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THE PROTON COUPLED ^{13}C NMR DIRECT DETERMINATION OF Z-,E-CONFIGURATION OF 4-BENZYLIDEN-2-PHENYL(METHYL)- Δ^{2}-OXAZOLIN-5-ONES AND PRODUCTS OF THEIR SOLVOLYSIS

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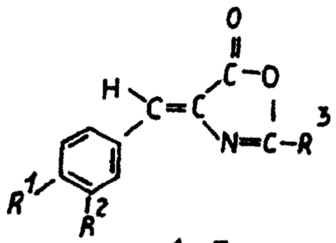
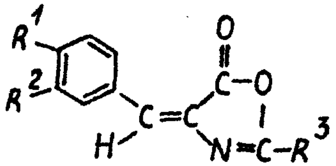
Although assignment of Z-,E-configuration in unsaturated azlactones 1 has been attracting attention of many investigators for a long time, a reliable solution of this problem is still lacking[1].

In the present paper such an assignment has been unequivocally made by means of the $^{3}J_{C_5,H_\beta}$ vicinal coupling constants between the carbonyl carbon of an azlactone and the olefinic H$_\beta$ proton. The vicinal couplings $^{13}C-C=C-H$ have been shown to be stereospecific: $^{3}J^{trans}_{C,H} > {}^{3}J^{cis}_{C,H}$ [2]. When the carbons are unaffected by γ-effect[3a] this inequality is strongly pronounced[2]. The significant difference between the $^{3}J^{trans}_{C_5,H}$ and $^{3}J^{cis}_{C_5,H}$ can be expected due to total absence of γ-effect in the case of the quaternary carbons[3]. Indeed, from the constants measured in the proton coupled ^{13}C NMR spectra obtained at 15.08 MHz by the gated decoupling technique on Brucker WP-60 spectrometer it followed that $^{3}J_{C_5,H_\beta}$ =5.5 Hz for the stable isomers 1a-j synthesised by Erlenmeyer method and $^{3}J_{C_5,H_\beta}$ = 12.5 Hz for the less stable isomeric forms 1k,l,m prepared according to [4] (see Table). It can therefore be concluded that 1a-j represent the Z-isomers while 1k,l,m are the E-isomers.

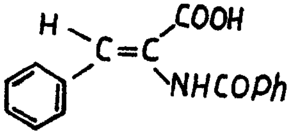
The signals of the C_5 carbon were located according to their chemical shifts and their doublet splitting (see Table). The adjacent signals of the C=N carbon (159.8-166.3 ppm) are quartets when $R^{3}=CH_3$ (^{2}J=8.5 Hz, coupling



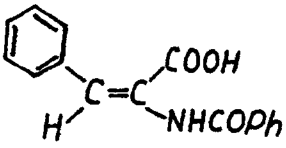
1 Z



1 E



2a Z



2b E

to the CH_3 protons) or triplets when R^3=Ph (^3J=5 Hz, coupling to the two Ph ortho-protons) and those of the C=O carbon of the AcO group (168.5–168.9 ppm) are quartets (^2J=7 Hz, coupling to the CH_3 protons).

The Z-configuration of 2a and E-configuration of 2b were determined in a similar manner. $^3J^{cis}_{COOH,H_\beta}$=5 Hz(2a) and $^3J^{trans}_{COOH,H_\beta}$ =10 Hz(2b). 2a and 2b were obtained by alkaline hydrolysis of 1f and 1k, respectively. The signals of the COOH carbon are doublets at 166.3 ppm (2a, CD_3OD) and 164.6 ppm (2b, $(CD_3)_2SO$). The adjacent signals of the NC=O carbon are triplets (^3J=3 Hz, coupling to the two Ph ortho-protons) at 167.8 ppm (2a,CD_3OD) and 163.9 ppm (2b, $(CD_3)_2SO$). The $^3J_{COOH,H_\beta}$constants were not determined for 2a in $(CD_3)_2SO$ and 2b in CD_3OD because of the overlapping of the COOH and NC=O resonances. The data obtained for 1f, 1k, 2a and 2b confirm the assumption of many investigators[1] that the unsaturated azlactones and the products of their solvolysis have the same configuration of the olefinic bonds.

For 1, an upfield shift of 2–3 ppm for C_5 resonances (see Table) and a considerably larger downfield shift of about 10 ppm for C_β resonances (double triplet at 130–132 ppm in the Z-isomers and 140–141 ppm in the E-isomers; $^1J_{C,H}$ =152–157 Hz; $^3J_{C,H}$=5 Hz, coupling to the two Ph ortho-protons) are observed in the E-isomers as compared to the Z-isomers. These shifts could be due to[5] a more effective conjugation of the olefinic bond and carbonyl group in the

Compound	R^1	R^2	m.p. °C	$\delta(C_5)^a$ ppm	$^3J_{C_5,H_\beta}{}^b$ Hz	Isomer
			R^3=Me			
1a	H	H	149–150	167.8	5.5	Z
b	AcO	H	135–137	167.7	5.5	Z
c	MeO	H	110–111	168.2	5.5	Z
d	AcO	MeO	149–151	167.8	5.5	Z
e	MeO	AcO	156–158	167.9	5.5	Z
			R^3=Ph			
f	H	H	165–166	167.6	5.5	Z
g	AcO	H	174–176	167.5	5.5	Z
h	MeO	H	157–159	167.9	5.5	Z
i	AcO	MeO	194–195	167.3	5.5	Z
j	HO	MeO	154–155	167.4	5.5	Z
k	H	H	146–147	164.6	12.5	E
l	MeO	H	149–151	165.1	12.5	E
m	HO	MeO	124–126	165.3	12.5	E

a. At t=30–45°C from TMS, 0.4–0.7mol/l in $CDCl_3$, **1**j,m in $(CD_3)_2CO$

b. FT measurement conditions: spectral width, 3750 Hz; data points, 8k; pulse flipping angle, 45°; delay between pulses, 5S; number of scans about 10^4.

E-isomers. The more effective conjugation can be assumed to lead to an increase of the positive charge on C_β in the E-isomers as compared to the Z-isomers. This assumption is in agreement with data[6] which show that the reaction of Grignard reagents with Z-isomer 1f leads to 1,2-adducts while that with E-isomer 1k yields 1,4-adducts.

A full description of the ^{13}C and ^{1}H NMR spectra as well as other NMR indications of the Z-,E-configurations of the compounds in question will be reported[7].

References and Notes

1. To make sure it is really so one has to compare the reviews (a) and (b) closely and to examine paper (c) and papers regarding the point in question and cited simultaneously in (a) and (b).
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4. 1k and 1l,m are obtained according to (a) and (b), respectively.
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