It should be noted that the capacities of the obtained sorbents with respect to C_{60} and C_{70} proved to be low. When the quantity of the fullerenes introduced increases, chromatographic peaks become asymmetrical, except for those on the sorbent based on TCA (sorbent **6**). The latter exhibited a high capacity, although the retention factors (k) attained on this sorbent are relatively low. In our opinion, this is due to the fact that TCA in sorbent **6**, unlike the grafted compounds in sorbents 1-5, is arranged flatly with respect to the silica gel surface. This ensures high density of the grafted TCA (10-12 % (w/w)) and, perhaps, more favorable conditions for the sorption of C_{60} and C_{70} .

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Received December 6, 1996; in revised form March 18, 1997

Acid-catalyzed decomposition of cyclohexanespiro-2-oxazolidine

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Heating cyclohexanespiro-2-oxazolidine at 160-200 °C in the presence of protic acids results in its decomposition to give N-(2-hydroxyethyl)cyclohexylamine, N-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole, and 2-cyclohexylidenecyclohexanone. The possible pathways leading to these compounds are discussed.

Key words: cyclohexanespiro-2-oxazolidine, N-(2-hydroxyethyl)cyclohexylamine, N-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole, 2-cyclohexylidenecyclohexanone, acid catalysis.

The outcome of acid-catalyzed transformations of oxazolidines depends markedly on the structure of the oxazolidine itself and on the nature of the catalyst. For example, heating N-phenyloxazolidines in the presence of TsOH or $R_3N \cdot HCl$ leads to low-molecular-weight poly(aminoethers);¹ N-alkyloxazolidines do not polymerize under these conditions. When N-propyloxazolidine is heated to 130 °C in the presence of HCl or H_2SO_4 , it is partly reduced to N-methyl-N-propylaminoethanol and it partly polymerizes.² Upon heating with polyphosphoric acid, N-substituted cyclohexanespiro-2-oxazolidines are cleaved to give cyclohexanone and N,N'-disubstituted piperazines.³

In conformity with published data,³ we expected that cyclohexanespiro-2-oxazolidine (1) would be converted under similar conditions into cyclohexanone and piperazine or their derivatives. However, it was found that at 160-200 °C in the presence of polyphosphoric acid,

oxazolidine 1 decomposes with elimination of ammonia and water to give a complex mixture of products (12 components, GLC). N-(2-Hydroxyethyl)cyclohexylamine (2), N-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole (3), and 2-cyclohexylidenecyclohexanone (4) formed as the major products and were isolated preparatively (Scheme 1). In addition, GLC analysis showed that the reaction mixture contained the initial oxazolidine 1, cyclohexanone, 2-aminoethanol, and contained no piperazine and no products of the reduction of cyclohexanone and ketone 4, *viz.*, cyclohexanol or 2-cyclohexylidenecyclohexanol.

This reaction outcome, which differs fundamentally from that of the acid-catalyzed cleavage of N-substituted cyclohexanespiro-2-oxazolidines, is apparently due to the fact that oxazolidine 1 is able⁴ to undergo tautomeric transformation into N-cyclohexylideneaminoethanol (1a).

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 8, pp. 1547-1548, August, 1997.

1066-5285/97/4608-1482 \$18.00 © 1997 Plenum Publishing Corporation



The formation of amino alcohol 2 unambiguously indicates that the cleavage of oxazolidine 1 involves redox processes. Tetrahydroindole 3 can be regarded as a product of the oxidation of oxazolidine 1. This product might be formed via dehydration of oxazolidine 1 (in its tautomeric form 1a) to 2,3,4,5,6,7-hexahydroindole (5), similarly to the process observed⁵ in the condensation of cyclohexanone with 2-aminoethanol in the presence of H₂SO₄. After that, compound 5 is oxidized to give 4,5,6,7-tetrahydroindole (6), whose hydroxyethylation by, for example, 2-aminoethanol or ethylene oxide formed from the latter, yields tetrahydroindole 3 (Scheme 2).

It was shown that the cleavage of oxazolidine 1 under consideration can also occur in the presence of TsOH, H_2SO_4 , and H_3PO_4 , whereas in the absence of acids, only slight resinification occurs without the formation of compounds 2 and 3 after heating to 200 °C for 8 h.

Ketone 4 is formed either via condensation (of crotonic type), which is known for oxazolidines,⁶ and subsequent hydrolysis of the product of this condensation or via condensation of the cyclohexanone resulting from the hydrolysis of oxazolidine 1.

Experimental

A mixture of oxazolidine 1 (28.8 g, 0.2 mol) and polyphosphoric acid (1.0 g) was refluxed for 10 h. The temperature of the reaction mixture was 200 °C at the beginning of the reaction and decreased spontaneously to 160 °C by the end. Benzene (100 mL) was added to the cooled reaction mixture, and the products were extracted with water (3×100 mL). Vacuum distillation of the extract gave 1.4 g of N-(2-hydroxyethyl)cyclohexylamine 2 (b.p. 91-95 °C (10 Torr),



m.p. 47-49 °C; cf. Ref. 7: m.p. 50 °C), 3.04 g of 2-cyclohexylidenecyclohexanone 4 (b.p. 103-106 °C (10 Torr), $n_{\rm D}^{20}$ 1.5058, d_4^{20} 1.0032; cf. Ref. 8: b.p. 273-275 °C (760 Torr), $n_{\rm D}^{20}$ 1.5062, d_4^{20} 1.004) and 1.72 g of N-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole 3, b.p. 134-136 °C (3 Torr), $n_{\rm D}^{20}$ 1.5402; d_4^{20} 1.0698 (cf. Ref. 9: b.p. 152-155 °C (6 Torr), $n_{\rm D}^{20}$ 1.5408; d_4^{20} 1.0800). The ¹H NMR and IR spectra of the isolated compounds were identical to those recorded for authentic samples.

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Received February 28, 1997