^{13}C NMR OF CARBONYL COMPOUNDS. 3. STRUCTURE AND DYNAMICS OF PROTONATED ENONES AND DIENONES

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Abstract The unsaturated ketones 1 - 10 were protonated at low temperatures and studied by dynamic ^{13}C NMR spectroscopy. Four interconverting stereoisomers were detected which differ in their conformation with respect to the CO and CC (enone) single bond.

We have recently studied the stereodynamic behaviour of conjugated enones, dienones and epoxyenones via different spectroscopic methods and achieved a profound knowledge of the relevant energy profiles[1,2]. The conformational properties of the title compounds appear to severely influence their thermal and photochemical reactivity[3,4]. Extension of this work to the corresponding protonation products appeared promising since (i) monoprotonated ketones serve as chromophores in photochemical studies and (ii) protonation was expected to deeply influence the electronic and conformational properties of the substrates[5]. We report on the protonation products derived from the conjugated ketones 1 - 10 whereby special emphasis is put on the prevailing stereoisomerism.

Protonation was performed with FSO_3H in SO_2ClF or SO_2[6,7]. Under the experimental conditions the unsaturated ketones are known to quantitatively transform into the monoprotonated derivatives with the proton attached to oxygen (without changing the configuration of the CC double bond)[5,7,8]. Most of the cations decompose above ca. -20°C; however, when the solutions were neutralized (at low temperatures) by the addition of pyridine, the starting compounds were recovered. Inspection of the Table leads to the following conclusions:

- upon going from the neutral to the cationic species the ^{13}C NMR signals of carbons C-9 (carbonyl), C-7 (C-β), and C-5 (C-δ) suffer from the most pronounced downfield shifts while those of C-8 (C-α) and C-6 (C-γ) can even experience an upfield shift (note the example of 2). One concludes, in accordance with the predictions from simple resonance theory[7], that the positive charge is largely localized (apart from oxygen) at C-9, C-7, and C-5. Thereby centres of high and low positive charge alternate along the chain;
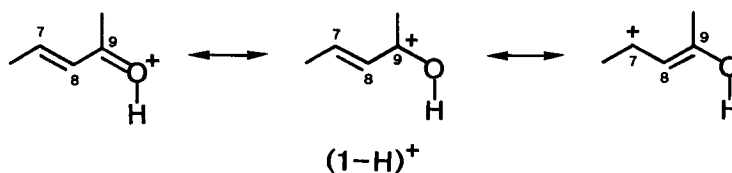

$(1-H)^+$

Table. ^{13}C NMR Chemical Shifts of **1** - **10** and their protonation products **(1-H)**$^+$ - **(10-H)**$^+$ [a,b,c]

Compound	Temp.	C-9	C-8	C-7	C-6	C-5	C-4	C-3	C-2	C-1	C-9a	C-8a	C-7a	C-5a	C-1a	C-6a[f]
1	r.t.	199.3	132.7	143.5							26.8	18.1				
(1-H)$^+$	0°C	218.6	128.8	181.8							23.8	22.8				
	-105°C	218.2	128.5 / 127.5	182.5 / 182.9							22.7	22.4				
		216.6	126.6	175.9							28.1	21.9				
2	-154°C	200.7 / 198.4	135.3 / 129.9	145.7 / 141.4	136.6	135.8 / 138.3	34.1	19.9	39.5	35.2	26.9 / 32.5			23.2	30.7 / 28.5	
(2-H)$^+$	-105°C	207.2	119.4 / 118.5	168.8	142.2	184.5 / 182.7	38.9^d	17.5	40.6^d	34.1	23.4			20.7	26.9	
		204.7	116.7	164.0		186.5	39.3^d				26.6^d			20.1	23.2^d	
3	-154°C	198.7 / 196.4	131.8 / 127.6	143.1	130.6	135.1	127.9	128.9	38.1	33.2	26.2 / 30.6			20.2	25.0	
(3-H)$^{+ e}$	-105°C	202.3	117.3	167.1^d	141.3	168.8	131.8	148.9^d	42.0	34.3	21.9			19.6	25.9	
		198.7	115.1	162.7^d	141.5	171.5	132.2	150.0^d			22.0					
4	r.t.	185.9	127.2	156.7	37.7											26.6
(4-H)$^+$	-105°C	191.1	122.0 / 121.2	182.0 / 181.4	46.6											22.2
5	r.t.	199.4	129.9	150.5	26.0	23.2	38.4									
(5-H)$^+$	-85°C	217.4 / 216.9	124.5 / 123.8	188.1 / 188.8	27.5 / 27.8	19.9 / 19.7	33.6 / 32.2									
6	r.t.	191.3	126.1	153.9									27.5/20.3			
(6-H)$^+$	-105°C	194.4	122.6 / 120.8	188.8 / 180.8									31.5/30.4 25.5/24.1			
7	r.t.	197.8	123.8	154.4							31.1		27.1/20.1			
(7-H)$^+$	-105°C	211.65	122.3	195.6							31.9		27.9/26.3			
8	r.t.	209.8	128.4	143.5	30.9	18.7	38.6	33.1			33.3		20.6	(C-3a: 28.4)		
(8-H)$^+$	-80°C	221.5	140.09	178.8	30.8	16.3	38.4	37.6			35.1		25.9	(C-3a: 26.3)		
9	r.t.	199.7	129.9	140.7	135.2	139.8	32.2	19.5	39.4	35.0	25.8	13.1		21.3	28.5	
(9-H)$^+$	-110°C	215.5	136.9^d	172.3	136.6^d	142.5	32.8	18.6	38.4	35.9	22.6	12.9		22.8	27.6 / 29.5	
10	r.t.	198.9	125.3^d	137.5	136.4^d	141.9^d	30.4^d	22.1^d	22.6^d	27.4^d	26.8	33.7		46.6	(C-8b: 25.6)	
(10-H)$^+$	-105°C	205.9	131.4^d	167.0	135.7^d	170.4	33.4^d	21.2^d	21.9^d	27.0^d	25.1	33.9		47.5	(C-8b: 22.8)	

a) Measured at 75.1 MHz on a Bruker WM 300 spectrometer in SO_2ClF or SO_2 (+FSO_3H). Details of the measurement of the neutral compounds are given in references 1 and 2. For **2** and **3** the chemical shifts of both s-cis and s-trans isomers have been listed. b) Assignments have been made from selective and off-resonance decoupling experiments. c) The chemical shifts of the protonated ketones are reported as follows: top row, s-trans (enone) isomer; bottom row, s-cis (enone) isomer. At low temperatures the s-trans isomers of **(1-H)**$^+$ and **(2-H)**$^+$ give rise to additional splittings due to the slow rotation around the CO-bond (see text). d) Assignment uncertain. e) The slow-exchange domain of the CO-rotation is not yet obtained. f) For better comparison the centres have been numbered as in β-ionone.

Structures **1**, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**
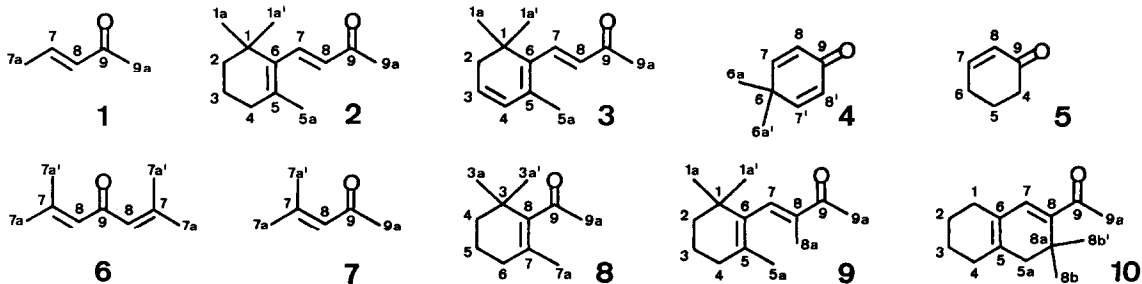
- when the conjugation between the enone moiety and the additional double bond(s) is inhibited for steric reasons (e.g. in **8** and **9**) the charge remains in the enone part;
- according to the low-temperature ^{13}C NMR spectra the title compounds classify into two groups; the members of one group (**1** - **6**) exhibit dynamic behaviour while the others (**7** - **10**) fail to reveal exchange effects down to -110°C.
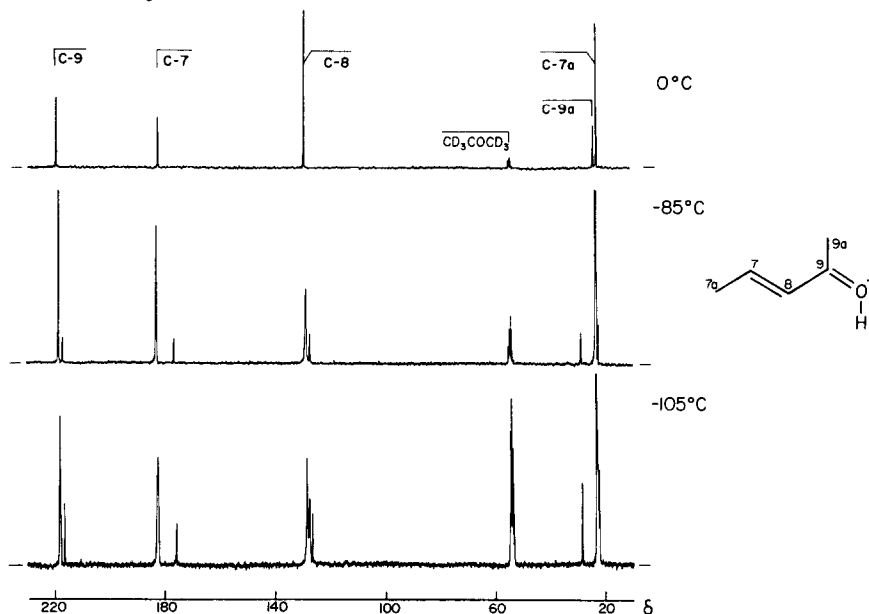

Figure. ^{13}C NMR spectra of (**1**-H)$^+$ at different temperatures (see Table)

The number of ^{13}C signals of **1** (spectrum taken at 0°C) corresponds to the constitutional formula. When lowering the temperature to ca. -85°C (see Figure) each resonance broadens and splits into two signals of relative intensities 3:1, thus, indicating the presence of two stereoisomers. When proceeding to even lower temperatures the (sharp) signals of the minor isomer are unaffected while those of the major isomer (which are still broad at -85°C) again split into two signals of relative intensities 1.5:1. One concludes that there is both a "high-temperature" and a "low-temperature" interconversion process. The related dienone **2** (β-ionone) and the trienone **3** show essentially the same behaviour. Compounds **4** - **5** indicate the presence of only the "low-temperature" exchange. All temperature-dependent line broadening effects are perfectly reversible. Which are the isomerization phenomena and how can one assign the spectra of the individual stereoisomers?

The enone **1** can undergo two stereodynamic processes[7,9,10]: rotation around the enone single bond (interconversion of s-cis/s-trans isomers) and isomerization around the CO-bond (interconversion of syn/anti-arrangements of the proton at oxygen and of C-8 with respect to the CO-bond; see Scheme below). Only the latter process is feasible in compounds **4** and **5**, so that in accordance with findings from ^{1}H NMR spectroscopy[7,11], the low-temperature process must be identified as the isomerization around the CO-bond. In **4** this conformational interconversion exchanges the magnetic sites of e.g. C-8 and C-8' while leaving the proton at the oxygen unaffected. When ascribing the high-temperature process e.g. in **1** and **2** to the s-cis/s-trans

s-trans / syn **a**   CO   **b** s-trans / anti

CC ⇅   ⇅ CC

s-cis / syn   **c**   CO   **d** s-cis / syn
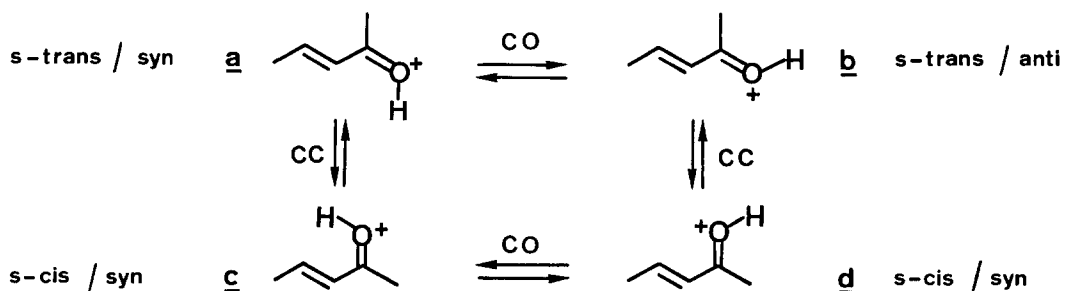
enone isomerism, we note that the same process has also been detected by us for the corresponding neutral compounds in the ^{13}C NMR spectra below -120°C[1]. Thereby, the s-trans conformers are energetically more favored. The higher activation barrier of the rotation in the cations is due to the increased π-bond order of the enone single bond.

The above Scheme reveals that among the four possible enone conformers **a** -**d** the structure **c** (s-cis enone and syn-arrangement) is much less favorable since it possesses the largest non-bonded interactions[7,10]. It is, therefore, reasonable to assume that (i) only the s-trans enone isomer exhibits the isomerism around the CO-bond at very low temperature and that (ii) the s-trans isomer must be identified as the more abundant component in the high-temperature process.

It is known from the study of the neutral compounds that substitution of the hydrogens at C-8 or C-7 by larger groups shifts the conformational equilibrium toward the s-trans or s-cis conformers, respectively[1,12]. When extending these arguments to the protonated species (assuming similar energy profiles for the s-cis/s-trans interconversion as in the neutral species) it is clear that the relative energies of the s-cis/s-trans conformers and syn/anti-arrangements differ significantly due to the prevailing non-bonded interactions. It is, therefore, no surprise that the protonation products of **7** - **10** exist in a single stereoisomeric form and fail to exhibit dynamic processes.

The full account of this work will include further unsaturated ketones as well as ^1H NMR and UV studies of the protonated species[13].

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