over ice, and the aqueous mixture was extracted with ether. The ether extract was washed successively with water, sodium bicarbonate solution, and water and dried with magnesium sulfate. The ether was removed by distillation, and the residual oil was recrystallized from petroleum ether (bp 70°) to give 2.8 g (70%) of a product with mp 94-95°. Found: Cl 9.7; S 17.7%. $C_{17}H_{20}ClNO_2S_2$. Calculated: Cl 9.6; S 17.3%.

5-Tosylamino-4-thiocyanato-2,3-tetramethylenethiophene (XVIII). This compound, with mp 117-118° (from methanol), was obtained in 69% yield by the method described in [2]. Found: C 52.4; H 4.4; N 7.4; S 26.6%. $C_{16}H_{16}N_2O_2S_3$. Calculated: C 52.4; H 4.4; N 7.6; S 26.8%.

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ACETYLENIC α-AZIRIDINOCARBINOLS AND THE MECHANISM OF THEIR CONVERSION TO β-AZIRIDINOACROLEINS

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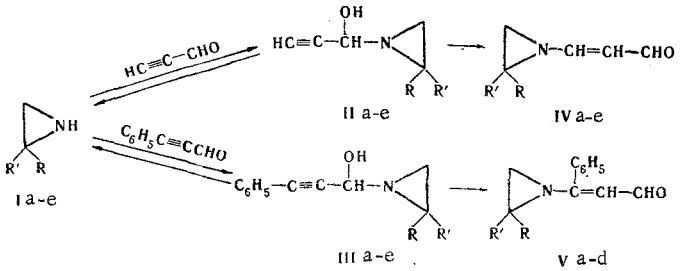
UDC 547.717:543.422.25.4

Acetylenic α-aziridinocarbinols were obtained by reaction of propiolaldehyde and phenylpropiolaldehyde with aziridine and its 2-substituted derivatives. The mechanism of the conversion of the latter to β-aziridinoacroleins was studied.

It is known [1-6] that aziridine and its 2-alkyl-substituted derivatives react with aliphatic and aromatic carbonyl compounds to give aziridinocarbinols, whereas only 3,4-addition products have been obtained up until now with α-unsaturated oxo compounds [5-7].

On the basis of PMR and IR spectroscopic studies we have established that α-aziridinocarbinols IIa-e and IIIa-e (Tables 1 and 2) are formed in 60-80% yields in the reaction of propiolaldehyde and phenylpropiolaldehyde with aziridines Ia-e at reduced temperature.



I-V a R = R′ = H; b R = H, R′ = CH_3; c R = R′ = CH_3; d R = H, R′ = C_2H_5; I-IV e R = H, R′ = $COOCH_3$

α-Aziridinocarbinols IIa-e and IIIa-e are colorless crystalline substances that at room temperature in both solutions and in the crystalline state undergo rearrangement to β-aziridinoacroleins IVa-e and Va-d, which exist in the form of cis-trans isomers in a ratio of 1:2.3 (Tables 3 and 4). The rate of isomerization

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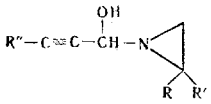
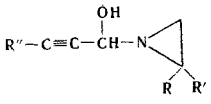
TABLE 1. Physicochemical Characteristics of IIa-e and IIIa-e



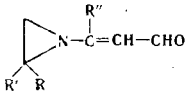
Compound	R	R′	R″	Characteristic frequencies in the IR spectra, cm^{-1}				mp, °C	Yield, %
				$\nu_{C\equiv C}$	ν_{O-H}	$\nu_{C=O}$	$\nu_{\equiv CH}$		
IIa	H	H	H	—	—	—	—	—	72
IIb	H	CH_3	H	2115	3190	—	3250	40—41	78
IIc	CH_3	CH_3	H	2115	3180	—	3245	33—34	75
IId	H	C_2H_5	H	2120	3180	—	3245	52—53	80
IIe	H	$COOCH_3$	H	2130	3150	1728	3290	74—76	85
IIIa	H	H	C_6H_5	2200 2230	3130	—	—	46—48	72
IIIb	H	CH_3	C_6H_5	2195 2230	3170	—	—	57—59	61
IIIc	CH_3	CH_3	C_6H_5	2195 2235	3100	—	—	71—73	70
IIId	H	C_2H_5	C_6H_5	2200 2245	3160	—	—	75—77	65
IIIe	H	$COOCH_3$	C_6H_5	2200 2230	3220	1738	—	82—84	84

TABLE 2. PMR Spectra of IIb, d and IIIa-d



Compound	R	R′	R″	Chemical shifts, τ, ppm					
				CH	OH	CH_2	R	R′	R″
IIb	H	CH_3	H	5,57 d 5,70 d	3,9 bs	8,0—8,3m	7,9 m	8,77 d	7,58 d
IId	H	CH_2CH_3	H	5,73 d 5,63 d	3,7 bs	8,1—8,4m	8,1—8,4 m	8,6 (CH_2) m 8,97 (CH_3) t	7,58 d
IIIa	H	H	C_6H_5	5,94 s	3,7 bs	8,25 s	8,25 s	8,25 s	2,6—2,8 m
IIIb	H	CH_3	C_6H_5	5,36 s 5,40 s	3,5 bs	8,1—8,5m	8,1—8,5 m	8,75 d	2,6—2,8 m
IIId	H	CH_2CH_3	C_6H_5	5,62 s 5,48 s	3,9 bs	8,1—8,4m	8,1—8,4 m	8,6 (CH_2) m 8,97 (CH_3) t	2,6—2,8 m
IIIc	CH_3	CH_3	C_6H_5	5,50 s	3,7 bs	8,6 s	8,85 s	8,85 s	2,6—2,8 m

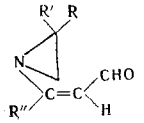
TABLE 3. Physicochemical Characteristics of β-Aziridinoacroleins IVa-e and Va-d

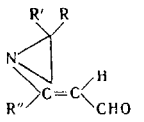


Compound	R	R′	R″	bp, °C (10^{-2} mm)	Found, %			Empirical formula	Calc., %			IR spectra, cm^{-1}	
					C	H	N		C	H	N	$\nu_{C=C}$	$\nu_{C=O}$
IVa	H	H	H	30—32	61,4	7,5	14,5	C_5H_7NO	61,8	7,2	14,4	1615	1670
IVb	H	CH_3	H	43—45	64,5	8,1	13,0	C_6H_9NO	64,9	8,1	12,6	1620	1680
IVc	CH_3	CH_3	H	50—53	66,9	8,7	11,3	$C_7H_{11}NO$	67,2	8,8	11,5	1610	1665
IVd	H	C_2H_5	H	55—58	66,8	8,8	11,2	$C_7H_{11}NO$	67,2	8,8	11,5	1615	1675
IVe	H	$COOCH_3$ H	H	60—62	53,9	6,1	9,4	$C_7H_9NO_3$	54,2	5,8	9,0	1625	1680 1750
Va	H		C_6H_5	77—80	76,7	6,7	8,4	$C_{11}H_{11}NO$	76,3	6,4	8,1	1595	1665
Vb	H	CH_3	C_6H_5	80—82	76,6	6,5	7,9	$C_{12}H_{13}NO$	77,0	6,9	7,5	1595	1665
Vc	CH_3	CH_3	C_6H_5	82—85	77,7	7,3	7,3	$C_{13}H_{15}NO$	77,5	7,5	7,0	1595	1665
Vd	H	C_2H_5	C_6H_5	87—89	77,8	7,3	7,0	$C_{13}H_{15}NO$	77,5	7,5	7,0	1595	1665

depends markedly on the character of the substituents both in the acetylenic and aziridine fragments of the molecules of IIa-e and IIIa-d. The aziridinocarbinols of phenylacetylene series IIIa-e are considerably more stable than derivatives IIa-e. In particular, IIa exists only at low temperature (from −10 to −20°C). The stabilities in solution of aziridinocarbinols IIe and IIIe, with an electron acceptor carbomethoxy group, are considerably lower than the stabilities of IIb-d and IIIb-d, which contain electron-donor substituents (alkyl groups) in the aziridine ring. We therefore were unable to record the PMR spectra of aziridinocarbinols IIe and IIIe.

TABLE 4. Parameters of the PMR Spectra of β-Aziridinoacroleins IVa-e and Va-d


cis

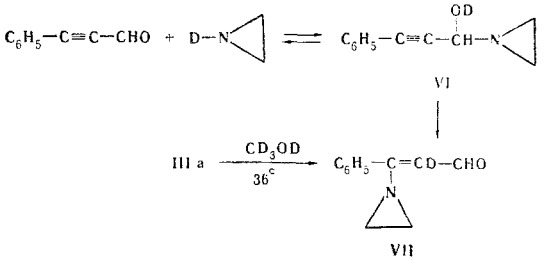

trans

Compound	R	R′	R″	Isomer	Chemical shifts, τ, ppm						SSCC	
					=CH	CHO	CH_2	R	R′	R″	=CHCHO	HC=CH
IVa	H	H	H	cis	4,80	−0,10	7,84 s	7,84 s	7,84 s	3,09 d	7,8	8,5
				trans	4,48	0,74	7,93 s	7,93 s	7,93 s	2,74 d	7,8	13,1
IVb	H	CH_3	H	cis	4,68	−0,03	7,8—8,2 m	7,7 m	8,64 d	3,12 d	7,3	7,6
				trans	4,40	0,64	7,8—8,2 m	7,7 m	8,68 d	2,72 d	7,8	13,0
IVc	CH_3	CH_3	H	cis	4,69	0,10	7,86 s	8,70 s	8,70 s	3,10 d	7,3	7,4
				trans	4,44	0,65	8,00 s	8,70 s	8,70 s	2,70 d	7,5	12,9
IVd	H	C_2H_5	H	cis	4,75	−0,02	7,8—8,2 m	7,7 m	8,96 (CH_3) t 8,2 (CH_2) m	3,14 d	7,2	7,5
				trans	4,43	0,70	7,8—8,2 m	7,7 m	8,96 (CH_3) t 8,4 (CH_2) m	2,73 d	8,0	13,0
IVe	H	$COOCH_3$	H	cis	4,50	0,02	7,62 m 7,50	7,10 q	6,28 s	3,14 d	6,0	8,0
				trans	4,34	0,62	7,62 m 7,50	7,10 q	6,25 s	2,58 d	7,8	13,0
Va	H	H	C_6H_5	cis	4,27	−0,15	7,73 s	7,73 s	7,73 s	2,6 m	7,3	—
				trans	4,38	0,57	7,95 s	7,95 s	7,95 s	2,6 m	8,0	—
Vb	H	CH_3	C_6H_5	cis	4,37	−0,10	7,8—8,1 m	7,7 m	8,70 d	2,6 m	7,6	—
				trans	4,43	0,64	7,7—8,1 m	7,7 m	8,86 d	2,6 m	7,8	—
Vc	CH_3	CH_3	C_6H_5	cis	4,36	0,01	7,73 s	8,83 s	8,83 s	2,6 m	8,0	—
				trans	4,52	0,58	7,95 s	8,94 s	8,94 s	2,6 m	8,1	—
Vd	H	C_2H_5	C_6H_5	cis	4,33	−0,15	7,8—8,2 m	7,8 m	9,06 (CH_3) t 8,6 (CH_2) m	2,6 m	7,6	—
				trans	4,40	0,55	7,8—8,2 m	7,0 m	9,12 (CH_3) t 8,6 (CH_2) m	2,6 m	8,0	—

When IIe is dissolved in CCl_4 it undergoes isomzerization to β-aziridinoacrolein IVe, whereas aziridinocarbinol IIIe undergoes decomposition to the starting components. It is interesting that aziridinocarbinols IIe and IIIe in the crystalline state are characterized by the maximum stabilities in the corresponding series IIa-d and IIIa-d. This is evidently associated with the presence of intermolecular hydrogen bonds between the oxygen atom of the carbomethoxy group and the hydrogen atom of the hydroxyl group in the crystalline state of IIe and IIIe.

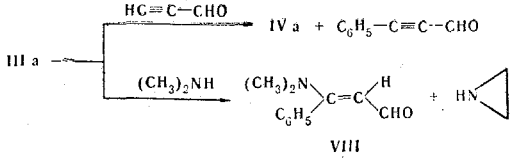
Carbinol VI, formed in the reaction of N-deuteroaziridine with phenylpropiolaldehyde, undergoes isomerization to acrolein VII. The latter was also obtained by isomerization of aziridinocarbinol IIIa in deuteromethanol.

During a study of the mechanism of the isomerization by PMR spectroscopy we established that the rate of isomerization of IIIa to Va in various solvents is constant and corresponds to a zero-order reaction. The isomerization rate constants at 36° were determined: $K_{CH_3Cl} = 2.90\ min^{-1}$, $K_{C_2H_5OH} = 2.85\ min^{-1}$, and $K_{CH_3CN} = 2.80\ min^{-1}$.



It might be assumed that the isomerization of aziridinocarbinols IIa-e and IIIa-d to β-aziridinoacroleins IVa-e and Va-d occurs via either an intramolecular mechanism or through an intermediate step involving the retrograde decomposition of IIa-e and IIIa-d to the starting aldehydes and aziridines with the subsequent formation of the acrolein derivative. On the basis of the literature data [8, 9] on the reversible dissociation of aziridinocarbinols in solutions and their tendency to undergo cleavage to the starting components, the latter pathway seems preferable.

Our experimental data on the conversion of IIIa in the presence of propiolaldehyde to acrolein derivative IVa constitute proof for this assumption.

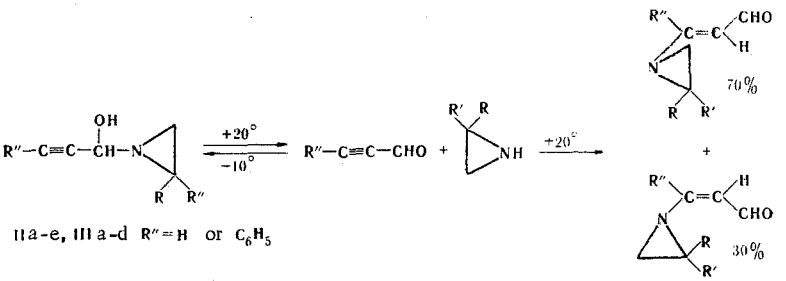


VIII

This persuasively proves the presence of an intermediate step involving retrograde decomposition of aziridinocarbinol IIIa to phenylpropiolaldehyde and aziridine Ia.

It is known [8] that aziridinocarbinols react with primary and secondary amines to give aminals through intermediate steps involving dissociation and transhydroxyalkylation. One might have expected that IIIa would also react with dimethylamine in a similar manner. We obtained 3-dimethylaminoacrolein VIII, the formation of which also occurs through a step involving dissociation of aziridinocarbinol IIIa to the starting components, but the reacting dimethylamine subsequently adds to the C≡C bond of phenylpropiolaldehyde. The structure of VIII was proved on the basis of data from the PMR spectrum and alternative synthesis.

In conformity with the results obtained above, the isomerization of aziridinocarbinols IIa-e and IIIa-d to β-aziridinoacroleins IVa-e and Va-d can be represented by the following scheme:



IIa-e, IIIa-d R″ = H or C_6H_5

IVa-e, Va-d

Of interest in the PMR spectra of unsymmetrically substituted aziridinocarbinols IIb, d and IIIb, d is the fact that the CH signal appears in the form of two identical singlets with an overall intensity of one proton unit. This is evidently due to the presence in such molecules of two chiral centers (i.e., to the presence of diastereoisomers).

In order to make a more detailed study of the three-dimensional and electronic structures of the acetylenic α-aziridinocarbinols, we investigated IIIa by means of PMR spectroscopy. Because of the average (with respect to the PMR time scale) rate of inversion of the nitrogen atoms at 36°, the protons of the aziridine ring absorb in the form of a broad singlet. The coalescence temperature (28°) can be easily determined by changing the temperature, after which the free energy of activation of the inversion process [10] for IIIa ($\Delta\nu$ = 12.0 Hz, ΔG_c = 15.6 kcal/mole) can also be determined. According to the data in [8], the depressed ΔG_c value in aziridinocarbinols as compared with 1-alkylaziridines [11] can be explained by reversible dissociation of the former. If this is so, the chemical shift of the aziridine protons of IIIa should change as the temperature is varied. This assumption was experimentally confirmed (Table 5).

By adopting the chemical shifts at 0° as the "standard" values, one can calculate the percentage of free aziridine at 30 and 50° and the equilibrium constants for the reversible reaction at these temperatures. The following values were determined: $K_{30} = 0.09$ and $K_{50} = 0.64$.*

The reaction of α-acetylenic aldehydes with aziridine can be used for the synthesis of acetylenic α-aziridinocarbinols and β-aziridinoacroleins.

*The percentage of carbinol IIIa at various temperatures was calculated from the formula $\rho_c = (\tau_{az} - \tau)/(\tau_{az} - \tau_c)$, where τ is the chemical shift of the protons of the aziridine ring observed at a given temperature, τ_{az} is the chemical shift of the ring protons of ethyleneimine, and τ_c is the chemical shift of the ring protons of aziridinocarbinol IIIa at 0°. The equilibrium constant was calculated from the formula $K_{t0} = (1-\rho_c)^2/\rho_c$, where ρ_c is the mole fraction of aziridinocarbinol IIIa at a certain temperature.

TABLE 5. Chemical Shifts of the Aziridine Protons at Various Temperatures (CCl_4)

Compound	0°	30°	50°
IIIa	8.14	8.20	8.27
	8.36	8.37	8.38

EXPERIMENTAL

The PMR spectra of 10% solutions of the compounds in CCl_4 were obtained with a Perkin–Elmer R12A spectrometer (60 MHz) with tetramethylsilane as the internal standard. The IR spectra of mineral oil and hexachlorobutadiene suspensions of the compounds or liquid films were obtained with a UR-20 spectrometer.

Acetylenic α-Aziridinocarbinols IIa-e and IIIa-d. A solution of 0.03 mole of aziridine Ia-e in 15 ml of absolute diethyl ether was added at −10° with stirring to 0.025 mole of propiolaldehyde or phenylpropiolaldehyde in 20 ml of absolute diethyl ether, and the resulting crystals were removed by filtration, dissolved in absolute ether, and crystallized by cooling the solution. The crystals were removed by filtration and vacuum dried. Compounds IIa-e and IIIa-d were colorless crystalline substances. The physicochemical characteristics are presented in Table 1.

1-Hydroxy-1-(2-carbomethoxyaziridino)-3-phenyl-2-propyne (IIIe). A solution of 3 g (0.03 mole of aziridine Ie in 20 ml of diethyl ether was added dropwise with stirring at −10° to a solution of 3.25 g (0.025 mole) of phenylpropiolaldehyde in 20 ml of absolute diethyl ether, after which the temperature was raised to room temperature, and the mixture was allowed to stand for 20 h. The ether was evaporated, and the residue was crystallized from absolute ether to give 4.7 g (84%) of a colorless crystalline substance with mp 82-84°.

β-Aziridinoacroleins IVa-e and Va-d. These compounds were obtained in quantitative yields by isomerization of the corresponding acetylenic α-aziridinocarbinols IIa-e and IIIa-d at room temperature. The physicochemical characteristics of IVa-e and Va-d are presented in Table 3.

1,O-Deutero-1-aziridino-3-phenyl-2-propyne (VI). This compound was obtained by the general method from phenylpropiolaldehyde and N-deuteroethyleneimine. As compared with the PMR spectrum of IIIa, the absorption at 3.7 ppm vanishes.

2-Deutero-3-phenyl-3-aziridinoacrolein (VII). This compound was obtained by isomerization of aziridinocarbinol VI in CCl_4 solution at 36° for 45 min. PMR spectrum: −0.15 and 0.57 (CHO, two broad s, 1H); 2.6 (C_6H_5, m, 5H); 7.73 and 7.95 ppm ( two s, 4H).

Reaction of 1-Hydroxyl-1-aziridino-3-phenyl-2-propyne (IIIa) with Propiolaldehyde. A 0.37-g (0.007 mole) sample of propiolaldehyde was stirred in 10 ml of absolute diethyl ether at room temperature with 1.1 g (0.007 mole) of aziridinocarbinol IIIa in 30 ml of absolute diethyl ether. The mixture was allowed to stand for 20 h, after which the ether was evaporated. In addition to signals corresponding to the cis and trans isomers of IVa, the parameters of which are presented in Table 4, the PMR spectrum of the residue contains a singlet at τ 0.70 (1H) and a multiplet at 2.4-2.7 ppm (5H) related to phenylpropiolaldehyde.

Reaction of 1-Hydroxy-1-aziridino-3-phenyl-2-propyne (IIIa) with Dimethylamine. A twofold excess of dimethylamine was added at room temperature to 1.1 g (0.07 mole) of aziridinocarbinol IIIa in 30 ml of absolute diethyl ether, and the mixture was allowed to stand for 10 h. The solvent was vacuum evaporated, and 3-phenyl-3-dimethylaminoacrolein (VIII) was detected in the residue. PMR spectrum, τ: 1.38 (d, J = 7.8 Hz, CHO, 1H); 2.5-2.8 (C_6H_5, m, 5H), 4.80 (d, J = 7.8 Hz, =CH-, 1H); 7.28 ppm (NCH_3, s, 6H).

3-Phenyl-3-dimethylaminoacrolein (VIII). A solution of 3.25 g (0.025 mole) of phenylpropiolaldehyde in 20 ml of absolute diethyl ether was added dropwise with stirring at 0° to a twofold excess of dimethylamine in 30 ml of absolute diethyl ether, after which the ether was evaporated, and the residue was identified as 3-phenyl-3-dimethylaminoacrolein.

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VINYLATION OF PYRROLES IN DIMETHYL SULFOXIDE

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and L. N. Balabanova

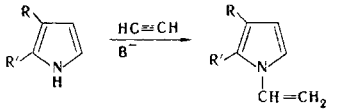
UDC 547.741.07

A number of 1-vinylpyrroles were obtained in up to 97% yields by base-catalyzed addition of substituted pyrroles to acetylene in dimethyl sulfoxide at 80-100°C.

N-Vinyl derivatives of heterocyclic compounds, which are valuable monomers and intermediates, find application in the manufacture of plastics and synthetic fibers, in radio technology, and in medicine (for example, see [1]). N-Vinylpyrroles are the most interesting derivatives of this sort but the least study has been devoted to them.

Methods for the synthesis of vinyl nitrogen heterocycles have been examined in a review [2]. They consist in dehydration of β-hydroxylethyl derivatives, dehydrohalogenation of haloethyl derivatives, or direct vinylation of heterocycles with an NH bond. Up until now the direct vinylation of nitrogen heterocycles has been accomplished at high temperatures (150-300°C) and pressures (20-40 atm) and has required a long time for completion [2].

Data from a study of the vinylation of a number of pyrroles obtained on the basis of the reaction of acetylene with ketoximes [3] are presented in this paper. 1-Vinylpyrroles I-XIV (table 1) were obtained in up to 97% yields:



I-XVI

R = H, alkyl, aryl; R' = alkyl, aryl

The reaction proceeds effectively in the presence of 30% KOH in aprotic polar solvents [dimethyl sulfoxide (DMSO), sulfolane, and hexamethylphosphoric triamide]; DMSO was found to be the best of the investigated solvents. The use of the latter made it possible to lower the reaction temperature to 80-100°, which is almost 100° lower than the temperature of classical vinylation of NH heterocycles, and 1-vinylpyrroles were obtained in practically quantitative yields. The use of DMSO makes it possible to carry out the vinylation of pyrroles at an acetylene pressure close to atmospheric (1.1-1.5 atm). It should be emphasized that up until now processes of this sort could not be put into practice because of the necessity of the use of acetylene under pressure and at high temperatures.

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