UNEXPECTED HYDROGENOLYSIS OF 2-ISOXAZOLINES

F. A. Lakhvich, E. V. Koroleva,
and I. P. Antonevich

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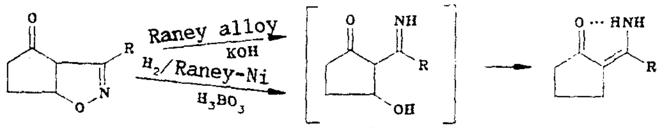
Reductive fission of 2-isoxazolines leads to β-hydroxyketones, γ-aminoalcohols or oximes [1, 2] depending upon the nature of the reducing agent.

We have found that 4,5-cyclopentanoisoxazolines I (bearing in mind their stability relative to many reducing agents [3]) undergo fission at the N—O bond using Raney alloy in alkaline solution to form the enaminoketones II in high yield. Hydrogenolysis of the isoxazolines I also occurs over Raney nickel in the presence of boric acid using the conditions described for the conversion of isoxazolines to β-hydroxyketones [1, 4]:



Ia,b IIIa,b IIa,b

I—III a $R=C_4H_9$, b $R=C_7H_{15}$

A solution of KOH (1M, 5 ml) was added dropwise to a solution of isoxazoline I (1 mmole) and Raney alloy (1 g) in methanol (15 ml) which had been heated to 45°C. The solution was stirred for 1 h at 50-55°C, cooled, filtered, evaporated, and the product extracted from the aqueous residue using ether. Purification by chromatography on Kieselgel 60 F_{254} plates (ether-hexane, 2:1) gave a yield of 80%. Catalytic hydrogenation according to [4] gave a 35% yield.

2-(1-Aminopent-1-en)cyclopentan-1-one (IIa).* IR spectrum (film): 3330, 3190, 1635, 1520 cm^{-1}. PMR spectrum ($CDCl_3$): 0.95 (3H, t, CH_3); 1.4 and 1.55 (4H, m, 3- and 4-H); 1.87 (2H, q, ring CH_2); 2.15 (2H, t, 2-H); 2.3 (2H, t, ring CH_2); 2.5 (2H, t, $H_2CC{=}O$); 4.8 (1H, br. s, free NH); 9.4 ppm (1H, br. s, bonded NH). M^+ 167.

2-(1-Aminooct-1-en)cyclopentan-1-one (IIb). IR Spectrum (film): 3340, 3190, 1635, 1520 cm^{-1}. PMR Spectrum ($CDCl_3$): 0.89 (3H, t, CH_3); 1.28 (8H, m, 4- to 7-H); 1.54 (2H, q, 3-H); 1.85 (2H, q, ring CH_2); 2.14 (2H, t, $\underline{H}_2CNH_2$); 2.31 (2H, t, ring CH_2); 2.51 (2H, t, $H_2CC{=}O$); 4.8 (1H, br. s, NH); 9.4 ppm (1H, br. s, NH). M^+ 209.

Formation of the enaminoketones was previously observed only upon fission of the cyclohexanoisoxazolines under conditions of catalytic hydrogenation in which, however, the cyclopentanone analog was stable [5]. This unexpected hydrogenolysis of 2-isoxazolines is evidently due to participation of the carbocyclic carbonyl group in the reaction. Formation of the enaminoketone II apparently occurs as a result of successive hydrogenolyses of the heterocycle and oximino ketone III and not hydrogenolysis-hydrolysis which typifies other examples.

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Bioorganic Chemistry Institute, Academy of Sciences of the Belorussian SSR, Minsk 220045.
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RECYCLIZATION OF 3-OXAZOLIOPROPANESULFONATES INTO 2,5-DIHYDRO-1,2,4-TRIAZINIO-4-PROPANESULFONATES

V. F. Lipnitskii and O. P. Shvaika

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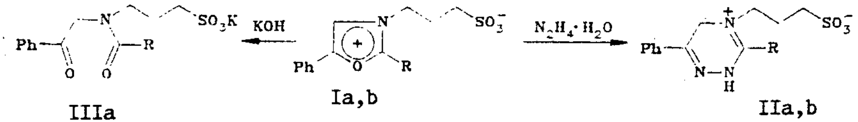
We obtained new oxazolium derivatives with a betaine structure Ia, b and showed that their recyclization by the action of hydrazine results in the synthesis of previously unknown triazinium betaines IIa, b.



I-IIIa R=4-PhC_6H_4: b R=Ph

The recyclization is carried out by boiling equivalent amounts of sulfobetaine I and hydrazine hydrate in methanol. This is a convenient method for the preparation of triazinium derivatives having a betaine structure with an attached alkanesulfonate group. The alkaline hydrolysis of betaines Ia,b with the formation of amides III, which would be expected to accompany the recyclization reaction, was not observed, and compounds III could be obtained only by the action of alkalies.

Sulfobetaines Ia,b were obtained by quaternization of the corresponding oxazoles with 1,3-propanesultone by heating in o-dichlorobenzene (170°C, 30 min).

The composition and structure of the synthesized compounds was confirmed by elemental analysis for C, H, N, S, and also by the IR and PMR spectral data.

3-[2-(4-Biphenylyl)-5-phenyloxazolio-3]propanesulfonate (Ia). Yield 93%. mp 279...280°C (dec., from acetic acid), IR spectrum (in Nujol): 1640, ($C{=}N^+$); 1600, 1560 (C=C); 1215, 1180, 1040 cm^{-1} (S=O). PMR spectrum (CF_3COOH, TMS): 2.83 (2H, m, CH_2), 3.57 (2H, t, J = 7 Hz, CH_2SO_3); 4.93 (2H, t, J = 8 Hz, CH_2N^+); 7.76 ppm (15H, m, aromatic protons).

3-(2,5-Diphenyloxazolio-3)propanesulfonate (Ib). Yield, 70%. mp 224...225°C (from ethanol). IR spectrum (in Nujol): 1630, ($C{=}N^+$); 1590, 1550 (C=C); 1210, 1160, 1035 (S=O). PMR spectrum (CF_3COOH, TMS): 2.77 (2H, m, CH_2), 3.50 (2H, t, J = 7 Hz, CH_2SO_3); 4.87 (2H, t, J = 8 Hz, $CH_2{-}N^+$); 7.83 ppm (11H, m, aromatic protons).

3-[3-(4-Biphenylyl)-6-phenyl-2,5-dihydro-1,2,4-triazino-4]propanesulfonate (IIa). Yield 81%, mp 278...280°C (dec., from methanol). IR spectrum (in Nujol): 3350 (NH); 1620 ($C{=}N^+$); 1600, 1575, 1540 (C=C); 1230, 1150, 1030 cm^{-1} (S=O). PMR spectrum (CF_3COOH, TMS): 2.60 (2H, m, CH_2); 3.27 (2H, t, J = 7 Hz, CH_2SO_3); 4.00 (2H, m, $CH_2{-}N^+$); 4.96 (2H, s, ring CH_2); 7.66 ppm (14H, m, aromatic protons).

3-(3,6-Diphenyl-2,5-dihydro-1,2,4-triazino-4)propanesulfonate (IIb). Yield 80%. mp 293...295°C (dec., from ethanol). IR spectrum (in Nujol): 3200 (NH), 1625 ($C{=}N^+$); 1600, 1580, 1545 (C=C); 1235, 1185, 1040 cm^{-1} (S=O). PMR spectrum (CF_3COOH, TMS): 2.47 (H, m, CH_2), 3.00 (2H, t, J = 7 Hz, CH_2SO_3); 3.83 (2H, t, J = 7 Hz, $CH_2{-}N^+$); 4.90 (2H, s, ring CH_2); 7.53 ppm (10H, m, aromatic protons).

3-[N-(4-Phenylbenzoyl)-N-phenacylamino]propane Potassium Sulfonate (IIIa). Yield 93%, mp 203...205°C. IR spectrum (in Nujol): 1690 (C=O); 1630 (C=O), 1610, 1600, 1580 (C=C),

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