

2-β-D-Ribofuranosyl-4-carbamoyl-1,2,3-triazole (X). A 0.12-g portion (0.41 mmole) of nucleoside VII is boiled in 15 ml of anhydrous methanol, containing 1.2 g of Raney nickel. The catalyst is filtered, washed with methanol, and the filtrate is evaporated. The residue is chromatographed in system B to yield 0.04 g (40%) of compound X, R<sub>f</sub> 0.26 (B). UV spectrum, λ<sub>max</sub> (ε): 227 nm (10,000).

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#### ESTIMATION OF THE σ<sub>R</sub>-CONSTANTS OF THE TETRAZOLYL GROUPS ON THE BASIS OF <sup>13</sup>C NMR SPECTRA OF VINYL TETRAZOLES

O. A. Ivashkevich, P. N. Gaponik,  
and V. N. Naumenko

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On the basis of <sup>13</sup>C NMR spectra of tetrazole-containing vinyl monomers, the resonance σ<sub>R</sub> constants of a series of tetrazolyl groups have been estimated.

Investigation of the reactivity of new monomers in polymerization processes requires some quantitative information on the electronic nature of the substituent at the vinyl group, especially on the σ<sub>I</sub> and σ<sub>R</sub> Taft constants which characterize the contribution of the inductive and resonance effects to the Hammett σ-constant. This information is especially important in the case of the monomers in which the substituent at the vinyl group is ambident. Recently, vinylazoles have been widely employed as such compounds. Their azolyl radicals appear to be electron-withdrawing groups; however, due to the conjugation they can also behave as electron donors and cause the appropriate polarization of the vinyl bond [1].

In the present work, we estimated the resonance σ<sub>R</sub> Taft constants on the basis of the <sup>13</sup>C NMR spectra of several tetrazolyl groups. Calculation of these constants using the Swain-Lupton equation is tedious and requires a complex mathematical treatment [2]. The calculation was carried out using a correlation relationship which satisfactorily correlates the <sup>13</sup>C NMR chemical shifts of the terminal vinyl carbon atoms (C<sub>β</sub>) of the olefins RCH = CH<sub>2</sub> with the inductive and resonance constants for substituents R [3, 4]:

$$\Delta\delta_{C_{\beta}} = 11.9\sigma_I + 63.5\sigma_R,$$

where Δδ<sub>C</sub> is the difference between the values of the chemical shifts of the vinyl derivative and ethylene (the δ<sub>C</sub> value for ethylene is equal to 123.3 ppm [4]).

The data concerning the chemical shifts of the carbon atoms in the <sup>13</sup>C NMR spectra of the investigated tetrazole containing monomers are presented in Table 1. The σ<sub>I</sub> values of the inductive constants for 1-tetrazolyl, 5-tetrazolyl, and N-methyl-5-tetrazolyl groups are taken from [6, 7] and those for 5-amino-1-tetrazolyl, and 5-methyl-1-tetrazolyl groups are calculated according to the pK<sub>a</sub> values of the corresponding tetrazolylacetic acids [6] using the Charton correlation equation [8]:

$$\sigma_I = -0.251pK_a + 1.186.$$

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TABLE 1. Chemical Shifts of the Carbon Atoms of Vinyltetrazoles and  $\sigma$ -Constants of the Tetrazolyl Groups

Tetrazole	$\delta C_{\alpha}$	$\delta C_{\beta}$	$\delta C_{(5)}$	$\delta(CH_3)$	$\sigma_I$	$\sigma_R$
1-Vinyl	127,86	109,86	142,72		0,65 [5]	-0,33
1-Vinyl-5-methyl	127,12	110,30	152,39	8,96	0,64	-0,32
1-Vinyl-5-amino	126,21	106,90	155,53		0,59	-0,37
5-Vinyl	120,48	125,74	155,32		0,45 [6]	-0,05
1-Methyl-5-vinyl	118,87	126,85	153,36	34,41	0,48 [6]	-0,03
2-Methyl-5-vinyl	123,75	122,33	169,46	39,83	0,32 [6]	-0,08

The values of the  $\sigma$ -constants for the tetrazolyl groups indicate that 1- and 5-tetrazolyl radicals should manifest a significant difference in their effect on the reactivity of the vinyl group, apparently due to the possibility of the conjugation between the lone electron pair of the nitrogen atom in the position 1 of the ring and the  $\pi$ -electron system of the vinyl group. The inductive and resonance values of the 1-tetrazolyl fragments are similar to those of these parameters for other N-azolyl groups [1, 4, 9], as well as those for halogens [2], which remains in agreement with the Kauffmann principle, according to which N-azolyl groups are similar in many aspects to the halogens. This allows one to assume that, similarly to vinyl halogens and N-vinylazoles, N-vinyltetrazoles will manifest a decreased reactivity in the copolymerization with styrene and with methyl methacrylate and a high activity in the copolymerization with vinyl acetate and acrylonitrile. The obtained values of the resonance constant of the C-tetrazolyl groups agree with the  $\sigma$ -constants characterizing the ability of the 5-tetrazolyl group to conjugate [7] and with the resonance constant calculated from the Swain Lupton equation [11].

It is known that the conjugation of the electron systems of the vinyl group and the substituent increases the activation energy of the chain growth and decreases to a greater extent the reactivity of the radical; it increases thereby the reactivity of the monomer. Thus, by increasing the conjugation energy of the monomer the reaction of the chain growth during homopolymerization should slow down [5]. This conclusion, taking into account the obtained results, allows one to assume a larger tendency of 5-vinyltetrazole to undergo homopolymerization than in the case of N-vinyl-tetrazoles.

#### EXPERIMENTAL

The  $^{13}C$  NMR spectra were taken on a WM-360 Bruker (90.56 MHz) instrument. Deuterated methanol was used as solvent and tetramethylsilane as internal standard. The accuracy of determination of the chemical shifts was  $\pm 0.025$  ppm.

1- and 5-Vinyltetrazoles were obtained according to the known procedures [12-14], respectively. 5-Vinyltetrazole was purified by recrystallization from an 1:1 chloroform-ethyl acetate mixture (mp 127.5°C). 5-Amino-1-vinyltetrazole was recrystallized from water (mp 158°C). 1-Vinyltetrazole [ $n_D^{20}$  1.5010, bp 94-96°C (66.7 Pa), mp 16°C], 5-vinyl-1-methyltetrazole [ $n_D^{20}$  1.5052, bp 94-95°C (66.7 Pa)], 5-vinyl-2-methyltetrazole [ $n_D^{20}$  1.4847, bp 56°C (930 Pa)], and 5-methyl-1-vinyltetrazole [ $n_D^{20}$  1.4914, bp 93-94°C (123 Pa)] were purified by vacuum distillation.

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#### STEREOCHEMISTRY OF NITROGENOUS HETEROCYCLES.

##### 61.\* SYNTHESIS AND CONFIGURATION OF AN EIGHTH ISOMER OF 2-METHYL-4-HYDROXYDECAHYDROQUINOLINE

G. S. Litvinenko and L. A. Voronenko

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Reduction of 1-benzoyl-2 $\alpha$ -methyl-4-oxo-cis-decahydroquinoline with sodium borohydride and sodium in alcohol has given 1-benzoyl-2 $\alpha$ -methyl-4 $\beta$ -hydroxy-cis-decahydroquinoline, which exists in the steroidal conformation with diaxial  $\alpha$ ,  $\alpha'$ -substituents in the piperidine ring and with an equatorial hydroxy-group. Debenzoylation of this has given the last of the eight theoretically possible isomers of 2-methyl-4-hydroxydecahydroquinoline, namely 2 $\alpha$ -methyl-4 $\beta$ -hydroxy-cis-decahydroquinoline, which exists in the nonsteroidal conformation with an axial hydroxy-group.

By reducing isomers of 2-methyl-4-oxodecahydroquinoline and its derivatives, we have previously obtained seven isomers of 2-methyl-4-hydroxyquinoline [2-6]. Three of the isomers of 2-methyl-4-oxodecahydroquinoline capable of existence (the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -isomers) and their N-benzoyl derivatives gave two epimeric alcohols each, and the fourth,  $\delta$ -isomer (2 $\alpha$ -methyl-4-oxo-cis-decahydroquinoline† in the form of its 1-benzoyl derivative (I), on hydrogenation over a nickel catalyst gave a single amidoalcohol (II) in 92% yield [3]. On heating this with benzoyl chloride followed by hydrolysis of the resulting benzoate, a seventh isomer of 2-methyl-4-hydroxyquinoline was obtained which existed in the nonsteroidal conformation (IIIa) with an equatorial hydroxy-group [7]. On the assumption at that time that the conformation of the amidoketone (I) was the same as in the alcohol (IIIa) (i.e., nonsteroidal (Ia)), we employed a method for the preparation of the epimeric alcohol (V) with an axial hydroxy-group which gives preferentially axial alcohols, namely reduction with aluminum isopropoxide (Barton's rule [8]). It was, however found that in this instance the same amidoalcohol (II) was obtained, in even greater (almost quantitative) yields [5].

The present article is devoted to the preparation of the final, eighth isomer of 2-methyl-4-hydroxydecahydroquinoline.

\*For communication 60, see [1].

†The trans- ( $\alpha$ -) and cis- ( $\beta$ -) dispositions of the substituents are relative to 9-H.

Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata 480100.  
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