3. B. Schrader and A. Ansmann, Angew. Chem., Int. Ed. Engl., 14, 364 (1975).
4. H. J. Oelichmann, D. Bougeard, and B. Schrader, Angew. Chem. Suppl., Int. Ed. Engl., 1404 (1982).
5. E. V. Sobolev and V. T. Aleksanyan, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1336 (1963).
6. V. A. Koptyug (ed.), Atlas of the Spectra of Aromatic and Heterocyclic Compounds [in Russian], Vol. 12, Novosibirsk (1976).

FORMATION OF 1,4- AND 1,5-REGIOISOMERS OF TRIAZOLINES IN REACTIONS OF 2-ETHOXYETHYL AZIDE WITH MONOSUBSTITUTED ETHYLENES

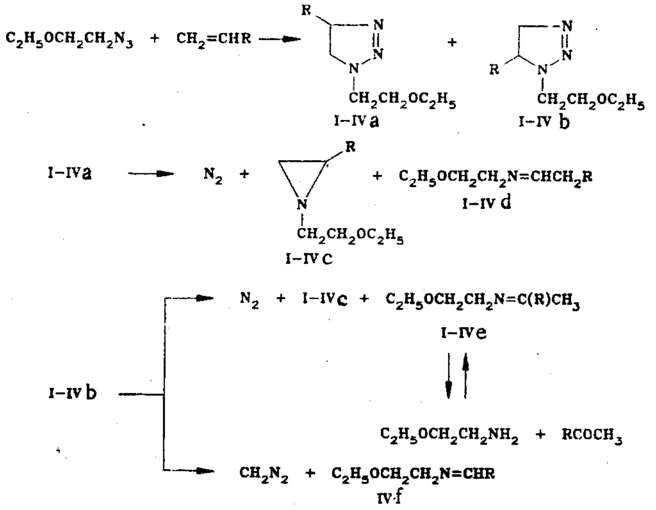
G. A. Lanovaya, V. F. Mishchenko, and E. D. Korniets

UDC 547.791.04:541.11'127'621.22:542.422.25

The structural specificity of the reactions of 2-ethoxyethyl azide with alkenes $RCH{=}CH_2$ [$R = CH_2C_6H_5$, $CH_2OC_6H_{13}$, $CH(OC_2H_5)_2$, C_6H_5] was studied. The formation of 1,4- and 1,5-substituted triazolines and the high stabilities of the latter were demonstrated by PMR spectroscopy, data from gas—liquid chromatography (GLC), and the kinetics of thermolysis.

The understanding of the structural possibilites of reactions involving the cycloaddition of azides to ethylene compounds $CH_2{=}CHR$ is far from complete. The formation of the 1,4- and 1,5-isomers that are possible in such reactions was demonstrated for the reactions of 4-nitrophenyl azide with styrene and 2-ethoxyethyl azide with alkenes [1, 2]. Only one isomer was described in the reactions of azides with vinyl ethers (1,5-isomers) and with methyl vinyl ketone, methyl acrylate, and acrylonitrile (1,4-isomers) (for example, see [3-5] and the literature cited therein).

In the present research we investigated the structural specificity of the reactions of 2-ethoxyethyl azide with four monosubstituted ethylenes with different polarities (see the scheme).



I $R{=}CH_2C_6H_5$; II $R{=}CH_2OC_6H_{13}$; III $R{=}CH(OC_2H_5)_2$; IV $R{=}C_6H_5$

In syntheses with the use of allylbenzene, allyl hexyl ether, and acrolein diethylacetal the elementary compositions of the isolated compounds corresponded to disubstituted 1,2,3-Δ^2-

---

Siberian Technological Institute, Krasnoyarsk 660049. Institute of Chemistry and Chemical Technology, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk 660049. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 798-803, June, 1987. Original article submitted December 2, 1985; revision submitted August 11, 1986.

0009-3122/87/2306-0660$12.50

TABLE 1. Physicochemical Characteristics of 1,4(5)-Di-substituted 1,2,3-Δ^2-Triazolines and Standard Compounds

Compound	bp, °C (mm)	d_{20}^{20}	n_D^{20}	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	Found, %			Empirical formula	Calculated, %		
					C	H	N		C	H	N
Ia+Ib	—	1,0603	1,5235	241 (3,60), 260 (2,60)	67,2	8,2	17,9	$C_{13}H_{19}N_3O$	67,0	8,2	18,0
IIa+IIb	—	1,0687	1,4620	239 (3,30), 260 sh	60,5	10,4	16,7	$C_{13}H_{27}N_3O$	60,7	10,5	16,3
IIIa+IIIb	—	1,0221	1,4550	241 (3,85), 260 (3,05)	54,0	9,4	16,9	$C_{11}H_{23}N_3O_3$	53,9	9,4	17,2
IIIb	116 (1)	1,0210	1,4546	241 (3,40), 260 (2,65)	53,3	9,3	17,0	$C_{11}H_{23}N_3O_3$	53,9	9,4	17,2
IIIc	65 (0,5)	0,9459	1,4350	—	60,6	10,5	6,6	$C_{11}H_{23}NO_3$	60,8	10,6	6,4
IVc	85—86 (1)	0,9886	1,5085	—	75,1	8,8	7,6	$C_{12}H_{17}NO$	75,4	8,9	7,3
IVe	114 (1,5)	1,0021	1,5250	—	75,2	8,8	7,7	$C_{12}H_{17}NO$	75,4	8,9	7,3
IVf	101 (1,5)	1,0110	1,5260	—	74,2	8,4	8,5	$C_{11}H_{15}NO$	74,6	8,5	7,9

triazolines Ia-IIIa and Ib-IIIb (Table 1). They could not be separated into individual isomer by fractionation or by means of column chromatography. The conclusions regarding the structure of the synthesized triazolines were drawn on the basis of the PMR spectra, data on the kinetic of thermal decomposition, and the determination of the compositions of the mixtures of thermolysis products.

The presence of 1,4- and 1,5-isomers of triazolines I and III is determined reliably from the PMR spectra. Two triplet signals of methyl groups of the OC_2H_5 radical of equal intensity with δ 1.05 and 1.11 ppm were observed in the spectrum of triazoline I. This result indicates unequivocally the presence in the mixture of isomers Ia and Ib in an equimolar ratio The presence in the PMR spectrum of doublet signals of nonequivalent methylidyne protons of a diethylacetal group at 4.32 (J = 5.3 Hz) and 4.63 ppm (J = 4.7 Hz) constitutes evidence for the structural isomerism of triazoline III. After the labile isomer is removed from the mixture of triazolines by thermolysis, only the doublet with δ 4.32 ppm, which belongs to the stable isomer, is retained in the spectrum. We were unable to detect isomers in the PMR spectrum of triazoline II because of masking of the signals of the CH_3 group in the OC_2H_5 radical by signals of the protons of the C_6H_{13} group. The thermolysis of triazolines I-III wa carried out at 170°C. The kinetics of decomposition were determined by gasometry, since, as we previously ascertained, triazolines liberate an equimolar amount of nitrogen. The kinetic dependences in the coordinates of a first-order equation included two rectilinear sections with different slopes (Fig. 1). The break on the graphical dependence for a monomolecular reaction constitutes evidence for the presence of two compounds that are characterized by different rates of decomposition. Consequently, the parallel formation of 1,4- and 1,5-substituted triazolines occurred during the synthesis. The kinetic data, like the PMR spectra of the triazolines, while demonstrating the presence of two isomers, do not make it possible to correlate the type of structure with its lability. The data necessary for such assignments were obtained in a study of the products of thermolysis of triazolines Ia-IIIa and Ib-IIIb, the labile and stable isomers. In analyzing the thermolytic mixtures we proceeded from the assumption that the decomposition of the triazolines obtained occurs as in the decomposition of 4(5)-alkyl-1-(2-ethoxyethyl)-1,2,3-Δ^2-triazolines, i.e., with the formation of nitrogen, identical aziridines Ic-IIIc, and different azomethines: aldimines Id-IIId from Ia-IIIa and ketimines Ie-IIIe from Ib-IIIb [2]. Thus the task of determining the structure of each of the isomers reduced to identification of the resulting azomethines. The time required for the complete decomposition of the triazolines at 170°C was determined from the kinetic dependences: 1h for I, 42 min for II, and 2 h for III. The stable isomer was isolated in the form of a residue after decomposition of the less stable isomer and removal of the products of its decomposition by distillation. The products that were removed by distillation were the thermolyzate of the labile isomer. The time necessary for decomposition of the bulk of the labile isomer was also found from kinetic data. For triazolines I-III the times were 1.5, 2.0, and 5.0 min. During these times the labile and stable isomers underwent decomposition to the extent of, respectively, 99% and 8% (Ia,b) 83% and 13% (IIa,b), and 81% and 13% (IIIa, b). The conditions of thermolysis of the stable isomers were the same as for mixtures of the isomers. The thermolysis products were identified from data from gas—liquid chromatography (GLC) and the PMR spectra.

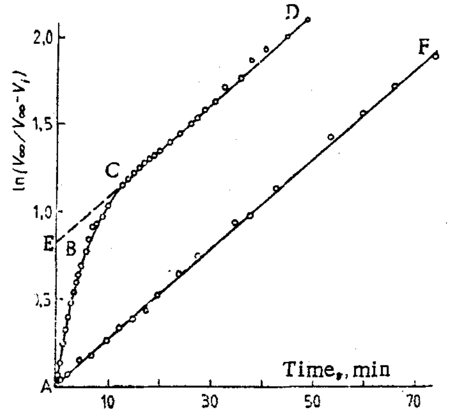


Fig. 1. Kinetic dependences of the thermal decomposition of 1-(2-ethoxyethyl)-4(5)-diethoxymethyl-1,2,3-Δ^2-triazolines (ABCD) and 1-(2-ethoxyethyl)-5-diethoxymethyl-1,2,3-Δ^2-triazoline (AF) at 170°C.

The chromatograms of the thermolyzates of the mixture of triazolines Ia + Ib and the corresponding stable isomer were identical — they each had two peaks. The peak with the greater retention time was assigned to the azomethine on the basis of an increase in its intensity when genuine ketimine Ie was added to the sample being analyzed. Ketimine Ie was used without isolation from the reaction mixture, since the peaks of the starting amine and ketone do not coincide with the peak of the azomethine. The peak with the shorter retention time was assigned to aziridine Ic in analogy with the data in [2]. Similar chromatograms were also obtained for the thermolyzates of triazoline II. The products of thermolysis of triazoline III emerged as one peak — the presence of the aziridine in the azomethine peak was established by means of genuine IIIc. As we see, the GLC data, while they do confirm the formation of aziridines and azomethines, do not enable one to determine the type of azomethine.

It has been previously shown for aldimines and ketimines (R = Alk) that are similar to Id-IIId and Ie-IIIe that they are satisfactorily distinguishable from the PMR spectra, in which one observes, respectively, a triplet at ~7.5 ppm (HC=N, J ~ 4.5 Hz) and a singlet at ~1.7 ppm (CH_2=N). The presence in the PMR spectra of the thermolysates of the labile isomers of triazolines I and III of intense triplet signals of aldimines at 7.52 (J = 3.9 Hz; Id) and 7.52 ppm (J ~ 4.6 Hz; IIId) proves structures Ia and IIIa for these isomers. A signal of aldimine IId was not observed in the spectrum of the thermolysate, obtained in the usual way, of the labile isomer of triazoline II; however, it was identified in the spectrum of a sample taken after heating triazoline II for 2 min [δ 7.65 ppm (t, J = 4.3 Hz)]. In the PMR spectrum of the thermolysate of isomer IIIa, in addition to signals belonging to aziridine IIIc (with respect to a genuine compound, Table 2) and aldimine IIId, we also observed three signals with equal integral intensities, viz., δ 5.46 (dd, J = 8.9 and 13.0 Hz), 6.78 (d, J = 13.0 Hz) and 7.59 ppm (d, J = 8.9 Hz), which were assigned to the possible product of splitting out of alcohol from a molecule of aldimine IIId ($C_2H_5OC_2H_4N{=}CHCH{=}CHOC_2H_5$).

The stable isomers evidently have 1,5-structures Ib-IIIb. For triazolines Ib-IIIb this is confirmed by the presence in the PMR spectra of their thermolyzates of singlet signals of ketimines (δ 1.62 and 1.70 ppm, respectively, for Ie and IIIe). Ketimine IIe was not detected in the spectrum of the thermolysate of isomer IIb, probably because of the presence at 1.6-1.7 ppm of intense signals of a hexyl radical.

The PMR spectra of the thermolysates of the labile isomers usually had low-intensity signals of ketimines, while signals of admixed aldimines were present in the spectra of the thermolysates of the stable isomers; this was associated with the method used to obtain the thermolysates.

A study of the triazoline obtained on the basis of styrene showed that the introduction of a phenyl substituent into the ring substantially changes both the stabilities of the isomers and the mechanism of their decomposition. Removal of the unchanged 2-ethoxyethyl azide and styrene from the reaction mixture by distillation gave a product consisting, according to the PMR spectral data, of an approximately equimolar mixture of aziridine IVc (Table 2). The equimolarity of the mixture was confirmed by the elementary composition (13.0% N found, and 13.3% N calculated) and the amount of gas liberated (48%) during thermolysis. The chromatogram of the thermolysate (170°C) showed the presence of aziridine IVc, aldimine IVf, and ketimine IVe (the identification was made with respect to genuine compounds). The presence of these thermolysis products was also confirmed by the PMR spectra of the thermolysate (the spectra of the genuine compounds in Table 2). The results provide evidence that the parallel

TABLE 2. Data from the PMR Spectra of Standard Compounds

Compound	δ, ppm
IIIc	1,08, 1,10 and 1,12 (9H, t, CH_3); 1,25—1,59 (3H, m, 2- and 3-H); 2,30 (2H, t, 1-CH_2); 3,40 (4H, q, OCH_2); 3,45 (4H, t, OCH_2); 3,97 (1H, d, J=5,1 Hz, CH)
IVc	1,04 (3H, t, CH_3); 1,52 (1H, dd, J=6,5 and 0,9 Hz, 3-H); 1,62 (1H, dd, J=3,4 and 0,9 Hz, 3′-H); 2,20 (1H, dd, J=6,5 and 3,4 Hz, 2-H); 2,41 (2H, t, 1-CH_2); 3,32 (2H, q, OCH_2); 3,45 (2H, t, OCH_2); 7,07 (5H, m, C_6H_5)
IVe	1,10 (3H, t, CH_3); 2,08 (3H, t, J=0,7 Hz, $N{=}CCH_3$); 3,43 (2H, q, OCH_2); 3,62 (4H, m, OCH_2CH_2N); 7,25—7,76 (5H, m, C_6H_5)
IVf	1,08 (3H, t, CH_3); 3,41 (2H, q, OCH_2); 3,63 (4H, m, OCH_2CH_2N); 7,27—7,67 (5H, m, C_6H_5); 8,15 (1H, br s, $HC{=}N$)

formation of 1,4- and 1,5-substituted triazolines IVa and IVb also occurs in this case. Under the conditions of thermostatting of the reagents (50°C) trizaoline IVa is evidently unstable and, with splitting out of nitrogen, is converted to aziridine IVc. The approximately equimolar ratio of aziridine IVc and triazoline IVb in the isolated reaction product can be considered to be indirect evidence for the closeness of the rates of formation of isomers IVa and IVb. Triazoline IVb undergoes decomposition via two pathways. One, which is the most typical for triazolines, coincides with the character of the decomposition of Ib-IIIb — nitrogen split out, and aziridine IVc and ketimine IVe are formed. The demonstrated formation of aldimine IVf (PMR, GLC) suggests a pathway of thermolysis of triazoline IVb with splitting out of diazomethane. This decomposition mechanism has been described for 1,5-substituted triazolines obtained on the basis of the reaction of sulfonyl and phosphoryl azides with vinyl ethers and enamines [4, 6].

The rate constants for the decomposition of each of the isomers were calculated from the kinetic dependences for the thermal decomposition of mixtures of the triazolines (Table 3). The error in the determination of the constants depended on the number of measurements of the volume of nitrogen (i) for sections AB (both isomers decompose) and CD (only the more stable isomer decomposes) (Fig. 1). At 170°C the labile isomers decomposed rapidly, and the root mean-square errors in the determination of their decomposition constants ranged from 1 to 35. The rate constants for the decomposition of the second isomer are more reliable. This confirm the coincidence of the constants obtained in experiments with individual isomer IIIb and a mixture of isomers IIIa and IIIb.

The volumes of nitrogen in the complete decomposition of the 1,4- (V_∞^a) and 1,5-isomers (V_∞^b) were obtained in calculations of the decomposition rate constants. Their ratio corresponds to the ratio of the regioisomers of triazolines obtained as a result of cycloaddition and indirectly characterized the difference in the rates of formation of the two isomers. This ratio is close to equimolar for trizaolines I, II, and IV. The increase in the amount of isomer IIIa in the reaction with acrolein diethylacetal is in agreement with data on the formation of only 1,4-triazolines from alkenes with strong electron-acceptor substituents [5]

EXPERIMENTAL

Chromatographic analysis of the thermolysis products and the standard compounds was carried out with KhL-69 (with helium as the carrier gas) and LKhM-72 chromatographs as described in [2]. The IR spectra were recorded with an IKS-22 spectrometer. The UV spectra of solution in hexane were recorded with an SF-4A spectrophotometer. The PMR spectra of solutions in CCl were recorded with a Tesla BS-467 spectrometer (60 MHz) with tetramethylsilane (TMS) as the internal standard.

The allylbenzene, allyl hexyl ether, acrolein diethylacetal, and 2-ethoxyethyl azide were obtained as in [7-9]. Industrially prepared styrene was purified by fractionation.

The 4(5)-benzyl-1-(2-ethoxyethyl)- (Ia + Ib), 4(5)-hexyloxy-1-(2-ethoxyethyl)- (IIa + IIb), 4(5)-diethoxymethyl-1-(2-ethoxyethyl)- (IIIa + IIIb), 4(5)-phenyl-1-(2-ethoxyethyl)- (IVa + IVb), 5-diethoxymethyl-1-(2-ethoxyethyl)-1,2,3-Δ^2-triazoline (IIIb), and 2-diethoxymethyl-1-(2-ethoxyethyl)-aziridine (IIIc) were obtained as in [2]. 2-Phenyl-1-(2-ethoxyethyl)-aziridine (IVc) was isolated by vacuum distillation from the reaction mixture obtained in the reaction of 2-ethoxyethyl azide with styrene with subsequent fractionation. N-Benzylidene (IVf), N-(1-phenylethylidene)- (IVe), and N-(2-phenyl-1-methylethylidene)-2-ethoxyethylamine

TABLE 3. Rate Constants for the Thermolysis of 1,4- (k^a) and 1,5-Substituted 1,2,3-Δ^2-Triazolines (k^b) at 170°C and Isomer Ratios

Triazoline	Thermolysis rate constants,* $k \cdot 10^4$, sec^{-1}		Ratio of the 1,4- and 1,5-isomers
Ia	k^a	612±35 (3)	0,91 (Ia : Ib)
IIa	k^a	147±4 (4)	
IIIa	k^a	54,7±1,2 (6)	
Ib	k^b	9,67±0,06 (20)	0,97 (IIa : IIb)
IIb	k^b	12,00±0,06 (17)	
IIIb	k^b	4,50±0,07 (18) [4,42±0,05 (18)]	1,28 (IIIa : IIIb)

---

*The number of measurements of the volume of nitrogen are presented in parentheses; the k^b value obtained in a experiment with individual isomer IIIb is given in brackets.

(Ie) were obtained in accordance with the method in [7]; however, the latter was not isolated from the reaction mixture. The physicochemical characteristics of the synthesized compounds are presented in Table 1. The method used to carry out the thermolysis of the triazolines was described in [2].

The results of the kinetic measurements were calculated in accordance with a first-order equation by the method of least squares [10]. For triazolines Ib-IIIb thermolysis rate constants k^b were found from the slopes of lines CD. The free term in the equation of line CD gives the value of ordinate AE = $\ln [V_\infty/(V_\infty - V_\infty{}^a)] = \ln (V_\infty/V_\infty{}^b)$, where V_∞ is the volume of nitrogen in the case of complete decomposition of a weighed sample of a mixture of triazolines, and $V_\infty{}^a$ and $V_\infty{}^b$ are the volumes of nitrogen in the complete decomposition of, respectively, 1,4- amd 1,5-disubstituted triazolines. Knowing the AE value and calculating V_∞ from the weighed sample of the triazoline we find $V_\infty{}^b$ and then $V_\infty{}^a = V_\infty - V_\infty{}^b$. From the equation $k^b\tau_i = \ln [V_\infty{}^b / (V_\infty{}^b - V_i{}^b)]$ we find $V_i{}^b$ for section AB, and then $V_i{}^a = V_i - V_i{}^b$. From the equation $k^a\tau_i = \ln [V_\infty{}^a/(V_\infty{}^a - V_i{}^a)]$ we determine k^a. Rate constant k^b for triazoline IIIb was calculated from the equation $k^b\tau_i = \ln [V_\infty{}^b/(V_\infty{}^b - V_i{}^b)]$ (Fig. 1, AF). The error in the measurements of k^a and k^b was estimated as the root-mean-square error [10].

LITERATURE CITED

1. R. Huisgen, R. Sustmann, and K. Bunge, Chem. Ber., 105, 1324 (1972).
2. G. A. Lanovaya, V. F. Mishchenko, and E. D. Korniets, Zh. Org. Khim., 10, 639 (1984).
3. G. A. Lanovaya and V. F. Mishchenko, Zh. Org. Khim., 15, 2203 (1979).
4. K. A. Ogloblin, V. P. Semenov, I. K. Zhurkovich, and I. M. Stroiman, Zh. Org. Khim., 9, 263 (1973).
5. G. Szeimies and R. Huisgen, Chem. Ber., 99, 491 (1966).
6. M. Regitz and G. Himbert. Ann. Chem., 734, 70 (1970).
7. Weygand-Hilgetag, Experimental Methods in Organic Chemistry [Russian translation], Khimiya, Moscow (1968).
8. B. I. Mikhant'ev, V. B. Mikhant'ev, V. L. Lapenko, and V. K. Voinova, Some Vinyl Monomers [in Russian], Izd. Voronezh. Univ., Voronezh (1970), p. 135.
9. G. A. Lanovaya, V. F. Mishchenko, A. S. Mashikhina, and Yu. D. Salov, The Chemistry and Technology of Polymers, Vol. 3, Izd. Sibirsk, Tekhnol. Inst., Krasnoyarsk (1974), p. 84.
10. L. M. Batuner and M. E. Pozin, Mathematical Methods in Chemical Technique [in Russian], Khimiya, Leningrad (1971), p. 665.