PROOF OF THE STRUCTURE OF 1-TOSYL-5-(2'-NITROVINYL)IMIDAZOLE

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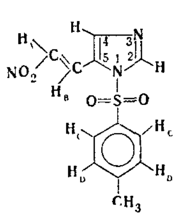
UDC 541.61:543.422.25:547.781

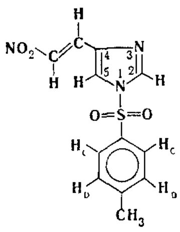
The structure of 1-tosyl-5-(2'-nitrovinyl)imidazole was established on the basis of its NMR spectrum [by means of tris(dipivaloylmethanato)europium as the "shift reagent"] and from the magnitude of the dipole moment.

1-Tosylformylimidazole and the products of its condensation with nitroparaffins are well known [1], but the position of the formyl group and, consequently, the nitroalkenyl groups has not been established. In this connection, we investigated the structure of 1-tosylnitrovinylimidazole.

In addition to signals that confirm the presence of tosyl and β-nitrovinyl groups, the PMR spectrum of the compound (Table 1) contains two signals that can be assigned to the H_2 and H_4 atoms of structure I or to the H_2 and H_5 atoms of structure II.



I



II

Inasmuch as the chemical shifts of H_2, H_4, and H_5 are close [3], while it is difficult to predict the effect of adjacent groups on them, it is impossible to choose between structures I and II on the basis of this spectrum.

TABLE 1. PMR Spectra

Protons	τ, ppm		Substrate/ $Eu(DPM)_3$ = 1,1
	in d_6-acetone	in $CDCl_3$	
CH_3	7,61	—	—
H_A*	2,13	2,41	3,21
H_B	2,21	2,50	1,65
H_C†	2,02	2,27	1,30
H_D	2,51	2,65	0,44
H_2 and H_4	1,71 and 1,88	2,02 and 2,14	3,08 and 3,06

*J_{AB} = 13.2 Hz, trans protons [2].

†J_{CD} = 8.5 Hz.

Using tris(dipivaloylmethanato)europium, $[Eu(DPM)_3]$, as a "shift reagent," we followed the appreciable weak-field shift of the signals ($\Delta\tau$) at 2.0-2.7 ppm.

Inasmuch as the nitrogen atom in the 3 position is more basic, the protons in the 2 and 4 positions should experience a greater shift (it is assumed [4] that the effect of the coordinated Eu ion is transmitted via a pseudocontact mechanism, the determining factors of which are the distance to the proton and the angle between the major axis of the molecule and the line connecting it with the lanthanide ion). Thus the shift of the H_2 signal is 28.3 ppm for 1-methylimidazone [5] for an equimolecular substrate-to-$Eu(DPM)_3$ ratio (as compared with 25 ppm for H_4 and 10 ppm for H_5).

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Novosibirsk Institute of Railroad Transportation Engineers. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 818-819, June, 1974. Original article submitted June 21, 1973.

Inasmuch as the signals at 2.02 and 2.14 ppm are shifted to an approximately equal extent, it can be assumed that we are dealing with structure I, in which the H_2 and H_4 protons are at about the same distances from N_3. The signal of the proton in the 5 position of structure II should experience considerably less of a shift as compared with the signal of the proton in the 2 position. The small shift in the H_2 and H_4 signals as compared with 1-methylimidazole [5] is explained by weakening of the basicity and, consequently, by a reduction in the capacity for complexing of the nitrogen atom in the 3 position through the two electron-acceptor substituents – the nitrovinyl group and the tosyl group. The reasons for the relatively large shift of the H_A signal are unclear.

The magnitude of the dipole moment (μ_{exp} 6.7 D, as compared with μ_{calc} 7.07 D for structure I and 5.89 D for structure II) also corresponds to structure I.

The establishment of the structure of 1-tosylnitrovinylimidazole proves that 1-tosyl-5-formylimidazole is formed by tosylation of 4(5)formylimidazole and that the nitropropenyl derivative obtained from it has the same orientation of the substituents.

EXPERIMENTAL

The PMR spectra were recorded with a Varian HA-100 spectrometer relative to hexamethyldisiloxane (HMDS). The spectra with $Eu(DPM)_3$ [6, 7] (10% solution in $CDCl_3$) were obtained with a Brucher – Fizik AG HX-90/8-15 spectrometer with homostabilization of the resonance conditions.

The following moments of the individual bonds and groups were used in the calculation of the dipole moments via a vector-additive scheme: $C_{sp3}-H$ 0.28, $C_{sp2}-H$ 0.70, $C_{sp3}-C_{sp2}$ 0.78 [8], NO_2 3.31 (calculated from the experimental dipole moment of nitrobenzene [9]), C =N 0.56, C =N 1.8 [10], S =O 3.76, C =S 0.44 [11], and C =O 2.3 D [12]. The geometrical parameters of pyrazole [13] were used.

The dielectric permeabilities of benzene solutions were determined at 25° by the heterodyne method with a Tangens apparatus. The orientation polarization was calculated by the Guggeneheim–Smith method [14] with α 16.44, γ 0, and $P_{exp\,\infty}$ 917.19.

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