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The ^{13}C NMR Spectra of Several 4-Amino-3-penten-2-ones and Their Palladium Complexes

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Synopsis. A ^{13}C NMR study of several 4-amino-3-penten-2-ones and their palladium chelate complexes is presented. The resonances of the carbonyl carbons of these complexed molecules moved upfield by about 20 ppm relative to the free ligands, while no significant shifts were observed for those of carbons bearing the amino groups.

Three kinds of structures—I, II, and III—are possible for α,β-unsaturated β-amino ketones. In an infrared study a tautomeric equilibrium has been reported to exist between those corresponding to I and II, with the III structure ruled out.[1] Cromwell *et al.*[2] have presented convincing evidence for the II structure in the infrared study of various α,β-unsaturated β-amino ketones. It was also indicated in the ^{1}H NMR spectra that these tautomers are present predominantly in the II form.[3] We wish to report here a ^{13}C NMR study of several 4-amino-3-penten-2-ones and their palladium chelate complexes.

The natural-abundance 25.15 MHz ^{13}C FT-NMR spectra were obtained using the ^{1}H noise-decoupling technique. The assignment of the resonances to the specific carbon atoms was made with the aid of ^{1}H off-resonance experiments. The chemical shifts thus obtained are listed in Tables 1 and 2.

The chemical shifts for the carbonyl carbons of alkyl methyl ketones are usually more than δ; 200.[4] The resonances for the α,β-unsaturated carbonyl carbons move upfield at around δ; 190,[5] while the imino carbons in the II structure are supposed to appear at less than δ; 170.[6] The resonances around δ; 190 are, therefore, assigned to the carbonyl carbons (C-2). The signal at δ; 95.13, which is assigned to the sp^2 hybridized carbon (C-3) of 4-methylamino-3-penten-2-one is split into a doublet in the off-resonance spectra. This evidence suggests that significant portions of these compounds are present in the α,β-unsaturated amino ketone structure, II. The methyl carbon signals (C-1 and C-5) appear separately depending on the structural environments. It has been reported that the methyl carbon resonances of the alkyl methyl ketones usually appear around δ; 28—30,[7] while those of the enol ethers appear around δ; 20.[8] Consequently, the methyl carbon signals at δ; 28.63—29.60 and δ; 18.56—21.90 may correspond to C-1 and C-5 respectively. These assignments are supported by the findings that the signals which are provided by C-5 experience a large upfield shift when the hydrogen on the nitrogen atom is replaced by the methyl group. This shift may be due to the γ-effect between C-5 and the *N*-methyl group. The resonances of the carbonyl carbons of acetylacetone, which is a fifty-fifty mixture of the I and II structures, appear at a field slightly higher than those of the α,β-unsaturated β-amino ketones.

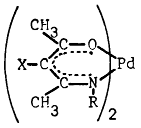
The structures of the palladium complexes are represented as IV or V and VI. The carbonyl carbon resonances of the palladium complexes appear at around δ; 170, at a field about 20 ppm higher than those of the free ligands. The resonances for the methyl carbon next to the carbonyl carbon (C-1) also move upfield, whereas the C-5 resonances move downfield compared with those of the corresponding free ligands. These results indicate the increasing contribution to the enol imine form, V, by the chelate com-

TABLE 1. ^{13}C CHEMICAL SHIFTS OF 4-AMINO-3-PENTEN-2-ONES(δ)[a]

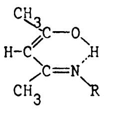
No.	$\mathrm{CH_3\underset{O}{\underset{\|}{C}}CH{=}\underset{NHR}{\underset{\mid}{C}}CH_3}$ R	C-1	C-2	C-3	C-4	C-5	*N*-substituent
1	H	28.75	196.02	95.37	163.02	21.90	
2	CH_3	28.63	194.26	95.13	164.11	18.56	29.36
3	C_6H_5	29.06	195.84	97.74	159.86	19.65	Subst.-C; 139.05 *o*-C ;(124.67) *m*-C ;(129.10) *p*-C ; 125.46
4	*p*-$NO_2C_6H_4$	29.60	197.84	101.26	157.13	20.56	Subst.-C;(145.36) *o*-C ;(125.16) *m*-C ;(121.76) *p*-C ;(143.38)
5	$\mathrm{CH_3\underset{O}{\underset{\|}{C}}CH_2\underset{O}{\underset{\|}{C}}CH_3}$	24.69	191.41	100.53			
		23.7	*191.6*	*100.3*			

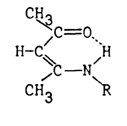
a) The values in italics are taken from J. C. Hammel and J. A. S. Smith, *J. Chem. Soc. A*, **1969**, 2883. The values in parentheses may be interchanged.

Table 2. ^{13}C chemical shifts of Pd-complexes of 4-amino-3-penten-2-ones(δ)[a]

No.	 R	X	C-1	C-2	C-3	C-4	C-5	*N*-Substituent
6	H	H	25.66	176.49	96.89	164.84	24.81	
7	H	Cl	27.78	174.36	103.26	164.47	25.84	
8	H	Br	30.76	174.51	103.29	164.34	28.75	
9	CH_3	H	24.14	173.39	99.01	164.17	22.14	36.64
10	$-CH_2$	H	25.29	177.28	98.95	161.74	20.56	55.87
11	$-CH_2$	Cl	27.24	175.32	104.46	162.02	19.77	57.03
12	$-CH_2$	Br	27.82	175.84	103.37	162.10	22.81	57.63
13	C_6H_5	H	23.78	176.18	97.80	162.71	23.47	Subst.-C; 148.70 *o*-C ;(126.07) *m*-C ;(127.77) *p*-C ; 124.55
14	$Pd(acac)_2$		25.29	187.17	101.44			
15	$Rh(acac)_3$		26.57	188.68	99.25			

a) The values in parentheses may be interchanged.


(I)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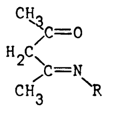
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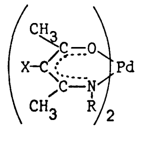
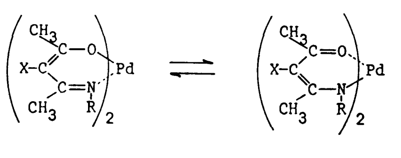

(IV)


(V) (VI)

plex formation. Similarly to the case of α,β-unsaturated β-amino ketones, the upfield shift of the C-5 resonances was observed upon the replacement of the hydrogen on the nitrogen atom with the methyl, the methylene, or the phenyl groups. When the hydrogen of C-3 is replaced by the halogen, the carbon resonances of the substituents on the nitrogen atoms as well as those of the skeletal carbons usually move downfield, with the exception of those of C-2, which reveal the opposite trend.

Experimental

NMR Spectra. The ^{13}C FT-NMR spectra were obtained at 25.15 MHz with a JEOL JNM-MH-100 instrument equipped with a JNM-MFT-100 Fourier transform accessory; the instrument was controlled with a JEC-6 spectrum computer. Samples were observed in 5-mm spinning tubes at 15±5% solutions in $CDCl_3$ at 28 °C. The solvent provided the internal lock signal. The measurement conditions were as follows: pulse width, 27.5 μs (*ca.* 45°); repetition time, 4 s; spectral width, 6.25 kHz; data point, 8192; acquisition time, 0.65 s. Noise modulated proton decoupling was carried out at a nominal power of 20 W. All the chemical shifts are expressed in δ (ppm downfield from internal Me_4Si). Each observed chemical shift is estimated to be accurate to δ ±0.06.

Materials. The compounds employed in this work have been previously prepared except **5**, which was commercially available; **1**,[9] **2**,[1] **3**,[10] **4**,[10] **6**—**13**,[11] **14**,[12] and **15**.[13]

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