

EXPERIMENTAL

The mass spectra of I-XIV were obtained with an MKh-1303 mass spectrometer equipped for direct introduction of the samples at 50-100°C and an ionizing-electron energy of 70 eV.

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ACETYLENIC α -AZIRIDINYLCARBINOLS IN REACTIONS WITH HYDRAZINE AND METHYL-SUBSTITUTED HYDRAZINES

A. V. Eremeev, D. A. Tikhomirov, V. A. Tyusheva, UDC 547.712'771:543.422.25.4:541.63
and Ē. Ē. Liepin'sh

It is shown that hydrazones of phenylpropiolaldehyde are formed in the reaction of an acetylenic α -aziridinylcarbinol — 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne — with hydrazine and methyl- and 1,1-dimethylhydrazine. The reaction of this carbinol with sym-dimethylhydrazine leads to the formation of phenylacetylene and 1-formyl-1,2-dimethylhydrazine, 1-aziridinyl-1-hydrazino-3-phenyl-2-propyne, or 3,6-diphenylethynyl-1,2,4,5-tetramethyltetrazine, depending on the reaction conditions. It was established that the reaction of 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne and 1-hydroxy-1-(2-methylaziridinyl)-2-propyne with hydrazine and methyl-substituted hydrazines is realized through an intermediate step involving the decomposition of the acetylenic aziridinylcarbinols to an α -alkynyl aldehyde and ziridine.

Acetylenic α -aziridinylcarbinols, which we have previously obtained [1], are the first representatives of α -aziridinylcarbinols of the unsaturated series. In the present research we studied the reactions of 1-hydroxy-1-(2-methylaziridinyl)-2-propyne (I) and 1-hydroxy-1-aziridinyl-3-phenyl-2-propyne (II) with hydrazine and methyl-substituted hydrazines.

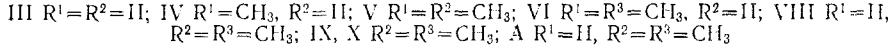
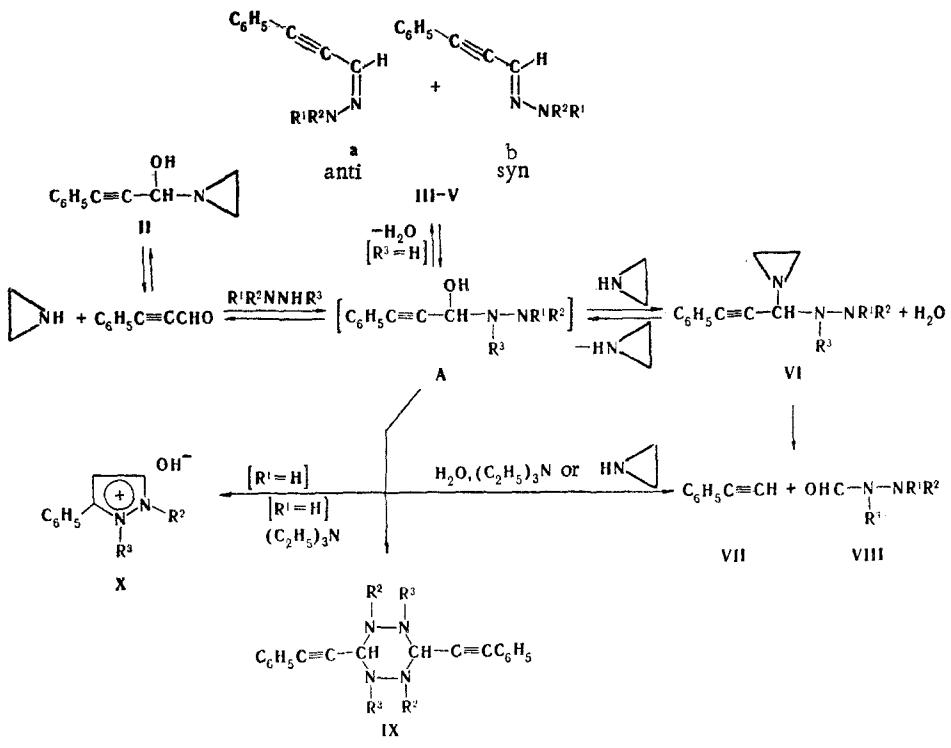
The currently available data [2] provide evidence that saturated α -aziridinylcarbinols react with primary and secondary amines to give aminals only through an intermediate step involving the decomposition of the aziridinylcarbinols to aldehydes and aziridines. However, no data at all are available on the reactivities of aziridinylcarbinols in reactions with hydrazine and its derivatives.

We have established by PMR and IR spectroscopy that the corresponding hydrazones of phenylpropiolaldehyde (III, IV, and V) are formed in the reaction of acetylenic α -aziridinylcarbinol II with hydrazine and methyl- and 1,1-dimethylhydrazine (see the scheme below). The hydrazones are oily liquids and were found to be mixtures of syn and anti isomers (Table 1). However, the less stable anti isomers gradually undergo isomerization to the syn isomers. The rate of conversion of the anti isomers to the syn isomers of hydrazones III, IV, and V increases as the number of methyl groups attached to the amine nitrogen atom increases.

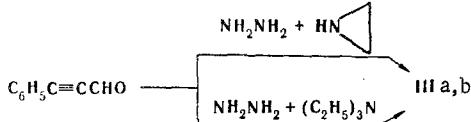
From the data in [1, 2] it may be assumed that the reaction of hydrazine and methyl-substituted hydrazines with acetylenic aziridinylcarbinol II is realized through an intermediate step involving the decomposition of the indicated aziridinylcarbinol to an aldehyde and aziridine (see the scheme below). The experimental data provide evidence for this premise.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
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The syn and anti isomers of phenylpropiolaldehyde hydrazone (III) are formed in the reaction of phenylpropiolaldehyde with hydrazine in the presence of an equimolar amount of aziridine, i.e., the result is the same as in the case of aziridinylcarbinol II.

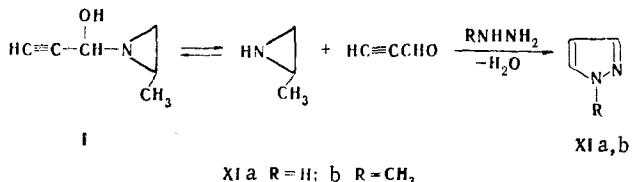


Replacement of the aziridine in this reaction by triethylamine, which excludes the formation of aziridinylcarbinol systems, also leads to IIIa, b.



This experiment provides evidence in favor of decomposition of aziridinylcarbinol II to the aldehyde and aziridine in the reactions with hydrazines.

The reaction of 1-hydroxy-1-(2-methylaziridinyl)-2-propyne (I) with hydrazine and methylhydrazine does not stop at the step involving the formation of hydrazones or propiolaldehyde, and the final products are pyrazoles XIa and XIb.



In contrast to hydrazine and methyl- and 1,1-dimethylhydrazines, the reaction with symmetrical hydrazines leads to the formation of different products. Thus the chief product in the reaction of sym-dimethylhydrazine with II at room temperature for 12 h is α -aziridinylalkylhydrazine VI (see the above scheme). Phenylacetylene (VII) and formylhydrazine VIII are formed when the reaction is carried out for a longer time (48 h). In addition to these compounds, small amounts (<10%) of 1,2-dimethylpyrazolium hydroxide (X) are present in the reaction mixtures in both cases.

The intermediate hydrazinocarbinol (A) formed in this reaction evidently undergoes conversion to α -aziridinylalkylhydrazine VI in the presence of aziridine. However, because of the reversibility of the reaction, the equilibrium is gradually shifted to the left, since hydrazinocarbinol A undergoes decomposition to phenylacetylene and formylhydrazine VIII under these conditions.

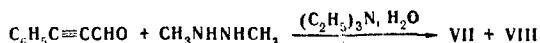
TABLE 1. Parameters of the PMR Spectra of Hydrazones III, IV, and V

Compound	Chemical shifts δ , ppm				Isomers
	C ₆ H ₅	CH=N	R ¹	R ²	
IIIa	7.1-7.5	6.99	5.9	5.9	anti
IIIb	7.1-7.5	6.50	6.5	6.5	syn
IVa	7.1-7.5	6.62	2.85*	6.3	anti
IVb	7.1-7.5	6.30	3.09†	6.3	syn
Va	7.2-7.6	6.39	2.94	2.94	anti
Vb	7.2-7.6	6.49	3.16	3.16	syn

*³J_{NHCH} ≈ 4 Hz.

†³J_{NHCH} ≈ 2 Hz.

It was established that a necessary condition for the decomposition of hydrazinocarbinol A to phenylacetylene and VIII is the presence of water and a base (aziridine or triethylamine) in the reaction mixture. Thus, for example, the reaction of sym-dimethylhydrazine with phenylpropiolaldehyde in the presence of an equimolar amount of triethylamine and water also leads to the formation of phenylacetylene and formylhydrazine VIII.



Data obtained by the direct hydrolysis of α -aziridinylalkylhydrazine VI, which in the presence of water undergoes decomposition to phenylacetylene and formylhydrazine VIII (see the above scheme), confirm the proposed reaction scheme.

When water is absent, the principal product of the reaction of phenylpropiolaldehyde with sym-dimethylhydrazine is tetrazine IX, which is evidently formed as a result of dimerization of hydrazinocarbinol A. The IR, PMR, and ¹³C NMR spectroscopic data and the dipole moment, which is zero for IX, provide evidence in favor of tetrazine structure IX. The molecular ion of tetrazine IX cannot be recorded in the mass spectrum, but a peak with m/e 172, which corresponds to half the mass of tetrazine IX, is observed. The tetrazine molecule evidently undergoes cleavage at the labile N-N bonds under the influence of electron impact.

The reaction of aziridinylcarbinol I with sym-dimethylhydrazine leads to the formation of 1-formyl-1,2-dimethylhydrazine (VIII). However, the corresponding α -aziridinylalkylhydrazine of the VI type cannot be isolated in this case.

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The PMR spectra of 10% solutions of the compounds in CCl₄, CDCl₃, and (CD₃)₂SO were recorded with a Perkin-Elmer R12A spectrometer (60 MHz) with tetramethylsilane as the internal standard. The IR spectra of mineral oil and hexachlorobutadiene suspensions or liquid films of the compounds were obtained with a UR-20 spectrometer. The ¹³C NMR spectra of ~20% solutions of the compounds were obtained with a Bruker WH-90 spectrometer. The mass spectrum was recorded with an AEI MS-905 spectrometer at an ionizing-electron energy of 70 eV with a heated direct-inlet port at an ionization-chamber temperature of 150°C. The temperature of the direct-inlet port was 100°C.

Phenylpropiolaldehyde Hydrazones (III, IV, and V). A solution of 0.03 mole of the corresponding hydrazine in 100 ml of absolute ethanol was added at -30°C to a solution of 0.03 mole of freshly prepared acetylenic aziridinylcarbinol II in 100 ml of absolute ethanol, and the temperature of the mixture was raised slowly (in 2 h) to 20°C. After 12 h, the alcohol solution was filtered, and the ethanol was removed from the filtrate by evaporation at 30°C. The residue was found to be a mixture of the syn and anti isomers of the hydrazones, which underwent isomerization to the syn isomers of hydrazones III, IV, and V on standing or under the distillation conditions. The constants of the compounds obtained are presented in Table 2.

Reaction of Phenylpropiolaldehyde with Hydrazine in the Presence of Aziridine or Triethylamine. A mixture of 0.96 g (0.03 mole) of hydrazine and 0.03 mole of aziridine or triethylamine in 50 ml of absolute ethanol was added with stirring at -30°C to a solution of 3.9 g (0.03 mole) of phenylpropiolaldehyde in 100 ml of absolute ethanol, and the temperature was raised slowly to 20°C (in 2 h), after which the mixture was allowed to stand for 12 h. The alcohol solution was filtered, the ethanol was removed from the filtrate by evaporation, and the residue was found to be a mixture of the syn and anti isomers of hydrazone III (Table 2).

TABLE 2. Constants of III, IV, and V

Compound	Isomer	bp, °C (0.01 mm)	mp, °C	Found, %			Empiri- cal for- mula	Calc., %			IR spectrum, cm ⁻¹ , C≡C	Yield, %
				C	H	N		C	H	N		
IIIa, b	syn-anti	60-62	—	74.5	5.8	19.4	C ₉ H ₈ N ₂	74.8	5.6	19.4	2190	86
IIIb	syn	—	58-59	74.5	5.8	19.4	C ₉ H ₈ N ₂	74.8	5.6	19.4	2190	86
IVa, b	syn-anti	42-43	—	75.8	6.3	17.7	C ₁₀ H ₁₀ N ₂	75.4	6.1	17.6	2190	80
IVb	syn	—	36-37	75.8	6.3	17.7	C ₁₀ H ₁₀ N ₂	75.4	6.1	17.6	2190	80
Va, b	syn-anti	38-39	—	76.5	6.8	16.0	C ₁₁ H ₁₂ N ₂	76.8	7.0	16.2	2210	84
Vb	syn	—	11-12	76.5	6.8	16.0	C ₁₁ H ₁₂ N ₂	76.8	7.0	16.2	2210	84

Reaction of 1-Hydroxy-1-aziridinyl-3-phenyl-2-propyne (II) with sym-Dimethylhydrazine.

A 3.1-g (0.05 mole) sample of sym-dimethylhydrazine was added at -40°C to a solution of 9 g (0.05 mole) of aziridinylcarbinol II in 200 ml of ether, and the temperature was raised slowly to 20°C (in 2 h).

A) The reaction mixture was allowed to stand for 12 h, after which it was filtered, the ether was removed from the filtrate by evaporation, and the residue was vacuum distilled to give 5.9 g (55%) of 1-(1,2-dimethylhydrazino)-1-aziridinyl-3-phenyl-2-propyne (VI) with bp 48-49°C (0.01 mm) and n_D^{20} 1.5665. Found: C 72.1; H 7.6; N 19.8%. C₁₃H₁₇N₃. Calculated: C 72.5; H 7.9; N 19.5%. IR spectrum: 2235 (C≡C); 3240 and 3400 cm⁻¹ (NH). PMR spectrum (CCl₄): δ 7.2-7.5 (5H, m, C₆H₅), 3.82 (1H, s, CH), 2.53 (6H, s, NCH₃), and 1.3-1.7 ppm (4H, m, C₂H₄N). ¹³C spectrum (CDCl₃): δ 26.2 and 25.2 (t*, aziridine C), 36.5 and 38.9 (q, NCH₃), 80.9 (d, -CH), 87.2 and 84.8 (s, acetylene C), 123.1 (s), 132.4, 128.4, and 128.9 (d) ppm (aromatic C).

B) The reaction mixture was allowed to stand for 48 h, after which the ether was removed by evaporation, and the residue was vacuum distilled at 30-32°C to give 5.9 g of a mixture of phenylacetylene VII and formylhydrazine VIII. IR spectrum: 2120 (C≡C), 3250 and 3305 (NH), and 1680 cm⁻¹ (C=O). PMR spectrum (CCl₄): δ 7.2-7.5 (5H, m, C₆H₅), 3.18 (1H, s, ≡C-H), 8.06 and 7.82 (two singlets with an overall intensity of 1H, CHO), 4.4 (1H, broad singlet, NH), 2.98 and 2.92 (two singlets with an overall intensity of 3H, CONCH₃), and 2.54 and 2.49 ppm (two doublets with an overall intensity of 3H, J = 5 and 2 Hz, NHCH₃).

1,2-Dimethylpyrazolium Hydroxide (X). The ether-insoluble oily substance formed in small amounts in the synthesis of VI, VII, and VIII was crystallized from acetone to give 0.6 g (7%) of a colorless crystalline compound with mp 57-59°C (acetone-ethanol). Found: C 69.0; H 7.1; N 14.5%. C₁₁H₁₄N₂O. Calculated: C 69.5; H 7.4; N 14.8%. IR spectrum: 3390-3490 and 1645 cm⁻¹ (OH). PMR spectrum [(CD₃)₂SO]: δ 8.70 (1H, d, J = 2.9 Hz, 3-H), 7.62 (5H, s, C₆H₅), 7.00 (1H, d, J = 2.9 Hz, 4-H), 4.20 (3H, s, 1-NCH₃), and 4.02 ppm (3H, s, 2-NCH₃).

Reaction of Phenylpropiolaldehyde with sym-Dimethylhydrazine in the Presence of Triethylamine and Water. A solution of 6.5 g (0.05 mole) of phenylpropiolaldehyde in 100 ml of ether was added with stirring at -40°C to a mixture consisting of 3.0 g (0.05 mole) of sym-dimethylhydrazine, 5 g (0.05 mole) of triethylamine, and 0.9 g (0.05 mole) of water in 100 ml of ether, and the temperature was raised slowly to 20°C (in 2 h), after which the mixture was allowed to stand for 48 h. The ether solution was separated from the small amount of water and dried with anhydrous sodium sulfate. The solvent was removed by evaporation, and the residue was vacuum distilled at 30-32°C (0.01 mm) to give 3.5 g of a mixture of phenylacetylene and 1-formyl-1,2-dimethylhydrazine (VIII).

Hydrolysis of 1-(1,2-Dimethylhydrazino)-1-aziridinyl-3-phenyl-2-propyne. Water [0.33 g (0.019 mole)] was added to a solution of 4 g (0.019 mole) of VI in 100 ml of ether, and the mixture was stirred at 20°C for 48 h. It was then dried with anhydrous sodium sulfate, and the ether was removed by evaporation. The residue was vacuum distilled at 30-32°C (0.01 mm) to give 2.2 g of a mixture of phenylacetylene and formylhydrazine VIII.

3,6-Diphenylethynyl-1,2,4,5-tetramethyltetrazine (IX). A solution of 6.5 g (0.05 mole) of phenylpropiolaldehyde in 50 ml of absolute ether was added slowly with stirring at -50°C to a mixture of 3.8 ml (0.05 mole) of sym-dimethylhydrazine and 5 ml (0.05 mole) of triethylamine in 100 ml of absolute ether, and the temperature of the mixture was slowly raised to 20°C (in 3 h). After 12 h, the ether solution was filtered, and the solvent was removed from the filtrate by evaporation. The residue was crystallized from acetone to give 3.8 g (45%)

*The multiplicity in off-resonance experiments is indicated.

of a colorless crystalline substance with mp 140-142°C. Found: C 76.5; H 7.0; N 15.9%. $C_{22}H_{24}N_4$. Calculated: C 76.8; H 7.0; N 16.2%. IR spectrum: 2230 cm^{-1} ($\text{C}\equiv\text{C}$). PMR spectrum (CCl_4): δ 7.2-7.6 (5H, m, C_6H_5), 4.98 (1H, s, C), and 2.74 ppm (6H, s, NCH_3). ^{13}C spectrum (CDCl_3): δ 36.9 (q, NCH_3), 68.3 (d, $-\text{CH}$), 87.9 and 85.0 (s, acetylenic carbon atoms), 122.3 (s), 132.2, 128.8, and 129.1 (d) ppm (aromatic carbon atoms).

Pyrazoles XIa, b. A 0.05-mole sample of hydrazine or methylhydrazine was added at -40°C to a solution of 5.6 g (0.05 mole) of freshly prepared aziridinylcarbinol I in 200 ml of ethanol, and the temperature was slowly raised to 20°C (in 2 h). The mixture was then allowed to stand for 12 h, after which the ethanol was removed by evaporation, and the residue was vacuum distilled.

A) The yield of pyrazole XIa, with bp 30-32°C (0.01 mm) and mp 69-70°C (from petroleum ether) [mp 69.5-70°C (from ligroin) [3]], was 1 g (30%). PMR spectrum (CDCl_3): δ 6.30 (1H, t, J = 2.0 Hz, h-H), 7.60 (2H, d, J = 2.0 Hz, 3-H and 5-H), and 12.0 ppm (1H, s, NH).

B) The yield of 1-methylpyrazole (XIb), with bp 26-28°C (3 mm) (bp 127°C [4]), was 1.7 g (42%). PMR spectrum (CDCl_3): δ 7.40 (1H, d, J = 1.9 Hz, 5-H), 7.31 (1H, d, J = 2.0 Hz, 3-H), 6.16 (1H, t, J = 2.0 Hz, 4-H), and 3.81 ppm (3H, s, NCH_3).

Reaction of 1-Hydroxy-1-(2-methylaziridinyl)-2-propyne (I) with sym-Dimethylhydrazine. A 3-g (0.05 mole) sample of sym-dimethylhydrazine was added with stirring at -40°C to a solution of 5.6 g (0.05 mole) of freshly prepared I in 200 ml of ether, and the temperature was slowly raised to 20° (in 2 h). The mixture was then stirred for 5 h, after which it was filtered. The ether was removed from the filtrate by evaporation, and the residue was vacuum distilled to give 1.6 g (36%) of 1-formyl-1,2-dimethylhydrazine (VIII) with bp 32°C (0.01 mm). Found: C 40.5; H 9.0; N 32.0%. Calculated: C 40.9; H 9.1; N 31.8%.

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