of 100 mg of  $\text{CrO}_3$  in 1.0 ml of aqueous 5% H<sub>2</sub>SO<sub>4</sub>. Stirring was continued for an additional 15 min at 0°. The reaction was quenched by the addition of water and the mixture was extracted with pentane. The organic layer was washed with 10% NaHCO<sub>3</sub> and water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give 138 mg (84% yield) of crude *cis*-jasmone (9). A pure sample was obtained by preparative tlc on silica gel plates using methylene chloride-methanol (99:1): ir (CHCl<sub>3</sub>) 1685 (C=O) and 1640 cm<sup>-1</sup> (C=C); nmr (CCl<sub>4</sub>)  $\delta$  1.00 (3 H, t), 2.0 (3 H, s), 2.1-2.6 (6 H, m), 2.85 (2 H, d), 5.25 (2 H, m). Ir and nmr spectra and retention time on vpc were identical with those of an authentic<sup>6</sup> sample of *cis*-jasmone.

**Registry No.**—1, 5307-99-3; 2, 13173-09-6; 3, 34638-25-0; 4, 34638-26-1; 5, 34638-27-2; 6, 34638-28-3; 7, 34638-28-3; 9, 4907-07-7.

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# Ketenimines. II.<sup>1</sup> Lone-Pair Effects on Nuclear Magnetic Resonance Properties of the Cumulenic $\pi$ System

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Allene (1) can be considered the parent molecule for a number of heterocumulene analogs of which the nitro-

(1) See G. Krow, Angew. Chem., 83, 455 (1971); Angew. Chem., Int. Ed. Engl., 7, 435 (1971), for a review of ketenimine chemistry.

gen compounds carbodiimides 2 and ketenimines  $3^1$  are representative examples. Evidence obtained from spectral measurements is in agreement with a dissymmetric ground state configuration having orthogonal  $\pi$  systems for each of these cumulenes 1-3.<sup>2</sup> The

$$\begin{array}{cccc} H_2C = C = C H_2 & RN = C = NR & R_2C = C = NR \\ 1 & 2 & 3 \end{array}$$

structural similarities of 1-3, however, tend to overshadow the inherent difference in the electronic properties of the heterocumulenes 2 and 3 resulting from the presence on nitrogen of invertible unshared electron pairs. We here wish to report the importance of interaction of the nitrogen lone pair electrons with cumulene  $\pi$  electrons on determining shifts in the nmr spectra of ketenimines.

From comparison of chemical shift data for comparably substituted allenes (Table I) and ketenimines (Table II), a greater shielding effect as measured by  $\Delta \delta$ 

TABLE I Chemical Shift Values ( $\delta$ ) for Allenic Hydrogen AS A FUNCTION OF GEMINAL SUBSTITUENT X IN ALLENES (R = R' = ALKYL)

	ACH=C=CRR	
	4	
Compd	Substituent $X$	Chemical shift, $\delta^a$
4a	H	$4.4 - 5.0^{b-d}$
4b	Alkyl	$4.8 - 5.1^{c-f}$
4c	$\rm CHMeCH_2OH$	$5.1^{g}$
4d	$\operatorname{COMe}$	$5.7^{h}$
4e	Cl	$5.8^i$
4f	Ph	5.90

<sup>a</sup> Spectra were reported neat or in dilute CCl<sub>4</sub>. It was reported that there were no marked solvent effects on shifts<sup>d,i</sup> <sup>b</sup> D. Koster and A. J. Danti, J. Phys. Chem., **69**, 486 (1965). <sup>e</sup> R. Fantazier and M. Poutsma, J. Amer. Chem. Soc., 90, 5490 (1968). <sup>d</sup> R. Ferguson, J. Phys. Chem., **68**, 1594 (1964). <sup>e</sup> R. Kullnig and F. Nachod, *ibid.*, **67**, 1361 (1963). <sup>f</sup> S. Landor, A. Patel, P. Whiter, and P. Greaves, J. Chem. Soc. C, 1223 (1966). <sup>e</sup> R. Macomber, J. Org. Chem., **36**, 999 (1971). <sup>h</sup> M. Martin, C. Martin, and P. Greuffernel, J. Chem. Buy. **40**, 1085 (1968). G. Martin, and R. Couffignal, J. Chem. Phys., 49, 1985 (1968). <sup>i</sup> G. Reddy, L. Mandell, and J. Goldstein, J. Amer. Chem. Soc., 83, 4729 (1961).

#### TABLE II

## Chemical Shift Values ( $\delta$ ) for Allenic Hydrogen AS A FUNCTION OF GEMINAL SUBSTITUENT X IN KETENIMINES (R = ALKYL) XCH=C=NR 5

Compd	Substituent X	Chemical shift, $\delta$ (CDCl <sub>3</sub> )	$\Delta \delta$ , ppm <sup>a</sup>
5a	$\rm CH_2CMe_2Cl$	3.5	$1.62^{b,c}$
5b	Isopropyl <sup>d</sup>	4.06	0.75 - 1.05
5c	COMe	4.4	1.3'
5d	Ph	$4.8^{g}$	1.1
5e	Cl	5.05	0.75°

<sup>a</sup>  $\Delta \delta = \delta$ (allene)  $- \delta$ (ketenimine). Shifts are to higher field for ketenimines. <sup>b</sup> Compared to allene  $X = CHMeCH_2OH$ . <sup>c</sup> R. Lloyd, Ph.D. Thesis, Clemson University, 1968. <sup>d</sup> N-phenyl. <sup>e</sup> CCl<sub>4</sub>. <sup>f</sup> R. Woodward and D. Woodman, J. Amer. Chem. Soc., 89, 3169 (1966). " The chemical shift of the allenic hydrogen varied less than 0.1 ppm between determinations of neat liquid and dilute solutions of CDCl<sub>3</sub> and CCl<sub>4</sub>. Since marked solvent shifts were not observed for allenes,  $\Delta\delta$  does not measure bulk diamagnetic susceptibility.



Figure 1.—A p-orbital representation of interaction of the lone pair orbital and the adjacent  $\pi$ -bond.

(Table II) for the allenic hydrogen in ketenimines is in-The difference  $\Delta \delta$  reflects variations in diadicated. magnetic shielding of the allenic hydrogen, and in the associated electric fields and diamagnetic anisotropies of the cumulenic systems.

In order to estimate the diamagnetic shielding effect of the ketenimine nitrogen on the shift of the allenic hydrogen, the hydridization at the terminal allenic carbons for allene and ketenimine were determined from the <sup>13</sup>C-H coupling constants, which are insensitive to medium and anisotropy effects.<sup>3</sup> A coupling value of 170 Hz for 3d indicates similar hybridization as found in allene,  ${}^{2}J_{{}^{18}C-H} = 168$  Hz. Hybridization differences can thus account for less than 0.1 ppm of shift.<sup>3,4</sup> The coupling  ${}^{3}J = 5.73$  Hz for **3b**, of similar magnitude to that in allenes.<sup>5</sup> is evidence for similar electron distribution for allenes and ketenimines at the terminal allenic carbon, and negligible deshielding electron withdrawal from this carbon by the electronegative nitrogen.

In addition to the similarity of electron distribution at the allenic carbon indicating little contribution from resonance form 6, which would result in a shielding

$$R_2C = C = NR \iff R_2\overline{C} - C \equiv \stackrel{+}{N}R$$

contribution, Anet<sup>2c</sup> has found a barrier to configurational inversion of aryl-alkyl ketenimines of 9-12 kcal/ mol, consistent with a dissymmetric ground state 3. By addition of Eu(fod)36 to N-isopropylphenylmethylketenimine we have confirmed the availability of the ketenimine nitrogen lone pair. The electron pair is, however, somewhat less available than that of a nitrile. The above data thus indicate little influence of nitrogen by diamagnetic shielding on shift of the allenic proton. On the basis of the Eu(fod)<sub>3</sub> coordination with nitrogen, the electrostatic effect would result in a downfield shift of the allenic proton resonance since the dipole moment vector has its negative end (shielding) toward the electron withdrawing nitrogen and its positive end (deshielding) toward the allenic hydrogen.<sup>8</sup>

$$+ \rightarrow -$$
  
R<sub>2</sub>C=C=NR

The enhanced shielding, which is sufficient to over-

(3) D. Rosenberg and W. Drenth, Tetrahedron, 27, 3893 (1971).

(4) J. W. Emsley, J. Feeney, and L. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, London, 1967, pp 1014, 1016, 1021. The effect of the  $\alpha$ -phenyl on <sup>13</sup>C-H coupling is minimal. Typical couplings are Ph-CH<sub>8</sub> = 126 Hz, Ph<sub>2</sub>CH<sub>2</sub> = 127 Hz. The allenic nitrogen might have been expected to cause a small change in hydridization; coupling  ${}^{13}C-H$  for  $CH_{3}CN = 136 Hz$ ;  $CH_{3}C \boxplus CH = 132 Hz$ . (5) See Table II, ref b, c, e, g;  ${}^{3}J = 4.75-6.65 Hz$  in allenes.

(6) Addition of Eu(fod)s to N-isopropylmethylphenylketenimine resulted in extrapolated shifts at Eu(fol)s to 1-solvedy interhyphylaterhy

(1971).

(8) J. W. ApSimon and H. Beierbeck, Can. J. Chem., 49, 1328 (1971), have found electrostatic and magnetic anisotropy effects equally important in a theoretical treatment of shielding effects for the carbonyl group.

<sup>(2)</sup> For the carbodiimide structure, see (a) G. Rapi and G. Sbrana, J. Amer. Chem. Soc., 93, 5213 (1971). (b) F. A. L. Anet, J. C. Jochims, and C. H. Bradley, *ibid.*, 92, 2557 (1970). (c) For the ketenimine structure, see J. Jochims and F. Anet, ibid., 92, 5524 (1970).



Figure 2.-Shielding of allenic hydrogens in ketenimines: Ho = applied field; a = induced magnetic lines of force shielding the allenic hydrogen;  $b = circulating \pi$  electrons.

come any diamagnetic or electric field deshielding contributions, can be attributed to an effect of electron donation from the rear lobe of the nitrogen sp<sup>2</sup>-hybridized lone-pair orbital to the coplanar  $\pi$  system of the allenic double bond (Figure 1). The charge increase at the central allenic carbon will reinforce the magnetic field of the ring current<sup>3</sup> by an increase in the rotating charge of the cumulene and will result in enhanced diamagnetic anisotropic shielding of the allenic hydrogen (Figure 2).

The present results indicate that, while analogy between the geometries of cumulenes and heterocumulenes is valid, heteroatom effects on electronic properties are not to be neglected. It can also be predicted that heteroatoms will effect rotational barriers and bond lengths and energies in cumulenes.<sup>9</sup>

(9) Although the double bond stretching frequencies for C=N (1690-1640 cm<sup>-1</sup>) and C=C (1680-1620 cm<sup>-1</sup>)<sup>10</sup> are similar, the stretching frequencies for C=C=C (1970-1950 cm<sup>-1</sup>),<sup>10</sup> N=C=C (2050-2000 cm<sup>-1</sup>),<sup>1</sup> and N= C=N  $(2155-2130 \text{ cm}^{-1})^{10}$  indicate a bond tightening effect of the heteroatom which might be attributed to lone pair- $\pi$  electron overlap.

### **Experimental Section**

Nmr spectra were recorded on a Varian XL-100-15. in 10% solutions with DCCl<sub>3</sub> or CCl<sub>4</sub> as solvents and tetramethylsilane as external standard.

Materials. N-Phenylisopropylketenimine (3b) was synthesized from N-phenylisovaleric acid amide<sup>11</sup> in 39% yield according to the general procedure of Stevens and French.<sup>12</sup> The yellow oil, bp 52-53° (0.15 mm), was characterized by its ketenimine absorption, 2025 cm<sup>-1</sup> (neat): nmr (CDCl<sub>3</sub>)  $\delta$  7.26, 4.06 (d, <sup>3</sup>J = 5.73 Hz), 4.49 (m), 1.10 (d, J = 7 Hz).

N-Isopropylphenylketenimine (3d) was similarly prepared from N-isopropylphenylacetamide in 54% yield. The yellow oil, bp 53-54° (0.15 mm), was identified by a 2010-cm<sup>-1</sup> (neat) absorption: nmr (CDCl<sub>3</sub>)  $\delta$  7.88, 4.76 (d, <sup>5</sup>J = 1.96 Hz), 3.81 (m), 1.30 (d, J = 7 Hz). Coupling <sup>13</sup>C-H of the allenic hydrogen of 170 Hz was determined from the <sup>13</sup>C side bands of the proton spectrum and was an average of four determinations. The allenic hydrogen had nmr  $\delta$  4.64 neat and at increasing dilutions with CCl<sub>4</sub>.

Anal. Calcd for  $C_{11}H_{15}NO$ : C, 74.56; H, 8.53; N, 7.90. Found: C, 74.28; H, 8.46; N, 7.78.

Ketenimines 3b and 3d could be reconverted to the corresponding amides by hydrolysis.

Registry No.---3b, 34621-16-4; 3d, 34621-17-5.

(10) C. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 34, 61, 263.

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  C. L. Stevens and J. C. French, J. Amer. Chem. Soc., 76, 4398 (1954).