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2-ETHYNYLAZIRIDINES

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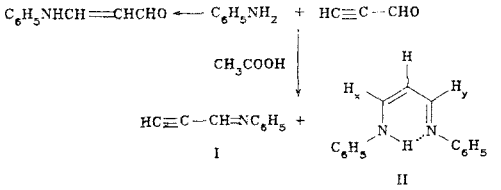
Methods for the synthesis of 2-ethynylaziridines by the cycloaddition of carbene to an α-ethynyl imine, cyclization of acetylenic β-amino alcohols in the presence of triphenylphosphine, and by means of the Gabriel reaction were developed.

2-(Phenylethynyl)aziridines were obtained in [1] by the cycloaddition of carbenes to N-(phenylpropynylidene)aniline and by cyclization of acetylenic β-amino alcohols by means of the $(C_6H_5)_3P—CCl_4$ complex in the presence of triethylamine.

In the present research we attempted to increase the number of ethynylaziridines by previously described methods [1] and carried out a search for other methods for the preparation of such compounds. Unsubstituted 2-ethynylaziridines are of particular interest. Only one representative of this series, viz., 2-vinyl-3-ethynylaziridine, has been described thus far [2].

α-Ethynyl imine I is necessary for the synthesis of 2-ethynylaziridines by the cycloaddition of carbenes to imines. It was established in [3] that the reaction of 2-propynal with aniline does not lead to the expected imine but rather to the product of addition of aniline to the triple bond, viz., an enamino aldehyde:



We obtained imine I by carrying out this reaction in the presence of acetic acid, which evidently facilitates dehydration of the initially formed unstable amino carbinol. In neutral media the latter decomposes to give the starting component with subsequent addition of aniline to the triple bond. The structure of imine I was confirmed by the IR and PMR spectra. N-(3-Phenylamino-2-propenylidene)aniline (II) — the product of the addition of aniline to the triple bond of imine I — is formed in addition to acetylenic imine I. The magnetic equivalence of the H_X and H_Y protons in II is explained by rapid intramolecular transfer of the N—H proton [4], which constitutes evidence for the formation of the cis-s-cis form. It should be noted that the yield of II increases as the time that the reaction mixture is allowed to stand is increased.

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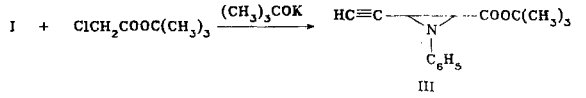
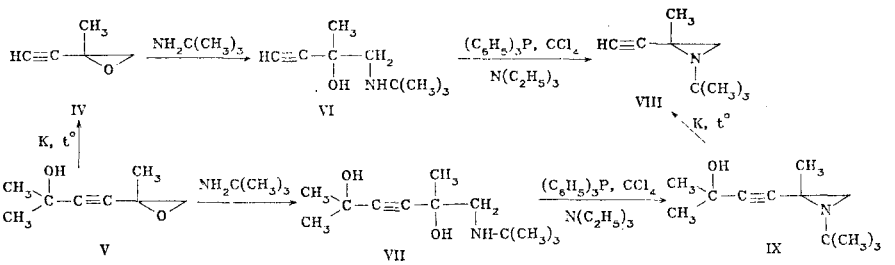
We obtained 1-phenyl-2-ethynyl-3-tert-butoxycarbonylaziridine (III) in the reaction of imine I with tert-butyl chloroacetate in the presence of potassium tert-butoxide. The cycloaddition of carbene proceeds regioselectively without involvement of the triple bond.



III

The structure of aziridine III was confirmed by the IR and PMR spectra; in accordance with [5], the J_{23} value of 2.6 Hz corresponds to the trans isomer.

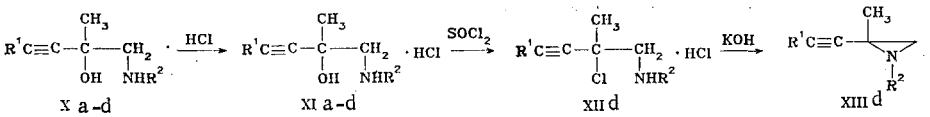
Another possible method for the synthesis of aziridines is the reaction of acetylenic amino alcohols with the $(C_6H_5)_3P—CCl_4$ complex in the presence of triethylamine. We used this method to obtain 1-tert-butyl-2-methyl-2-ethynylaziridine (VIII):



It is apparent from this scheme that two approaches were used for the synthesis of aziridine VIII. The first approach consists in cyclization of terminal acetylenic amino alcohol VI, whereas the second consists in pyrolysis of aziridine IX, which was similarly obtained from amino alcohol VII and contains a tertiary hydroxy group. The structure of aziridine VIII was confirmed by the IR and PMR spectra. Starting amino alcohols VI and VII were obtained by opening of the corresponding acetylenic oxiranes IV and V with tert-butylamine.

We attempted to synthesize functionally substituted (at the nitrogen atom) 2-ethynylaziridines via the same scheme. The corresponding amino and hydrazino alcohols were obtained by the reaction of oxiranes IV and V with ammonia, methoxyamine, and hydrazine. However, we were unable to synthesize aziridines from them by the method indicated above.

We also studied the possibility of the synthesis of 2-ethynylaziridines by the Gabriel method by alkaline cyclization of the corresponding β-halo amines:



X a-d XI a-d XII d XIII d

X—XIII a $R^1=H$, $R^2=C(CH_3)_3$; b $R^1=H$, $R^2=OCH_3$; c $R^1=C(OH)(CH_3)_2$, $R^2=OCH_3$; d $R^1=C_6H_5$, $R^2=C(CH_3)_3$

Treatment of amine XIId with potassium hydroxide in ethanol leads to 1-tert-butyl-2-methyl-2-phenylethynylaziridine (XIIId). This scheme was not applicable to the synthesis of 2-ethynylaziridines XIIIa-c, since the hydrochlorides (XIIa-c) of the corresponding β-chloro amines cannot be obtained from the β-amino alcohol hydrochlorides and thionyl chloride.

EXPERIMENTAL

The PMR spectra of 10% or 5% solutions of the compounds in $CDCl_3$ or d_6-DMSO were recorded with a Perkin-Elmer R12A (60 MHz) or Brucker WH-90 spectrometer with tetramethylsilane as the internal standard. The IR spectra of suspensions in mineral oil or hexachlorobutadiene or liquid films of the compounds were obtained with a UR-20 spectrometer.

Reaction of Propynal with Aniline. A solution of 25.5 g (0.27 mole) of aniline in 200 ml of absolute ether and a solution of 16.5 g (0.27 mole) of acetic acid in 200 ml of absolute ether were added simultaneously with stirring at —40°C in the course of 1 h to a solution of 14.8 g (0.27 mole) of propynal in 300 ml of absolute ether, after which the temperature of the mixture was raised to room temperature, and it was washed successively with three 150-ml portions of water and 150 ml of 10% potassium bicarbonate solution. The yellow

precipitate was removed by filtration to give 17.4 g (29%) of N-(3-phenylamino-2-propenylidene)aniline (II) with mp 65-66°C. IR spectrum: 3400 (NH), 1650 (C=C), and 1640 cm^{-1} (C=N). PMR spectrum, δ: 8.00 (2H, d, J = 10 Hz, H_X and H_Y), 7.18 (10H, m, C_6H_5), 6.47 (1H, broad s, NH), and 5.77 ppm (1H, t, J = 10 Hz, =CH). Found: C 81.3; H 6.5; N 12.9%. $C_{15}H_{14}N_2$. Calculated: C 81.1; H 6.5; N 12.9%.

The ether solution was dried with sodium sulfate and passed through a column packed with aluminum oxide. The ether was removed by distillation, and the residue was distilled *in vacuo* to give 13.5 g (31%) of N-propynylideneaniline (I) with bp 50°C (0.01 mm). IR spectrum: 3280 (≡C—H), 2100 (C≡C), and 1600 cm^{-1} (C=N). PMR spectrum, δ: 7.53 (1H, d, J = 1.2 Hz, CH=N), 7.09 (5H, m, C_6H_5), and 3.20 ppm (1H, d, J = 1.2 Hz, ≡CH). Found: C 83.6; H 5.3; N 11.1%. C_9H_7N. Calculated: C 83.7; H 5.4; N 10.9%.

1-Phenyl-2-ethynyl-3-tert-butoxycarbonylaziridine (III). A solution of 13.5 g (0.09 mole) of tert-butyl chloroacetate in 100 ml of THF and a solution of 5.2 g (0.04 mole) of acetylenic imine I in 100 ml of THF were added simultaneously with stirring at —40°C to 10.1 g (0.09 mole) of potassium tert-butoxide in 50 ml of absolute THF, and the reaction mixture was maintained at this temperature for 5 h, after which the temperature was slowly raised to room temperature, and the mixture was maintained at this temperature for another 5 h. It was then filtered and evaporated, and the residue was washed with hexane. The hexane solution was passed through a column packed with aluminum oxide and evaporated, and the residual oil was crystallized from hexane to give 4.4 g (45%) of aziridine III with mp 64-65°C. IR spectrum: 3260 (≡C—H), 2130 (C≡C), and 1730 cm^{-1} (C=O). PMR spectrum, δ: 7.11 (5H, m, C_6H_5), 3.25 (1H, t, 2-H), 2.98 (1H, d, J = 2.6 Hz, 3-H), 2.18 (1H, d, J = 1.6 Hz, ≡CH), and 1.45 ppm [9H, s, $C(CH_3)_3$]. Found: C 73.8; H 6.9; N 6.0%. $C_{15}H_{17}NO_2$. Calculated: C 74.1; H 7.0; N 5.8%.

Starting acetylenic oxirane V was obtained by the method in [6]. Oxirane IV was synthesized by pyrolysis of V [7].

Acetylenic amino alcohols VI, VII, and XIIa-d were obtained by the method in [8].

1-tert-Butylamino-2-methyl-3-butyn-2-ol (VI). This compound was obtained in 89% yield and had mp 67-69°C. IR spectrum: 3310 (NH), 3280 (≡C—H), 3180 (OH), and 2100 cm^{-1} (C≡C). PMR spectrum, δ: 2.38-3.10 (2H, broad s, NH and OH), 2.83 and 2.42 (2H, AB system, J = 10.6 Hz, CH_2), 2.34 (1H, s, ≡CH), 1.47 (1H, s, CH_3), and 1.10 ppm [9H, s, $C(CH_3)_3$]. Found: C 69.4; H 10.7; N 9.3%. $C_9H_{17}NO$. Calculated: C 69.5; H 11.0; N 9.0%.

1-tert-Butylamino-2,5-dimethyl-3-hexyne-2,5-diol (VII). This compound was obtained in 90% yield and had mp 53-55°C. IR spectrum: 3300-3500 (NH, OH) and 2110 cm^{-1} (C≡C). PMR spectrum, δ: 2.87 (2H, s, OH), 2.76 and 2.42 (2H, AB system, J = 11.3 Hz, CH_2), 2.68 (1H, broad s, NH), 1.48 [6H, s, $C(CH_3)_2$], 1.38 (3H, s, CH_3), and 1.09 ppm [9H, s, $C(CH_3)_3$]. Found: C 67.3; H 10.5; N 6.9%. $C_{12}H_{23}NO_2$. Calculated: C 67.6; H 10.8; N 6.6%.

1-tert-Butyl-2-methyl-2-ethynylaziridine (VIII). A) A mixture of 1.24 g (0.008 mole) of amino alcohol VI, 1.1 ml (0.01 mole) of carbon tetrachloride, 2.62 g (0.01 mole) of triphenylphosphine, 1.4 ml (0.01 mole) of triethylamine, and 2 ml of acetonitrile was maintained at —3°C for 20 h and at room temperature for 10 h, after which 50 ml of hexane was added, and the precipitate was removed by filtration. The hexane solution was fractionated with collection of the fraction with bp 96-98°C to give 0.4 g (31%) of aziridine VIII. IR spectrum: 3310 (≡C—H) and 2110 cm^{-1} (C≡C). PMR spectrum, δ: 2.09 (1H, s, ≡CH), 1.91 and 1.42 (2H, AB system, J = 1.9 Hz, 3-H), 1.33 (3H, s, CH_3), and 1.13 ppm [9H, s, $C(CH_3)_3$]. Found: C 78.6; H 10.8; N 10.4%. $C_9H_{15}N$. Calculated: C 78.8; H 11.0; N 10.2%.

B) A 0.03-g sample of potassium metal was dissolved in 4.1 g (0.021 mole) of aziridine IX at 50°C, and the mixture was heated *in vacuo* (50 mm) to 110°C (bath temperature) to remove the reaction product, which was distilled at atmospheric pressure to give 1 g (36%) of aziridine VIII with bp 96°C.

1-tert-Butyl-2-methyl-2-(3-methyl-3-hydroxy-1-butynyl)aziridine (IX). A mixture of 8.5 g (0.04 mole) of amino alcohol VII, 4.3 ml (0.045 mole) of carbon tetrachloride, 11.8 g (0.045 mole) of triphenylphosphine, 6.3 ml (0.045 mole) of triethylamine, and 20 ml of acetonitrile was maintained at room temperature for 30 h, after which the precipitate was removed by filtration, the filtrate was evaporated, and the residue was washed with hexane. The hexane solution was passed through a column packed with aluminum oxide and evaporated. The residual oil was distilled *in vacuo* to give 2.3 g (33%) of aziridine IX with bp 70°C (0.01

mm). IR spectrum: 3350 (OH) and 2210 cm^{-1} (C≡C). PMR spectrum, δ: 2.69 (1H, s, OH), 1.89 and 1.60 (2H, d, J = 1.1 Hz, 3-H), 1.45 [6H, s, $C(CH_3)_2$], 1.35 (3H, s, CH_3), and 1.16 ppm [9H, s, $C(CH_3)_3$]. Found: C 74.1; H 10.8; N 7.3%. $C_{12}H_{21}NO$. Calculated: C 73.8; H 10.8; N 7.2%.

1-tert-Butylamino-2-methyl-4-phenyl-3-butyn-2-ol Hydrochloride (XId). Hydrogen chloride was passed through a solution of 1.5 g (6.5 mmole) of amino alcohol Xd for 30 min, and the resulting precipitate was washed with acetone to give 1.6 g (91%) of hydrochloride XId with mp 161-163°C.

1-tert-Butyl-2-methyl-2-(phenylethynyl)aziridine (XIIId). A mixture of 1 g (3.7 mmole) of hydrochloride XId, 0.58 g (4.8 mmole) of thionyl chloride, and 20 ml of chloroform was maintained at room temperature for 24 h, after which it was evaporated, and the residue was washed with ether. A 0.62-g (11 mmole) sample of potassium hydroxide and 10 ml of ethanol were added to crude hydrochloride XIId, and the mixture was stirred for 1 h. The precipitate was removed by filtration, and the filtrate was evaporated. The residue was chromatographed with a column packed with aluminum oxide by elution with pentane, and the pentane solution was evaporated to give 0.24 g (30%) of aziridine XIIId. IR spectrum: 3090 (ring C–H) and 2230 cm^{-1} (C≡C). PMR spectrum, δ: 7.29 (5H, m, C_6H_5), 2.06 and 1.72 (2H, d, J = 1.2 Hz, 3-H), 1.47 (3H, s, CH_3), and 1.23 ppm [9H, s, $C(CH_3)_3$]. Found: C 84.2; H 9.0; N 6.8%. $C_{15}H_{19}N$. Calculated: C 84.5; H 8.9; N 6.6%.

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DIMERIZATION OF BIRADICALOID HETEROCYCLIC COMPOUNDS. NITRO DERIVATIVES OF PYRROLO[1,2-a]BENZIMIDAZOLE

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A new type of easily dimerized heterocyclic compound, viz., nitro derivatives of 2-phenylpyrrolo[1,2-a]benzimidazole, was discovered. The reaction proceeds by heating the latter in acetic acid. A radical mechanism for the dimerization that takes into account partial protonation of the starting compound is discussed on the basis of electrochemical data, the high π-donor capacity of 2-phenyl-4-methylpyrrolo[1,2-a]benzimidazole, the coloration that is characteristic for self-complexes, and EPR spectroscopy.

In 1978 Gorelik and co-workers [1] found that 1-methyl-2-hydroxybenzindolequinone (I) is converted to dimer II in 65% yield when it is heated in acetic acid:

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