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STUDY OF THE REACTION BETWEEN 2-IMINO-5-(CHLOROMETHYL) OXAZOLIDINE-1, 3 AND METALLIC SODIUM OR DISODIUM ACETYLIDE

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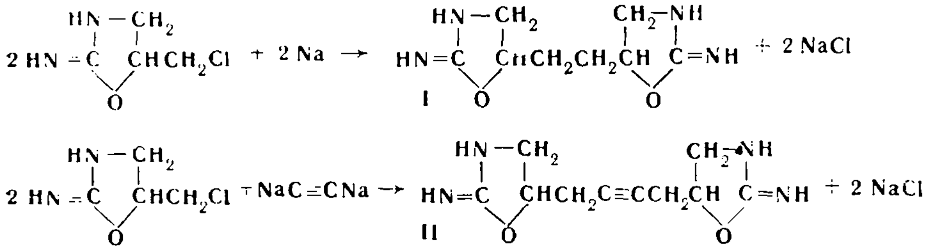
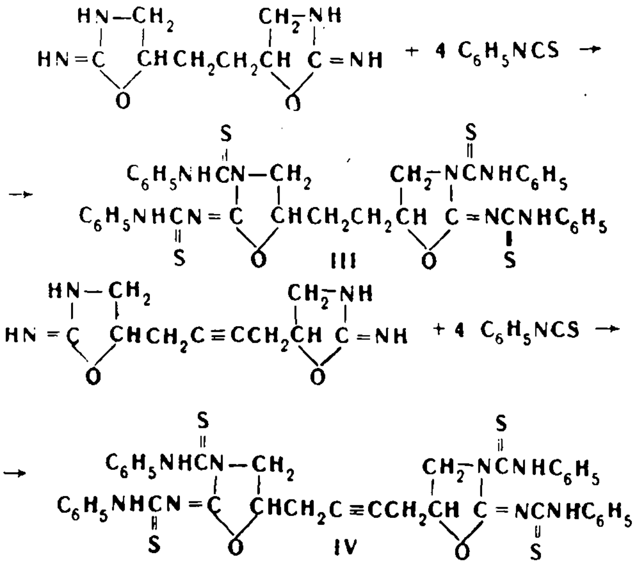
The reaction of 2-imino-5-(chloromethyl) oxazolidine-1, 3 with metallic sodium or disodium acetylide is investigated. Conditions are found for obtaining 1, 2-bis(2-iminooxazolil-5'-yl)-ethane and 1, 4-bis(2'-iminooxazolid-5'-yl) but-2-yne, respectively saponified to 1, 6-diaminohexane-2, 5-diol and 1, 8-diaminooct-4-yne-2, 7-diol. It is intended to use these compounds as monomers for preparing polyamide resins.

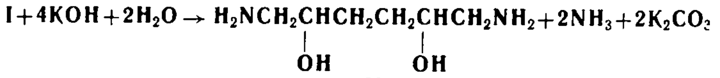
Continuing systematic research on oxazolidine and oxazoline derivatives, with a view to discovering new types of monomers for preparing polyamide resins, a study has been made of the reaction of 2-imino-5-(chloromethyl) oxazolidine-1, 3 with metallic sodium and disodium acetylide [1].



The compounds obtained were orange resinous substances. Compounds I and II are readily soluble in water, methanol, and dimethylformamide, but less soluble in ethanol, while they are almost insoluble in other organic solvents. This makes it difficult to purify them from the sodium chloride formed in the reaction, which makes their nitrogen contents a little low. I and II were identified as compounds III and IV, obtained by reacting I and II with phenylisothiocyanate.

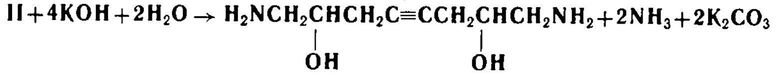


The structures of I and II follow from their modes of formation, and are confirmed by saponification [2, 3], to give give 1, 6-diaminohexane-2, 5-diol(V) and 1, 8-diaminoct-4-yne-2, 7-diol(VI), respectively, along with ammonia.



$$I+4KOH+2H_2O \rightarrow H_2NCH_2\underset{OH}{C}HCH_2CH_2\underset{OH}{C}HCH_2NH_2+2NH_3+2K_2CO_3$$

V



$$II+4KOH+2H_2O \rightarrow H_2NCH_2\underset{OH}{C}HCH_2C{\equiv}CCH_2\underset{OH}{C}HCH_2NH_2+2NH_3+2K_2CO_3$$

VI

Experimental

1, 2-Bis(2-iminoxazolid-5-yl) ethane (I) and 1, 4-bis (iminoxazolid-5-yl)-but-2-yne (II). In a 3-necked flask fitted with a thermometer and stirrer, 270 g (2 mole) 2-imino-5-(chloromethyl) oxazolidine-1, 3 was dissolved in 500 ml dry dimethylformamide, then 55 g (2.4 g at) finely-divided sodium introduced for the preparation of I, but 77 g (1.1 mole) disodium acetylide for preparation of II, and the mixture stirred at 80°C for 6 hr. After cooling, the reaction products were filtered to remove excess sodium, and the dimethylformamide in the filtrate extracted with ether. The reaction product was dissolved in dry methanol, the precipitate of NaCl filtered off, and the methanol distilled off.

Compound I: yield 96%, d_4^{20} 1.2500, n_D^{20} 1.5300. Found: N 27.46, 27.50%; M 198.0, 191.0 (Rast); 207.8, 207.1 (nonaqueous titration); MR_D 49.01. Calculated for $C_8H_{14}N_4O_2$: N 28.28%; M 198.2; MR_D 49.16.

Compound II: yield 95%, d_4^{20} 1.1991, n_D^{20} 1.5210. Found: N 24.90, 24.94%; M 224.6, 226.8 (Rast); 219.9, 220.6 (nonaqueous titration); MR_D 57.45. Calculated for $C_{10}H_{14}N_4O_2$: N 25.21%; M 222.3; MR_D 57.81.

1, 2-Bis [(2-N-phenylthiocarbaminoylimino-3-phenylthiocarbaminoyl)-oxazolilyl-5] ethane (III), and 1, 4-bis [2-N-phenylthiocarbaminoyl-3-phenylthiocarbaminoyl)-oxazolid-5-yl] but-2-yne (IV). Compound IV was prepared by carefully mixing 25 g (0.112 mole) II and 85 g (4.4 mole) phenylisothiocyanate, and compound III by carefully mixing 27 g (0.1 mole) I and 59.48 g (4.4 mole) phenylisothiocyanate, followed by heating at 200° C for 40 min with occasional stirring. After cooling the reaction products, excess phenylisothiocyanate was extracted with ether.

Compound III: yield 90%, mp 143–144° C (decomp, ex EtOH). Found: N 14.99, 15.29%. Calculated for $C_{38}H_{34}N_8O_2S_4$: N 15.17%.

Compound IV: yield 97.8%, mp 180–182°C (decomp, ex EtOH). Found: N 14.48, 14.49%. Calculated for $C_{36}H_{34}N_8O_2S_4$: N 14.68%.

1, 6-Diaminohexane-2, 5-diol (V). 198.2 g (1 mole) I was dissolved in 572 ml water-MeOH (1 : 2.36), and 134.4 g (2.2 mole) KOH carefully added in small portions. The reactants were refluxed together for 1 hr, the MeOH then distilled off, 91.5 ml H_2SO_4 (d 1.835) carefully added to the residue, the water vacuum-distilled off, and 1, 6-diaminohexane-2, 5-diol (viscous brown mass) extracted from the residual mixture with dry MeOH. Yield 140 g (98%). Three distillations gave pure V, bp 130°C (2 mm); d_4^{20} 1.1292; n_D^{20} 1.5010. Found: N 18.98, 18.92%; MR_D 38.65. Calculated for $C_6H_{14}N_2O_2$: N 18.90%; MR_D 39.80.

Saponification of 0.8001 g substance I in a Kjeldahl nitrogen apparatus gave 0.1105 g NH_3; calculated 0.1224 g.

1, 8-Diaminooct-4-yne-2, 7-diol (VI). 171 g (0.8 mole) II was dissolved in 250 ml water, 86 g (1.5 mole) KOH added, and the whole heated for 3 hr. After cooling, the reaction products were saturated with CO_2, the precipitate filtered off, the water vacuum-distilled off, and 1, 8-diaminooct-4-yne-2, 7-diol (viscous brown mass) extracted from the residue with anhydrous MeOH. Yield 84 g (97.7%). Four distillations gave pure VI, bp 152–154°C (2 mm); d_4^{20} 1.0680; n_D^{20} 1.4990. Found: N 16.44, 16.41%; MR_D 47.33. Calculated for $C_8H_{16}N_2O_2$: N 16.26%; MR_D 47.04.

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