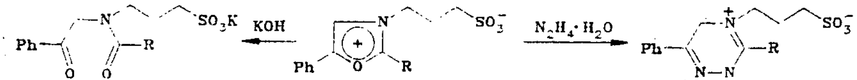
4. F. A. Lakhvich, V. A. Khripach, A. N. Pyrko, I. P. Antonevich, T. V. Yankova, E. V. Koroleva, and A. A. Akhrem, Khim. Geterotsikl. Soedin., No. 7, 972 (1988).
5. A. A. Akhrem, F. A. Lakhvich, V. A. Khripach, and I. I. Petrusevich, Khim. Geterotsikl. Soedin., No. 7, 891 (1976).

RECYCLIZATION OF 3-OXAZOLIOPROPANESULFONATES INTO 2,5-DIHYDRO-1,2,4-TRIAZINIO-4-PROPANESULFONATES

V. F. Lipnitskii and O. P. Shvaika

UDC 547.873.07'787.04'269.3'233.3

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.



IIIa Ia,b 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),

---

Institute of Physical Organic Chemistry and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1425-1426, October, 1989. Original article submitted November 29, 1988.

0009-3122/89/2510-1196$12.50

1205, 1180, 1050 cm^{-1} (S=O). PMR spectrum (CF_3COOH, TMS): 2.33 (2H, m, CH_2); 3.13 m, (2H, m, CH_2N); 3.87 (2H, m, CH_2SO_3); 5.17 (2H, s, $CH_2C{=}O$); 7.50 ppm (14H, m, aromatic protons).

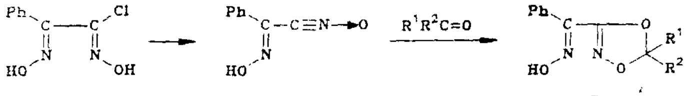
NONCATALYTIC ADDITION OF NONACTIVATED CARBONYL DERIVATIVES TO α-OXIMINOPHENYLACETONITRILE OXIDE

V. G. Andrianov and A. V. Eremeev

UDC 547.793.8.07

Nitrile N-oxides undergo a cycloaddition reaction with carbonyl compounds, activated by electron-acceptor substituents. Nonactivated aldehydes and ketones react only in the presence of a boron trifluoride etherate catalyst [1].

We studied the properties of α-oximinophenylacetonitrile oxide, formed by the dehydrochlorination of phenylchloroglyoxime, and found that in contrast to other nitrile oxides, this compound reacts readily with nonactivated aldehydes and ketones with the formation of the corresponding 1,4,2-dioxazoles:



Ia-e

a $R^1{=}R^2{=}H$; b $R^1{=}H$, $R^2{=}CH_3$; c $R^1{=}R^2{=}CH_3$; d $R^1{=}CH_3$, $R^2{=}C_2H_5$; e $R^1R^2{=}(CH_2)_5$

Even formaldehyde undergoes this reaction, but its cycloaddition products could not be obtained previously. In the reaction with cyclic ketone – cyclohexanone, the corresponding spiro-derivative Ie is formed.

The reaction is carried out at room temperature by adding a dehydrochlorinating agent (a solution of sodium bicarbonate or triethylamine) to a solution of chlorophenylglyoxime and the carbonyl derivative in alcohol (compounds Ia,b,e) or in an excess of the same carbonyl derivative (compounds Ic,d).

Oxime of 3-Benzoyl-1,4,2-dioxazole (Ia). mp 215...216°C (from alcohol). PMR spectrum (here and below in $DMSO-D_6$): 5.75 (2H, s, CH_2); 7.47 (3H, m, m-, p-H); 8.44 (2H, m, o-H); 10.78 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5-methyl-1,4,2-dioxazole (Ib). mp 164...165°C (from benzene). PMR spectrum: 1.62 (3H, d, CH_3); 5.96 (1H, q, CH); 7.47 (3H, m, m-, p-H); 8.46 (2H, m, o-H); 10.73 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5,5-dimethyl-1,4,2-dioxazole (Ic). mp 189...191°C (from benzene). PMR spectrum: 1.69 (6H, s, CH_3); 7.44 (3H, m, m-, p-H); 8.44 (2H, m, o-H); 10.73 ppm (1H, s, OH).

Oxime of 3-Benzoyl-5-methyl-5-ethyl-1,4,2-dioxazole (Id). mp 159...161°C (from alcohol). PMR spectrum: 0.73 (3H, t, CH_3); 1.67 (3H, s, CH_3), 2.04 (2H, q, CH_2); 7.48 (3H, m, m-, p-H); 8.49 (2H, m, o-H); 10.79 ppm (1H, s, OH).

Oxime of 3-Benzoyl-1,4,2-dioxazole-5-spirocyclohexane (Ie). mp 246...248°C (from alcohol). PMR spectrum: 1.80 (10H, m, C_5H_{10}); 7.48 (3H, m, m-, p-H); 8.50 (2H, m, o-H); 10.80 ppm (1H, s, OH).

LITERATURE CITED

1. C. Grundman and P. Grunanger, The Nitrile Oxides, Springer-Verlag, Berlin (1971), p. 120.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1426-1427, October, 1989. Original article submitted January 3, 1989.

0009-3122/89/2510-1197$12.50