^{13}C NMR spectra of some 1,2-disubstituted *N*-vinyl-1*H*-1,2,4-triazoles

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^{13}C NMR spectra (20 and 75 MHz, in DMSO-d_6) of a series of 1,3-diaryl-3-(1*H*-1,2,4-triazol-1-yl)- and 1,3-diaryl-2-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones were registered. It was shown that the chemical shifts of both the carbon atom of the alkene group and C(3) reflect regio- and stereoisomerism of these compounds. Taking this into account the isomeric structures of several 1,3-diaryl-3-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones were identified and the configurations relative to the double bond of a number of 1,3-diaryl-2-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones were determined.

Key words: 1,2-disubstituted *N*-vinyl-1*H*-1,2,4-triazoles; ^{13}C NMR; increments of chemical shifts; isomerism.

Recently it has been found that 1,2-disubstituted *N*-vinyl-1*H*-1,2,4-triazoles, prepared by condensation of 2-chlorophenyl-(1*H*-1,2,4-triazol-1-yl-methyl)ketone with aldehydes,[1] possess high biological activity. On the other hand, although it is possible to obtain regioisomers, as well as *Z*- and *E*-isomers, the configuration of these compounds relative to the double bond is still open to question. This work deals with the search for a dependence of some ^{13}C chemical shifts on regio- and stereoisomerism of 1,2-disubstituted *N*-vinyl-1*H*-1,2,4-triazoles. A number of 1,3-diaryl-3-(1*H*-1,2,4-triazol-1-yl)- and 1,3-diaryl-2-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones (compounds **5**—**14** and **15**—**17**, respectively) have been investigated. ^{13}C NMR spectra of model compounds **1**—**3** have been studied. The spectrum of **4** was calculated using the α- and α'-increments of Br for chemical shifts of the carbon nucleus at the double bond.[2]

Experimental

^{13}C NMR spectra for DMSO-d_6 10—20 % solutions (δ 39.5) were measured on a Bruker AS-80 (20 MHz) and on an AM-300 (75.5 MHz) Fourier spectrometer under conditions of complete proton decoupling. To determine the degree of protonation of the carbon atoms, the standard multi-impulse conditions JMODXH and INEPTRD were used. In the case of JMODXH, the delay time was 10—25 sec.

Results and Discussion

In Table 1 the chemical shifts of the ^{13}C nuclei of the investigated *N*-vinyltriazoles and model compounds are given. The signals were assinged on the basis of calculations by additive schemes using the increment values of the substituents[2] and taking the degree of C atom protonation into account. In compounds **5**—**17** the triazolyl radical (Tr), whose α- and α'-increments are unknown, is bonded to C(2) or C(3) atoms. We estimated these increments by a comparison between the chemical shifts of the corresponding ^{13}C nuclei of 1-vinyltriazole[3] and ethylene (δ 123.3) to afford α = 6.5 ppm and α' = −19.2 ppm.

However, the chemical shifts of the ^{13}C(2) and ^{13}C(3) nuclei calculated using these values differ considerably from the experimental chemical shifts, and the differences depend on the position of the attached triazolyl radical and on its steric configuration (*Z*-, *E*-isomers). The calculated chemical shifts of the ^{13}C(2) and ^{13}C(3) nuclei are 111.4 ppm and 149.9 ppm, respectively, in the case of compound **5** (model analog is **4**), the same values for **6** are 108.4 and 148.9 ppm, and for **15** (model analog is **1**) they are 134.1 and 123.2 ppm. The substantial deviations of the calculated chemical shifts from the experimental ones attest to large steric and electronic interactions between R(1) and R(3) radicals.

Examination of the data given in Table 1 reveals that the chemical shifts of the C atom nucleus in the alkene group are the most useful with respect to information about regioisomerism. Thus, the 140—144 ppm signal of this nucleus attests to the introduction of the triazolyl radical to the C(2) atom of compounds **15**—**17**, and in the case of their regioisomers **5**—**14**, the nucleus of the methine C atom of the alkene group resonates up-field (114—125 ppm). When the chemical shifts of the ^{13}C nuclei in isomer pairs **5**—**6**, **7**—**8**, **9**—**10**, and **11**—**12** (the *E*-configuration of **5** and **7** is established[4]) are compared, one can easily believe that the chemical shifts of ^{13}C(2) and ^{13}C(6) make it possible to find the

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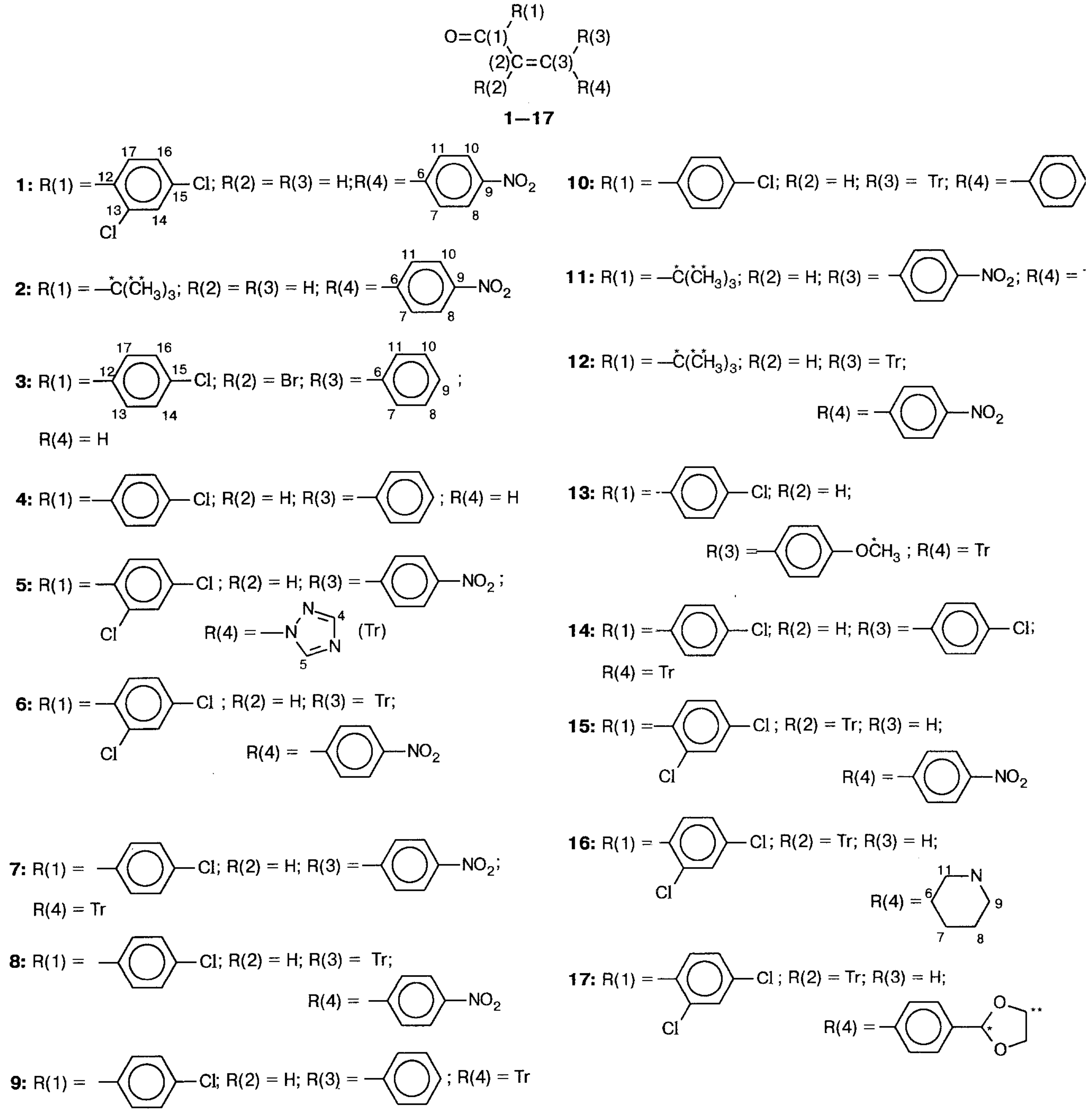

configuration of 1,3-diaryl-3-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones relative to the double bond: the ^{13}C(2) and ^{13}C(6) signals for all of the *E*-isomers are shifted up-field. The phenyl substituent at the keto group makes a substantial contribution to the diamagnetic shift of the ^{13}C(6) signal. In fact, when this substituent is absent (pair of isomers **11—12**), the chemical shifts of ^{13}C(6) give no information about *Z*-, *E*-isomerism, since their values are about the same (139.0 and 139.8 ppm).

Analysis of the geometrical structure of the *Z*- and *E*-isomers of 1,3-diaryl-3-(1*H*-1,2,4-triazol-1-yl)prop-2-en-1-ones using the Stuart—Briegleb models shows that in *E*-isomers (except for compound **11**) internal rotation of the phenyl substituents is hindered: they can not orient themselves in space independently from each other, *i.e.*, only coordinated rotation about the C(1)—C(12), C(1)—C(2), and C(3)—C(6) bonds is possible. This indicates the existence of steric strains in above-mentioned molecules, and it is most likely that

Table 1. Chemical shifts (δ) of ^{13}C nuclei of 1,2-disubstituted *N*-vinyltriazoles and their model analogs

Atom	Compound																
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
C(1)	191.4 191.0	202.9 206.5	190.5	191.0	189.7	189.0	188.5	188.0	188.7	188.3	203.4	204.0	187.6	187.7	189.4	189.1	189.5
C(2)	127.6 127.3	125.5 127.3	121.9 119.3	130.5	117.7	124.8	115.9	124.2	115.4	119.9	114.4	123.5	117.1 115.9	114.9 115.9	131.7	127.3	132.0
C(3)	142.4 141.3	141.7 141.3	142.5 140.3	143.4	144.7	141.0	144.4	140.4	145.3	143.3	143.4	140.7	143.3 144.5	144.5 144.5	141.1	140.9	143.8
C(4)					153.2	152.6	152.3	151.3	152.9	152.2	152.9	152.3	151.7	152.6	152.7	152.7	152.7
C(5)					145.7	146.7	145.6	146.9	145.0	146.5	145.2	146.8	146.1	144.8	146.3	146.0	145.7
C(6)	140.4 143.8	139.5	133.3 138.0	138.0	136.8	139.9	136.0	140.9	131.9	135.6	139.0	139.0	126.6 130.6	135.1 135.5	134.9	131.4 139.2	131.9 135.6
C(7)	129.1 127.4	129.5	128.6 126.5	126.5	131.5	129.5	131.4	129.2	128.5	127.6	131.1	128.7	129.3 127.5	128.3 127.6	131.4	136.6 134.7	130.6 130.4
C(8)	124.2 123.9	124.1	128.9 128.7	128.7	123.4	123.1	123.6	124.0	128.9	128.8	123.4	123.9	114.2 114.3	130.1 128.6	123.8	123.8 123.8	126.5 126.2
C(9)	148.8 148.6	148.6	130.6 128.0	128.0	148.2	148.6	148.2	148.7	130.2	131.4	148.0	148.4	161.7 159.4	133.0 134.0	148.4	151.2 147.8	142.3 148.3
C(10)	124.2 123.9	124.1	128.9 128.7	128.7	123.4	123.1	123.6	124.0	128.9	128.8	123.4	123.9	114.2 114.3	130.1 128.6	123.8		126.5 126.2
C(11)	129.1 127.4	129.5	128.6 126.5	126.5	131.5	129.1	131.4	129.2	128.5	127.6	131.1	128.7	129.3 127.5	128.3	131.4	151.8 149.9	130.6 130.4
C(12)	132.0 136.4		134.8 136.0	136.0	136.6	132.2	135.3	138.9	136.2	134.3			135.9	135.9	134.7	132.8	133.3
C(13)	136.8 137.7		131.2 131.5	131.5	136.9	135.3	130.3	130.6	130.3	130.4			130.0	131.4	136.5	134.9	135.8
C(14)	130.4 129.1		130.4 128.7	128.7	129.7	130.2	129.1	129.0	129.8	128.9			128.4	128.6	129.9	129.7	127.7
C(15)	137.7 139.6		139.1 138.3	138.3	137.8	136.8	139.0	138.0	138.6	138.5			138.3	138.5	137.6	136.8	136.7
C(16)	127.6 126.8		130.4 128.7	128.7	127.5	127.3	129.1	129.0	129.8	128.9			128.4	128.6	127.8	127.3	126.9
C(17)	130.7 132.8		131.2 131.5	131.5	131.6	131.9	130.5	130.6	130.3	130.4			130.0	131.4	131.2	131.9	129.9
C*		43.3									43.8	44.0	55.3				102.5
C**		25.5									25.7	25.6					65.2

Note. Denominator shows the calculated values.

these strains cause the diamagnetic shifts of ^{13}C(2) and ^{13}C(6). In all of the *Z*-isomers and in the *E*-isomer of compound **11**, three of the substituents rotate in a more free and independent way. In addition, all of the substituents in the compounds given in Table 1 are magnetically anisotropic groups, and their over-all influence on the chemical shifts of the olefin carbons substantially differs from the influence inherent only in the triazolyl radical in 1-vinyltriazole.

A comparison of the chemical shifts of ^{13}C(2) and ^{13}C(3) in the *E*- and *Z*-isomers of compounds **5**—**12** and the chemical shifts of the corresponding nuclei in **1** (*Z*-isomer) and **4** (*E*-isomer) made it possible to determine the α- and α'-increments of the triazolyl radical for the series of compounds under consideration. It was found that $\alpha = 1.1$ and $\alpha' = -14.6$ ppm for the *E*-isomer, while $\alpha = -1.0$ and $\alpha' = -4.5$ ppm for the *Z*-isomers. It should be pointed out that the increments obtained cannot be used for calculating the chemical shifts of ^{13}C(3) in the case of *Z*-regioisomers (compounds **15**—**17**). The R(4) radicals of these compounds are considerably different, and therefore the α- and α'-increments of the triazolyl substituent were not found.

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