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STABLE 1-ALKOXYAZIRIDINE INVERTOMERS

(Isolation by preparative GLC methods)

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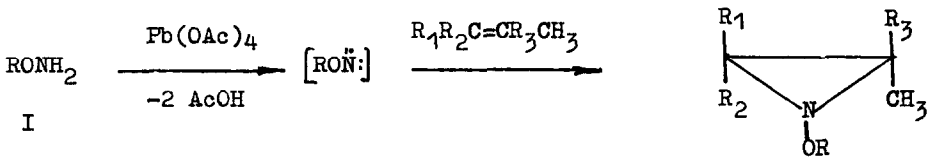
The possibility of O-nitrene addition to olefins was shown recently[1] when methoxyamine was oxidised in presence of tetramethylethylene. Quantum chemistry calculations of simple O-nitrene electronic structures[2] proved the structure and reactivity to be similar to those of carbenes. To use the O-nitrene addition to the double bond to yield earlier unknown 1-alkoxyaziridines appeared quite promising in the light of the similarity. Oxidation of methoxy-, ethoxy-, and isopropoxy- amines (1 a-c) with lead tetraacetate in presence of 2-methylpropene-1, trans-butene-2, 2-methylbutene-2, and 2,3-dimethylbutene-2 was studied, respective 1-alkoxyaziridines (II-Va-c)*



I

a) R = CH_3

b) R = C_2H_5

c) R = i-C_3H_7

II $R_1 = R_2 = H$, $R_3 = CH_3$

III** $R_1 = CH_3$, $R_2 = R_3 = H$

IV*** $R_1 = R_2 = CH_3$, $R_3 = H$

V $R_1 = R_2 = R_3 = CH_3$

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* All new compounds had correct elemental analyses (%N) and infrared and NMR spectra were consistent with assigned structures.

** Addition to trans-butene-2 was at least 95% stereospecific.

*** Mixture of stereoisomers.

being obtained in all cases. Gas chromatography data indicated 9-35% yield of the aziridines.

NMR methods were used to reveal the aziridine structures. NMR spectra of 1-alkoxy-2,2,3,3-tetramethylaziridines (Va-c) showed signals of alkoxyl groups at 3.4-3.8 δ and 1.02-1.06 δ as well as singlets in the range of 1.00-1.12 δ originating from the two geminal dimethyl groups. 1-Alkoxy-2,2,3-trimethylaziridines (IVa-c) were mixtures of two stereoisomers which did not convert into each other at room temperature. The mixtures were separated by GLC procedures (a 4 m column with diaphorite and 10% span-80) and yielded 85-100% samples of each of the stereoisomers with stable pyramid nitrogen. The isolation of two such invertomers from mixtures had been performed in the case of 1-chloro-2-methylaziridine only[3-5].

The following arguments served to determine configurations of the obtained stereoisomeric 1-alkoxyaziridines (IVa-c) with NMR spectral data:

1. Chemical shifts of the geminal dimethyl groups of the samples were compared with the previously reported data for simple aziridines (see Table 1). The comparison showed that only dimethyl- and one of the stereoisomeric trimethyl- derivatives originated signals of weakly shielded methyl protons at $\approx$1.2 δ. Shielding conditions of the 2,2-dimethylaziridine methyl groups at 1.2 δ were found similar to those of 1,2,2-trimethylaziridine methyl groups trans-oriented with respect to the substituent at the N-atom, 1-methoxy-2,3-trans-dimethylaziridine (IIIa) and 1-methoxy-2,2-dimethylaziridine (IIa) as well as of "d"-groups in the 1-alkoxy-2,2,3-trimethylaziridine syn-forms*. The conclusion allowed to assign signals of the range of 1.16-1.26 δ to the methyl groups cis-oriented with respect to the protons of the aziridine ring and the lone-pairs of nitrogen. On the same grounds isomeric 1-alkoxy-2,2,3-trimethylaziridines originating such signals were considered syn-forms. Thus the latter's signals at 0.96-1.05 δ were assigned to geminal methyls cis-oriented with respect to the substituent at the N atom. Hence alkoxyl groups at the N atom and methyls shield the adjacent cis-oriented methyl groups stronger than

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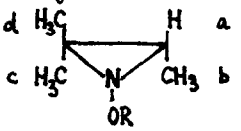
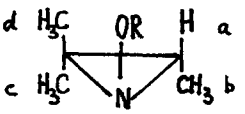
* The terms of syn and anti were used after the analogy of those of stereoisomeric cyclopropanes [6].

lone-pairs of nitrogen.

TABLE 1

Chemical Shifts of the Geminal Dimethyl Group in Aziridines*

Aziridines	δ, ppm		
2,2-dimethylaziridine [7]	1.20		
1,2,2-trimethylaziridine [8]	1.05	and	1.16
1-methoxy-2,2-dimethylaziridine (IIa)	1.01	and	1.26
1-methoxy-2,3-trans-dimethylaziridine (IIIa)	1.03	and	1.22
1-alkoxy-2,2,3-trimethylaziridines (IVa-c)			
 syn-form	0.96-1.02	and	1.20-1.26
 anti-form	1.00-1.04	and	1.02-1.09
1-alkoxy-2,2,3,3-tetrametylaziridines (Va-c)	1.03-1.05	and	1.09-1.12

* Spectrometer VARIAN - HA 100; internal standard HMDS

2. Since chemical shifts of methyl group doublets of stereoisomeric trimethylderivatives differed by 0.05-0.07 ppm (anti: δ 1.08-1.10, syn: 1.01-1.05) because of different shielding by alkoxyls and by lone-pair nitrogen, the isomer originating a doublet at a smaller δ might be considered a syn-form. This was confirmed by comparison with the geminal dimethyl signals.

All the isomers which the syn-configuration was assigned to, had shorter retention time. GLC data showed that anti : syn ratio increased from 1.1 to 1.5 as we passed from methoxy- to isopropoxy- aziridine (IVa-c). It might be regarded a result of important steric hindrances due to the isopropyl group. It also confirmed the NMR spectral determination of the invertomers con-

figuration as there was no evidence to suppose the content of the more hindred syn-isomer to increase as the size of the substituent at the sextet nitrogen of O-nitrenes becomes greater.

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