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^{13}C-NMR OF CARBONYL COMPOUNDS

1. STEREODYNAMIC BEHAVIOUR OF ACYCLIC AND CYCLIC DIENONES

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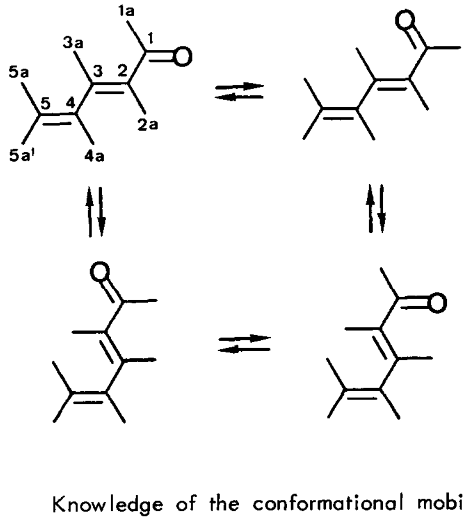
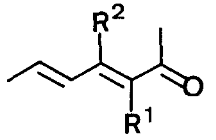
Abstract The conformational mobility of a series of conjugated dienones is investigated by low-temperature NMR- and IR-spectroscopy and interpreted in terms of substituent effects.

The stereochemical characterization of conjugated dienones, subject of various spectroscopic studies[1-4], has to consider the configurations of the C=C-double bonds and the s-cis / s-trans conformational isomerism within both the enone and diene moieties. While NMR-investigations have only dealt with the (average) fast-exchange spectra of the systems we have succeeded via low-temperature ^{1}H- and ^{13}C-measurements in slowing down dynamic interconversions and in characterizing separately the structures of the isomers.





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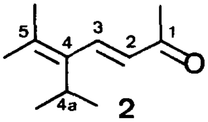
5 $R^1 = H$ $R^2 = CH_3$



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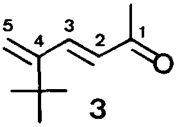

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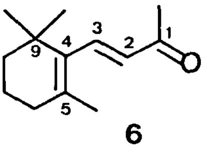

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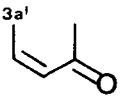

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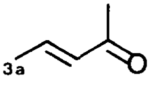

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Knowledge of the conformational mobility is of fundamental importance for the understanding of conjugated dienones[3,4]. Of special interest is the stereochemical behaviour of ß-ionone (6), a key compound of scientific and industrial problems[5]. In addition to the dienones 1, 2, and 4 - 6 we have in-

Table ^{13}C-NMR-chemical shifts of 1 - 6 [upper row: major isomer, lower row: minor isomer] a)

	T[°C]	C-1	C-2	C-3	C-4	C-5	C-1a	C-5a (C-5a')	
1	-156	199.17	128.67	145.14	129.57	140.33	25.18	18.87	
		197.17	b)	141.20	129.57	140.33	30.61	18.87	
2	-156	199.50	130.16	142.19	136.54	134.67	24.87	21.76(20.75)	C-4a: 28.58
		197.19	127.94	137.44	140.67	134.67	30.70	21.76(20.75)	C-4b: 19.95
3	-155	199.05	129.46	144.21	152.57	111.93	25.43		C-4a: 34.71
		196.66	b)	140.58	152.57	b)	30.01		C-4b: 27.98
4	-150	199.33	133.01	140.00	127.23	138.72	25.40	19.09	C-2a: 10.83
5	-154	199.05	124.13	149.79	134.34	134.24	32.12	18.76	C-3a: 12.79
6	-150	200.64	135.27	145.65	135.82	136.61	26.86	23.19	C-9a: 30.83
		198.35	129.88	141.32	138.37	136.61	32.54	23.19	28.56
									C-9 : 35.22

a) Measured in vinylchloride, TMS as internal standard (Varian CFT 20). Signal assignments have been achieved from selective decoupling experiments (except for 5, where ^{1}H-signals overlap) and from non-decoupled spectra. b) Covered by solvent-signals.

cluded in this investigation the novel compound 3, whereby the structures of 2 and 3 seem to be appropriate acyclic reference compounds for 6.

The enone units of dienones having hydrogens at C-2 and C-3 can be shown from ^{1}H-NMR data to exist as equilibrium mixtures of s-cis and s-trans conformers [3]. As is readily anticipated from the Scheme, methyl substitution at C-2 or C-3 will shift the equilibrium toward the s-trans or s-cis side, respectively. Within the diene moiety, on the other hand, a 5a-substituent will favour the s-trans, whereas a bulky 4a-substituent will favour the s-cis isomer. Molecular-mechanics calculations indicate the relevant activation energy to be significantly higher for rotation around the (enone) C-1-C-2 single bond [6].

The carbonyl chemical shift (see Table) appears essentially unchanged throughout the series; it adopts a value similar to the one in the enone case and, therefore, does not reflect the extended conjugation. In accord with previous experience [1] C-3 absorbs significantly downfield from C-2.

The low-temperature ^{13}C-measurements will be considered for 2 as a representative example: on cooling to temperatures below ∼-90°C the signals of C-1, C-1a, C-2, C-3 and C-5 broaden progressively and split into two signals with a relative intensity of ∼1 : 3. Signals of other nuclei are not affected by the exchange process, and the slow-exchange limit is obtained at ∼-150°C. Related signals can easily be identified from the temperature-dependance of the lineshape, so that both stereoisomers are fully characterized by their ^{13}C-spectra. It is significant that compounds 1, 3, and 6 behave analogously to

2. This finding is deduced from : a) the type of nuclei whose signals show line broadening [7], b) the relative chemical shifts of identical nuclei within both isomers, c) the equilibrium constants, and d) the temperature range involved.

Either a diene or an enone isomerization is expected to modify the mode of π-conjugation, thus influencing the magnetic sites of the olefinic carbons. However, the observed changes are most pronounced for signals of the enone part and, more importantly, affect the signals of methyl substituents in the enone (C-1a), but not in the diene (C-4a, C-4b, C-5a, C-5a') moiety. These findings, together with the fact that structures 1, 2, 3 and 6 are analogous only in the enone unit, lead one to the conclusion that the observed dynamic process is the interconversion of the s-cis and s-trans enone isomers.

Further support for this interpretation is provided by the failure of 4 and 5 to exhibit any exchange broadening down to ~-160°C: 4 and 5 seem to exist exclusively as s-trans and s-cis enone isomers.

Comparing the subspectra of both stereoisomers of 2 one notices the significant upfield shift of the C-1a methyl signal in the major form; the trans enone produces some "peri-type" arrangement of the 1a-methyl group and the hydrogen at position 3 (see Scheme). From the expected steric shielding one might conclude that the trans enone constitutes the favorable isomer [8]. Within the ^{1}H-NMR spectrum of 2 at -156°C, one can identify the minor isomer by its well separated signal of H-2 which is 0.5 ppm downfield from the one of the major isomer (the signal of H-3 is influenced to a lesser extent). The interpretation of the ^{13}C- and ^{1}H-spectra is only compatible if H-2 is believed to resonate farther downfield in the (less favorable) s-cis enone. This assignment is in accord with previous considerations of the magnetic anisotropy of the carbonyl group [9] and with the ^{1}H-resonances of the isomeric pentenones 7 and 8. The methyl substituents at positions 3a or 3a' strongly favour the s-trans or s-cis conformation, respectively [10]. The relatively large downfield absorption of H-2 observed in the enone 7 can hardly be due to some inherent substituent effect, but should rather be ascribed to the conformational change [11 - 13].

Independent evidence for this interpretation can be derived from IR-spectroscopy since it is well established that in enone [11] and dienone [3] species the s-cis and s-trans conformers differ by their C=O- and C=C-stretching frequencies. FTIR-spectra (0.012 mm film,KBr) indicate compounds 2 and 3 to exist as equilibrium mixtures of s-cis and s-trans enone structures [2 s-trans enone: ν(CO) 1655, ν(CC) 1608; 2 s-cis enone: ν(CO) 1670, ν(CC) 1581; 3 s-trans enone: ν(CO) 1668, ν(CC) 1645; 3 s-cis enone: ν(CO) 1675, ν(CC) 1620 cm^{-1}] [14]. Cooling the samples (25°C to -130°C) however, causes the (C=O- and C=C-) bands of the s-trans enone conformers to increase in intensity and those of the s-cis form to decrease. Following the arguments proposed by Noack and Jones [11] one concludes from the spectra that, at low temperatures, the s-trans enone constitutes the dominant stereoisomer.

From a preliminary lineshape analysis of the ^{13}C-NMR-spectra of 2 we obtain the free enthalpy of activation as $\Delta G^{\ddagger}$(s-trans $\rightarrow$ s-cis, T= -144°C) = 6.6 kcal/mole and the difference in the free enthalpy of the enone conformers as ΔG°(T = -144°C) = 0.27 kcal/mole.

There is no evidence in favour of an exchange process within the diene units. Whereas the vicinal

H,H-coupling constant J_{34} of 1 indicates the dominance of the s-trans diene[3], such information is less readily available for compounds 2, 3 and 6. Homonuclear NOE-measurements however, characterize the s-trans (diene) isomer to be the major component in 2, but not in 3. Thus, although dienone 2 from the type of substituents can be described as a true acyclic analogue of ß-ionone (6), it differs from the latter[15] by dominantly possessing a s-trans diene moiety.

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6. We thank Prof. J. Lindner, Technische Hochschule Darmstadt, for making available calculations based on a π-SCF-force-field procedure (program PIMM).
7. It should be noted that no broadening of the C-5 signal is observed for 1 and 6. Moreover, line broadening in 1, 3 and 6 occurs at somewhat lower temperature than in 2. A detailled comparison of the spectra of related dienones as well of the synthesis of 3 will be given in a forthcoming paper.
8. Comparing the ^{13}C-chemical shifts of related s-cis and s-trans isomers it appears noteworthy that the upfield shift of the carbonyl resonance in the former is accompanied by an upfield shift of the resonances of C-2 and C-3. Thus, a conclusion as to the mode of π-conjugation (e.g. the extent of charge separation) is not straightforward. This finding does not come unexpected, however, since various additional effects, such as the influence of solvent and temperature, have to be considered.
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