REACTIONS EXPANDING THE AZIRIDINE RING

V.* N-[β-(PYRIDIN-2-YL)ETHYL]AZIRINE AND ITS REACTIONS

F. N. Shomina, V. S. Étlis,
and A. P. Sineokov

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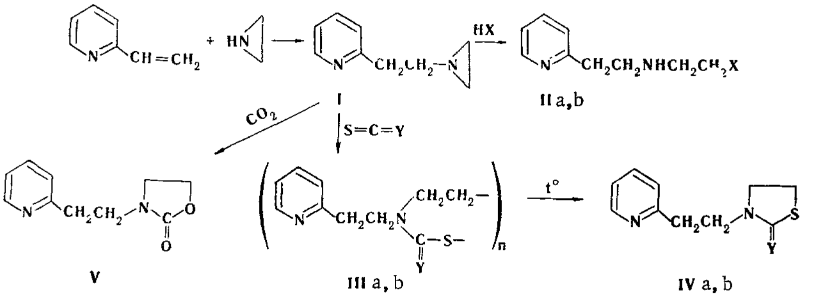
Azirine reacts with 2-vinylpyridine in the presence of metallic sodium with the formation of N-[β-(pyridin-2-yl)ethyl]azirine. The reaction of the latter with HBr and H_2S leads to N-(β-bromoethyl)- and N-(β-mercaptoethyl)-N-[β-(pyridin-2-yl)ethyl]amines. Carbon oxysulfide and carbon disulfide react at room temperature with N-[β-(pyridin-2-yl)ethyl]azirine to form copolymers in a ratio of 1 : 1. Carbon dioxide forms only N-[β-(pyridin-2-yl)ethyl]-oxazolinone under similar conditions.

Azirine adds to styrene in the presence of metallic sodium [2,3]. We have observed the addition of azirine to 2-vinylpyridine under similar conditions with the formation of N-[β-(pyridin-2-yl)ethyl]azirine (I). The three-membered ring of the azirine (I) is easily cleaved under the action of hydrobromic acid, giving the dihydrobromide of the amine (IIa), which was also obtained by treating with hydrobromic acid the product of the ethoxylation of N-[β-(pyridin-2-yl)ethyl]amine.

The reaction of the azirine (I) with hydrogen sulfide formed the aminoethyl mercaptan (IIb), which was also prepared by the alkaline treatment of the dihydrobromide of N-{β-[β-(pyridin-2-yl)ethylamino]-ethyl} isothiouronium bromide.

Under the action of catalytic amounts of hydrohalic acids, (I) polymerizes, giving a water-soluble low polymer. The reaction of the azirine (I) with carbon dioxide, carbon oxysulfide, and carbon disulfide, unlike that of the N-arylazirines, takes place without a catalyst. Carbon oxysulfide and carbon disulfide react very vigorously at room temperature, giving the peculiar copolymers (III).



IIa X=Br; b X=SH; III,IV a Y=O; b Y=S

The pyrolysis of the copolymers (III) in vacuum led to the formation of the thiazolidinone (IVa) and the thiazolidinethione (IVb). The latter were synthesized independently from the aminoethyl mercaptan (IIb) and phosgene or thiophosgene.

The heating of equimolecular amounts of the azirine (I) and CO_2 gave N-[β-(pyridin-2-yl)ethyl]oxazolidin-2-one (V).

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*For Communication IV, see [1].

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Thus, the nature of the reaction of the azirine (I) with carbon dioxide and its sulfur analogs is in agreement with the results that we have published previously for N-arylazirines [1,4] and also with those of other authors [5].

EXPERIMENTAL

The IR spectra* were taken on a UR-10 spectrophotometer in KBr tablets.

N-[β-(Pyridin-2-yl)ethyl]azirine (I). A mixture of 8.6 g (0.2 mole) of azirine, 0.2 g of sodium, and 10.5 g (0.1 mole) of 2-vinylpyridine was vigorously stirred at 55°C for 1 h. The unchanged azirine was distilled off, and the residue was fractionated in vacuum. This gave 10.3 g (70%) of (I). bp 77-79°C (1-2 mm), n_D^{20} 1.5210, d_4^{20} 1.0083. IR spectrum, cm^{-1}: 765, 1480, 1575, 1600 (pyridine ring), 3060 (ν_{C-H} in azirine). Found, %: C 73.0; H 8.1; N 19.0. $C_9H_{12}N_2$. Calculated, %: C 73.0; H 8.1; N 18.9.

(β-Bromoethyl)[β-(pyridin-2-yl)ethyl]amine (IIa). A. With stirring and cooling (5°C), 10.35 g of (I) was carefully added to 40 ml of 42% hydrobromic acid. The solution was evaporated and the residue was recrystallized from a mixture of methanol and ether. This gave 25 g (92%) of the dihydrobromide of the amine (IIa). mp 165°C. Found, %: C 27.6; H 3.8; Br 59.9; N 7.2. eq. 198. $C_9H_{15}BrN_2 \cdot 2HBr$. Calculated, %: .C 27.6; H 3.8; Br 61.3; N 7.1. eq. 195.

B. The reaction of (β-hydroxyethyl)[β-(pyridin-2-yl)ethyl]amine [6] with HBr was performed in a similar manner to the synthesis of β-bromoethylamine [7]. After the elimination of the water, the reaction product was recrystallized from a mixture of methanol and ether (1:1). Yield 66%. mp 165°C. The product gave no depression of the melting point with that of the reaction of (I) and HBr.

β-{[β-(Pyridin-2-yl)ethyl]amino}ethyl Mercaptan (IIb). A. To a mixture of 17 g (0.5 mole) of hydrogen sulfide in 50 ml of methanol at −50°C was added 7.4 g (0.05 mole) of (I) in 50 ml of methanol. The mixture was kept with cooling for 1 h, and then the temperature was brought up to that of the room, the excess of hydrogen sulfide was blown off, and the mixture was left overnight. After the elimination of the solvent, the product was fractionated in vacuum, giving 5.8 g (65%) of a substance with bp 120-122°C (2 mm); n_D^{20} 1.5552. Found, %: C 59.0; H 7.6; N 15.2; S 17.2; SH iodometrically 18.0; eq. 181.5. $C_9H_{14}N_2S$. Calculated, %: C 59.3; H 7.7; N 15.4; S 17.6; SH 18.2; eq. 182.

B. A mixture of 3.9 g (0.01 mole) of the amine (IIa) and 0.76 g (0.01 mole) of thiourea in 20 ml of methanol was boiled for 4 h. The methanol was driven off, and from the residue was isolated 4 g (86%) of the dihydrochloride of N-{β-[β-(pyridin-2-yl)ethyl]aminoethyl} isothiouronium bromide with mp 238°C. Found,%: N 12.1; S 6.8; Br (ionic) 34%; eq. (with respect to Br^-) 231. $C_{10}H_{19}BrN_4S \cdot 2HBr$. Calculated,%: N 12.0; S 6.8; Br (ionic) 34.3%; eq. (with respect to Br^-) 233.5.

A mixture of 11.7 g (0.03 mole) of the isothiouronium salt and 50 ml of 40% NaOH was boiled for 30 min. The cooled solution was extracted with chloroform. The chloroform extract was dried with $MgSO_4$, the solvent was evaporated off, and the residue was fractionated in vacuum. This gave 1 g (22%) of the amine (IIb) with bp 120°C (2 mm); n_D^{20} 1.5550.

Copolymer of the Azirine (I) with Carbon Oxysulfide (IIIa). A. A mixture of 3.7 g (0.025 mole) of (I) and 1.5 g (0.025 mole) of COS was made at −70°C and was then kept at room temperature for 5 h, during which time it solidified. The product was washed repeatedly with ether, and the ethereal washings yielded 2 g of unchanged azirine. The weight of the copolymer was 2 g (98% on the azirine that had reacted). Softening point 160°C. Found,%: N 13.4; S 15.3; eq. 207. $C_{10}H_{12}N_2SO$. Calculated,%: N 13.4; S 15.4; eq. 208. In the IR spectrum: $\nu_{-\overset{|}{N}-\underset{\underset{O}{\|}}{C}-S-}$ 1660-1670 cm^{-1}. The copolymer was insoluble in organic solvents and soluble in dilute hydrochloric acid. The hydrochloride of the copolymer is a hygroscopic substance with a softening point of 168-170°C.

N-[β-(Pyridin-2-yl)ethyl]thiazolidin-2-one (IVa). A. A mixture of 3.6 g (0.02 mole) of the amino mercaptan (IIb) and 4.04 g (0.04 mole) of triethylamine in 40 ml of chloroform was carefully added to a cooled (−20°C) solution of 1.98 g (0.02 mole) of phosgene in 20 ml of chloroform. The mixture was stirred at room temperature for 1 h and was then washed with water and dried with $MgSO_4$. The chloroform was driven off, and the residue yielded 1.5 g (36%) of compound (IVa) with mp 67-68°C (from hexane). It gave no depression of the melting point with the product of the pyrolysis of the copolymer, and their IR spectra were identical.

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B. The copolymer (IIIa) (1 g) was kept in an evacuated tube at 170°C for 2 h. On cooling, the melt crystallized, giving 0.7 g (70%) of compound (IVa) with mp 67-68°C (from hexane). Found, %: C 57.7; H 5.8; N 13.4; S 15.3. eq. 207. $C_{10}H_{12}N_2OS$. Calculated,%: C 57.6; H 5.8; N 13.4; S 15.4. eq. 208. IR spectrum: 1670 cm^{-1} (>N–COS).

Copolymer of the Azirine (I) with Carbon Disulfide (IIIb). A. At –70°C, 7.4 g (0.05 mole) of (I) and 3.8 g (0.05 mole) of CS_2 were mixed, and the mixture was kept at room temperature for 1 h. Then it was washed with ether and methanol, and from the washings was obtained 4 g (36%) of N-[β-(pyridin-2-yl)ethyl]-thiazolidine-2-thione (IVb). IR spectrum: 1460-1465 cm^{-1} (>N–CSS). mp 86-87°C (from a mixture of methanol and ether). Found, %: N 12.5; S 28.0; eq. 224. $C_{10}H_{12}N_2S_2$. Calculated,%: N 12.5; S 28.6; eq. 224. The residue was insoluble in organic solvents and soluble in 10% hydrochloric acid. Softening point 167-168°C. IR spectrum: 1470 cm^{-1} (>N–CSS). Found,%: N 12.8; S 26.6; eq. 221. $C_{10}H_{12}N_2S_2$. Calculated, %: N 12.5; S 28.6; eq. 224.

B. At –70°C, 3.7 g (0.025 mole) of (I), 1.9 g (0.025 mole) of CS_2, and 10 ml of benzene were mixed, and the mixture was then kept at room temperature for 5 h. The polymer that deposited was washed repeatedly with ether and methanol and was dried in vacuum. Yield 5.4 g (97%); the hydrochloride of the copolymer was a hygroscopic substance with a softening point of 158-159°C.

N-[β-(Pyridin-2-yl)ethyl]thiazolidine-2-thione (IVb). A. The copolymer (1.1 g) was kept in an evacuated tube at 180-190°C for 2 h. On cooling, the melt of the copolymer crystallized, giving 0.70 g (64%) of crystals with mp 87-88°C (from a mixture of hexane and methanol). It showed no depression of the melting point with the reaction product, and their IR spectra were identical.

B. To a mixture of 3.6 g (0.02 mole) of the amino mercaptan (IIb) and 4.04 g (0.04 mole) of triethylamine in 40 ml of chloroform at –5°C was added 2.3 g (0.02 mole) of thiophosgene in 20 ml of chloroform. The mixture was stirred at room temperature for 1 h and was then washed with water and dried with $MgSO_4$. The chloroform was driven off, and the residue yielded compound (IVb) with mp 87-88°C; yield 3 g (70%). It gave no depression of the melting point with the product of the reaction of I and CS_2, and their IR spectra were identical.

N-[β-(Pyridin-2-yl)ethyl]oxazolidin-2-one (V). A. A mixture of 2.96 g (0.02 mole) of (I) and 0.88 g (0.02 mole) of CO_2 was heated in a tube at 95°C for 20 h. The mixture was repeatedly washed with ether, and the ethereal washings yielded 1.41 g (0.009 mole) of unchanged (I). The residue yielded 2 g (72% on the I that had reacted) of the oxazolidinone (V). IR spectrum: $\nu_{C=O}$ 1740-1750 cm^{-1}, mp 99.5-100°C. Found, %: C 62.5; H 6.2; N 14.4; eq. 192. $C_{10}H_{12}N_2O_2$. Calculated, %: C 62.5; H 6.2; N 14.6; eq. 192.

B. A mixture of 3.32 g (0.02 mole) of (hydroxyethyl)[β-(pyridin-2-yl)ethyl]amine, 2.36 g (0.02 mole) of diethyl carbonate, and 0.1 g of sodium methoxide was kept at 150°C for 15 h. The ethanol was distilled off, and the residue yielded 2.7 g (70%) of the oxazolidinone (V) with mp 99-100°C (from acetone–hexane). It gave no depression of the melting point with the product of the reaction of (I) and CO_2, and their IR spectra were identical.

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