FORMATION OF NITROGEN HETEROCYCLES IN REACTIONS OF O-NITRENES. STRUCTURES AND PROPERTIES OF ALKOXYAZIRIDINES (REVIEW)

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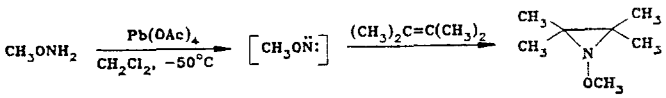
The results of research on the synthesis of 1-alkoxyaziridines and 1-alkoxypyrrolines with the hypothetical participation of O-nitrenes generated by oxidation of o-alkylhydroxylamines are correlated.

The chemistry of carbenes and nitrenes is attracting the attention of researchers because of the great synthetic possibilities: the diversity of the products of the reactions, many of which lead to heterocycles, and the isomeric transformations of these unstable intermediate particles [1-9]. The formation of heterocyclic compounds in the addition of carbenes to the carbon—heteroatom double bond was described in [2, 3], and the reactions of C-nitrenes with unsaturated compounds that lead to five-membered nitrogen-containing rings were examined in [1, 4-6]. Reviews [7, 9] and individual sections of a monograph [8] devoted to the chemistry of N-nitrenes correlate data on the participation of aminonitrenes in the formation of heterocyclic systems. However, the role of O-nitrenes in similar syntheses of heterocyclic compounds has not been examined, although a rather large number of studies, the results of which are set forth in the present review, have been devoted to this problem.

Among the processes that lead to an aziridine ring, the addition of O-nitrenes to the C=C bond is of greatest interest. This reaction takes on special significance, since it leads to 1-alkoxyaziridines that have a stable (at room temperature) nitrogen pyramid.

In 1970 1-methoxy-2,2,3,3-tetramethylaziridine (Ia) was obtained in 30% yield in the oxidation of methoxyamine with lead tetraacetate in the presence of 2,3-dimethyl-2-butene [10].



Ia

This was the first example of the synthesis of a pyramidally stable 1-alkoxyaziridine, in the formation of which, according to the assumption of Brois [10], an intermediate methoxynitrene participated.

The structure of the aziridine obtained was proved on the basis of the set of spectral data (IR, PMR, and mass-spectral). In addition to the signal of a methoxy group (3.36 ppm), the PMR spectrum contained two singlets of nonequivalent methyl groups with δ 1.04 and 0.97 ppm. It was found that merging of the resonance signals does not occur even when the temperature is raised to 130°C, while at 20°C the nitrogen atom in alkoxyaziridines exists in the form of stable pyramids that have a significant barrier to inversion ($\Delta G^{\neq}$ = 92 kJ/mole) [11].

1-Ethoxy- (Ib) [12,13], 1-isopropoxy- (Ic) [12], and 1-butoxy-2,2,3,3-tetramethylaziridine (Id) [14, 15] were obtained somewhat later by oxidation of the corresponding O-alkylhydroxylamines with lead tetraacetate in a fivefold excess of 2,3-dimethyl-2-butene. The preparative yields of Ia-d ranged from 27% to 45%, depending on the radical of the alkoxy group. It is interesting that the simplest nitrogen analog of O-nitrenes — dimethylaminonitrene — does not add at all to 2,3-dimethyl-2-butene but is stabilized by dimerization with the formation of tetramethyltetrazene [16].

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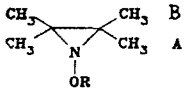
TABLE 1. Physical Properties of Aziridines I-III

Aziridine	bp, °C (mm Hg)	d_4^{20}	n_D^{20}	n_C^{20}	Δ_{FC}	ω_{FCD}	μ_D	Literature
Ia	97...98 (766)	0,8407	1,4194	1,4159	87,7	20,8	1,42	[12, 15]
Id	62...64 (32)	0,8499	1,4292	1,4269	80,1	18,6	—	[15]
IIa	—*	0,8896	1,4111	1,4089	78,0	18,6	1,50	[13, 15]
IIIa	—*	0,8885	1,4166	1,4143	79,7	19,1	1,44	[13, 15]

*Isolated by preparative GLC.

TABLE 2. PMR Spectra of 1-Alkoxy-2,2,3,3-tetramethylaziridines



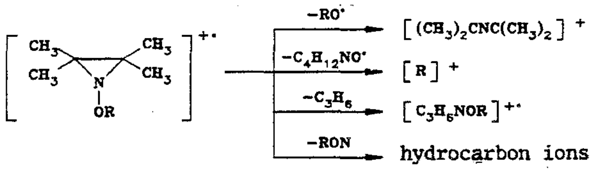
Aziridine	Chemical shifts (in CCl_4), δ, ppm (J, Hz)			Literature
	A, s	B, s	R	
Ia	0,97	1,04	3,36 s	[10]
	1,05	1,09	3,40 s	[13]
	1,09	1,11	3,40 s	[15]
Ib	1,06	1,09	1,06t (7); 3,64 q (7)	[13]
Ic	1,03	1,06	1,05d (6); 3,81 sept (6)	[13]
Id	1,15	1,19	0,7...1,8 m; 3,65t (6)	[14]
	1,13	1,16	0,7...1,8 m; 3,63t (6)	[15]

The physical constants (Table 1) of the synthesized aziridines have been determined, the IR [12-14], PMR [13-15, 17] and mass spectra [15] have been measured, and the Kerr constant has been determined for the simplest representative Ia [18]. The data on the relative dispersion of alkoxyaziridines correspond to the ω_{FCD} values of small carbon rings (cyclopropanes and cyclobutanes). The virtually identical values of the dipole moments for tetra- and trimethyl-substituted 1-methoxyaziridines constitute evidence for the absence of a substantial polar contribution of the methyl groups.

In all of the Ia-d the pyramidal stability of the nitrogen atom is confirmed by the nonequivalence of the geminal methyl groups, which is manifested in the development of two singlets with a difference of 0.02-0.06 ppm in the chemical shifts (Table 2). The assignment of the signals was made on the basis of an analysis of the data for N-alkyl-, amino-, and haloaziridines with different degrees of substitution with the assumption of the greater shielding effect of the alkoxy group as compared with the unshared electron pair of the nitrogen atom [13, 17].

The IR spectra of alkoxyaziridines are not very informative, since the weak bands of vibrations of the aziridine ring lie at 1220-1260 cm^{-1} and 885-920 cm^{-1}.

Somewhat greater information regarding the structures and stabilites of aziridines Ia-d is given by their behavior upon electron impact [15]. The principal fragmentation pathway is cleavage of the labile N—O bond with the formation of an ion with m/z 98 [10, 14, 15].



The $[M - OR]^+$ ions have the maximum intensity, and their contribution to the total ion current reaches 40%. These ions are characteristic for 1-alkoxyaziridines with different degrees of substitution and can be used for mass-fragmentographic identification.

TABLE 3. Homologous Groups and Spectra of Ionic Series of Alkoxyaziridines, Alkenylalkoxyaziridines, Alkoxypyrrolines, and Oxime Ethers [19]

Homologous series	Empirical formula	Group No.	Spectrum of the ionic series
Alkyl-1-alkoxyaziridines	$C_nH_{2n+1}NO$	1	40_{10}, 28_{11}, 5_3, 5_4, 2_2, 0, 0, 0, 0, 0, 0, 2_1, 2_1, 16_3
Aldoxime ethers	$C_nH_{2n+1}NO$	3	16_6, 33_{13}, 12_5, 13_9, 6_4, 0, 0, 0, 0, 0, 0, 2_1, 1_1, 17_5
Ketoxime ethers	$C_nH_{2n+1}NO$	3	23_8, 24_{13}, 11_4, 22_{10}, 6_4, 0, 0, 0, 0, 0, 0, 1_1, 2_1, 11_2
Alkenyl-1-alkoxyaziridines	$C_nH_{2n-1}NO$	1	15_8, 7_1, 2_1, 0, 0, 0, 0, 1_1, 0, 5_3, 4_2, 17_2, 28_4, 21_5
1-Alkoxy-3-pyrrolines	$C_nH_{2n-1}NO$	1	32_9, 21_4, 2_1, 1_1, 0, 1_1, 0, 0, 0, 1_1, 5_2, 12_4, 13_5, 12_4

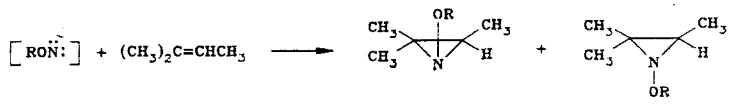
TABLE 4. Ratios of the Retention Times of the Invertomers II/III of 1-Alkoxy-2,2,3-trimethylaziridines with Columns with Different Sorbents

II/III	R	Span-80	Apiezon L	Polyox-100	SE-30
IIa/IIIa	CH_3	0,79	0,83	0,76	0,86
IIb/IIIb	C_2H_5	0,83	0,87	0,73	0,87
IIc/IIIc	C_3H_7	0,79	0,83	0,74	0,85
IId/IIId	*iso*-C_3H_7	0,82	0,88	—	0,89
IIe/IIIe	C_4H_9	0,79	0,87	0,84	0,87
IIf/IIIf	*iso*-C_4H_9	0,78	0,84	0,79	0,86
IIg/IIIg	*sec*-C_4H_9	0,77	0,84	0,75	0,88

In chromatographic mass-spectrometric analysis of complex reaction mixtures alkoxyaziridines are reliably identified from the spectra of ionic series [19], which are characterized by constancy for compounds of the same homologous series and differ substantially from the spectra of other possible components of the reaction mixtures (see Table 3).

Attempts to predict the reactivities of nitrenes on the basis of quantum-mechanical calculations of the simplest hydroxynitrenes were unsuccessful, since the results obtained by different methods were ambiguous and did not make it possible to draw a definite conclusion regarding the chemical character of these intermediate particles [20-23]. According to calculations by Hayes and coworkers [23] O-nitrenes have a singlet ground state and, like carbenes, should add stereospecifically to olefins.

The use of 2-methyl-2-butene as a trap for O-nitrenes made it possible to synthesize stable syn and anti invertomers of 1-alkoxy-2,2,3-trimethylaziridines (IIa-g and IIIa-g, respectively) [12, 13, 15, 17, 24].



IIa-g IIIa-g

II, IIIa R=CH_3, b R=C_2H_5, c R=C_3H_7, d R=*iso*-C_3H_7, e R=C_4H_9, f R=*iso*-C_4H_9, g R=*sec*-C_4H_9

Individual invertomers II and IIIa-c were isolated by preparative GLC [13, 15, 17]. Their structures were confirmed by PMR spectroscopic data using the Overhauser effect to establish the absolute configuration [13, 17, 24]. The refractive indexes, densities, and dipole moments have been measured for aziridines IIa and IIIa, and the molecular refractions and relative dispersions have been determined.

The physical constants of the invertomers are close (Table 1), while the refractive indexes, which are a little higher for the anti isomers than the indexes for the syn forms, differ more appreciably [13, 15, 17]. The dipole moments and Kerr constants have been determined to establish the polarity and anisotropy of the polarizability of the N—O bond,

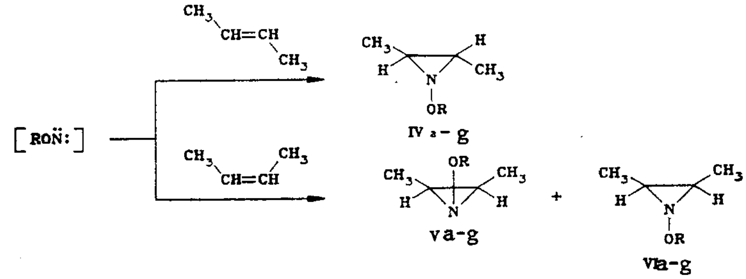
TABLE 5. Yields of 1-Alkoxyaziridines As a Function of the Structures of the Olefins $R^1R^2C{=}CR^3R^4$

R^1	R^2	R^3	R^4	Yield, %
CH_3	CH_3	CH_3	CH_3	27...45
CH_3	CH_3	CH_3	H	14...43
cis- trans- CH_3	H	CH_3	H	7...23

which could give an independent assignment of the configurations of the invertomers. However, the measured dipole moments virtually coincide, whereas the data on the parameters of polarizability of the aziridine ring were insufficient for the solution of the problem of the configurations [18]. The observed slight differences in the intensities of the peaks of the stereoisomeric aziridines exclude the possibility of the mass-spectral identification of the syn and anti invertomers [15].

The ratios of the retention times of the syn and anti forms of the aziridines IIa-g/IIIa-g in the case of chromatography under isothermal conditions with columns with different sorbents, the constancy of which makes it possible to use them for the configurational assignment of the invertomers, have been determined (Table 4). In all cases of oxidation of O-alkylhydroxylamines the C(1)—C(4) invertomers are formed in approximately equal amounts, and their ratios are virtually independent of the volume of the alkoxy group, although the overall content of aziridines in the reaction mixtures ranges from 43% to 14% on passing from methoxynitrene to butoxynitrene.

The stereochemical aspects of the reactions are extremely valuable for the solution of the problem of the existence of O-nitrenes and the characteristics of their reactivities. The addition of alkoxynitrenes to stereoisomeric 2-butenes has been studied to ascertain the stereochemistry of the closing of the aziridine ring [13-15, 24-28].

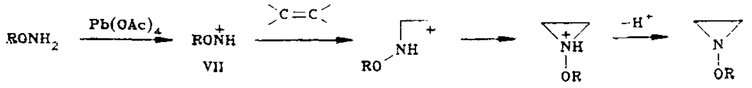


IV—VI a $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$, d $R=iso\text{-}C_3H_7$, e $R=C_4H_9$, f $R=iso\text{-}C_4H_9$, g $R=sec\text{-}C_4H_9$

The oxidation of methoxyamine with lead tetraacetate in the presence of trans-2-butene led to the formation of IVa, whereas aziridines Va and VIa with a cis orientation of the methyl substituents with respect to the plane of the ring were obtained in cis-2-butene as the medium. All three isomeric aziridines were isolated by preparative GLC [15, 17, 26, 28]. Proton magnetic resonance spectroscopy and the Overhauser nuclear effect (ONE) were used to prove their configurations [17, 14]. In addition to a singlet of a methoxy group (δ 3.42 ppm) and a multiplet of ring protons (1.40-1.62 ppm), two identical doublets of a nitrogen atom shielded differently by the methoxy group and the unshared electron pair at 1.05 and 1.26 ppm (J = 5 Hz) were observed in the PMR spectrum of IVa. A 12 ± 0.5% increase in the intensity of the doublet with the lower chemical shift was observed in the case of saturation of the methoxy group by its resonance frequency, and the signal at 1.26 ppm was therefore ascribed to the methyl group that is anti-oriented with respect to the methoxy group. In addition to identical signals of the methoxy group and the ring protons, in the spectra of Va and VIa there was only one doublet (1.05 and 1.13 ppm), each of which corresponded to six protons. In analogy with the spectrum of IVa the weak-field signal (1.13 ppm) was assigned to a methyl group in an anti orientation with respect to the methoxy group. Aziridines Va and VIa retain the configuration of the starting olefin and are invertomers of

1-methoxy-cis-2,3-dimethylaziridine. The structure of the anti invertomer was assigned to aziridine VIa, which has relatively weakly shielded signals of methyl groups.

The stereospecificity of this reaction is retained over the entire series of $C_{(1)}-C_{(4)}$ alkoxynitrenes; this is in agreement with the conclusion of Hayes and coworkers [20, 23] regarding the singlet ground state of O-nitrenes (under the condition of the applicability of the Skell postulate to nitrenes) but conflicts with the results of experiments by these researchers on the oxidation of butoxyamine with lead tetraacetate in the presence of stereoisomeric 2-butenes [14]. The oxidation of O-butylhydroxylamine led to the formation of two isomeric products (with a different ratio for the cis and trans-2-butene), to which they assigned the structures of stereoisomers IVe and VIe on the basis of the IR and mass spectra. It was concluded that the addition is nonstereospecific, and the hypothesis of the formation of alkoxynitrenium ion VII, which participates in the closing of the aziridine ring via the following scheme, was advanced:



Ioffe and coworkers [25], in repeating the experiments in [14] under identical conditions, used chromatographic mass-spectrometric analysis and mass fragmentography for monitoring and selected conditions for the complete chromatographic separation of stereoisomers IVa-VIa. As a result of the experiments it was demonstrated that there is no basis for denying the participation of O-nitrenes in this process, since the reaction proceeds strictly stereospecifically [25], while the product that was assumed to be the stereoisomeric aziridine in [14] is its structural isomer — butyraldehyde O-butyloxime. As regards the formation of oxime alkyl ethers VIII in the synthesis of aziridines from olefins and alkylhydroxylamines, they are obtained as a result of migration of a radical from the oxygen atom to the nitrogen atom in a molecule of the intermediate nitrene [29-31].

$$\left[RR'CHO\ddot{N}:\right] \xrightarrow{1,2\sim RR'CH} RR'CHN{=}O \xrightarrow{1,3\sim H} RR'C{=}N{-}OH$$

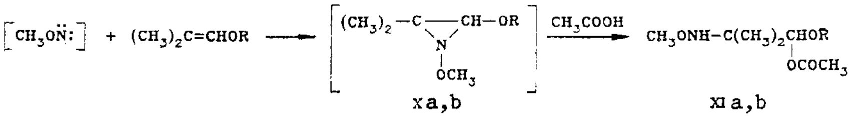
$$RR'C{=}N{-}OH + RR'CHONH_2 \longrightarrow \underset{VIII}{RR'C{=}NOCHRR'}$$

The formation of similar products was previously observed in the oxidation of aryl-substituted hydroxylamines [14, 32]. However, if the structure of the resulting nitroso compound excludes the possibility of rearrangement to an oxime, oxidation leads to dimer IX of the nitroso compound [31].

$$(CH_3)_3CONH_2 \xrightarrow[CH_2Cl_2,\ -45^\circ C]{Pb(OAc)_4} \underset{IX}{\left[(CH_3)_3CN{=}O\right]_2}$$

The tendency of nitrenes to undergo rearrangement increases with an increase in the length of the chain and the volume of the radical of the alkoxy group [31, 33]. The yields of the products of 1,1-cycloaddition of O-nitrenes to the double bond of an olefin decrease in the order tetra- > tri- > dimethylethylene and on passing from methoxy- to butoxynitrene. The yields of 1-alkoxyaziridines in this reaction are evidently determined both by the nucleophilicity of the multiple bond and the tendency of the alkoxynitrene to undergo intramolecular rearrangement (Table 5).

In an attempt to add methoxynitrene to the double bound of vinyl ethers, which have greater nucleophilicity as compared with olefins, cyclic products were not isolated, probably as a consequence of the facile opening of the dialkoxyaziridine ring of X under the influence of acetic acid [34].

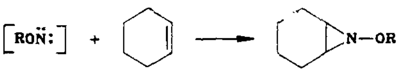


xa,b   xIa,b

X, XI a $R{=}CH_3$, b $R{=}C_2H_5$

The yields of the corresponding acetates XI (up to 60%) exceeded the yields of alkoxyaziridines in similar reactions; this is in agreement with the assumption of the more effective capture of O-nitrenes by vinyl ethers.

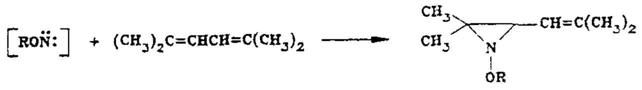
In contrast to carbenes and aminonitrenes, alkoxynitrenes were found to be quite inert with respect to an endocyclic double bound, and the yields of 7-alkoxyazabicyclo[4.1.0]-heptanes XII did not exceed 40% even with a tenfold excess of cyclohexene [35].



XIIa-d

XIIa $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$, d $R=C_4H_9$

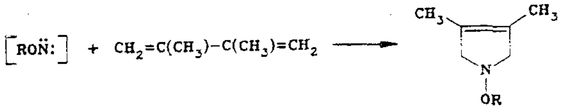
Nitrogen-containing heterocyclic compounds that correspond in molecular mass to a 1:1 adduct of the nitrene and its acceptor are formed in the oxidation of a mixture of the O-alkylhydroxylamine and a diene hydrocarbon. The only products of the reaction of alkoxynitrenes with 2,5-dimethyl-2,4-hexadiene are aziridines XIIIa-d, the structures of which were reliably established from the mass spectra of ionic series (Table 3) [19, 35, 36].



XIII a-d

XIII a $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$, d $R=C_4H_9$

On passing to unsymmetrically substituted 2,4-dimethyl-2,4-pentadiene, in addition to the principal reaction products, viz., the corresponding aziridines, isomeric (with respect to the unsaturated aziridines) compounds, to which 3-pyrroline structures were assigned on the basis of the mass spectra, were detected [19, 35, 36]. The latter proved to be the chief components in the oxidation of alkylhydroxylamines in excess 2,3-dimethyl-1,3-butadiene [35]:



XIV a-d

XIV a $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$, d $R=C_4H_9$

The formation of pyrroline XIVd under similar conditions was previously observed [14]; however, no details regarding the isolation, characteristics, and proof of the structure of the reaction product were presented. Products of addition of O-nitrenes to both bonds of the conjugated system of the diene were not observed in any of the investigated examples.

Attempts to add O-nitrenes to carbon—carbon multiple bonds of 2-methyl-2-buten-4-yne were unsuccessful because of the facile oxidation of the enyne hydrocarbon under the reaction conditions.

Information regarding the addition of alkoxynitrenes, direct evidence for the existence of which is not yet available (evidence was recently obtained for aminonitrenes [37]), is limited to what we have presented above. However, the reactions examined are of interest as a method for the synthesis of nitrogen-containing heterocycles that are difficult to obtain by other methods.

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