SYNTHESIS OF DIAZOXYFURAZANES

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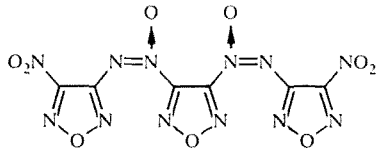
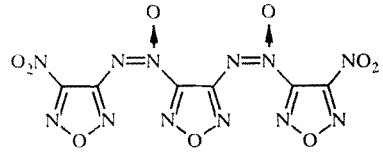
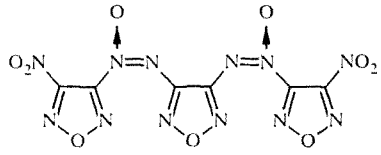
In a continuation of our investigation of methods of preparing polyazoxyfurazanes by our previously proposed two stage process [1] we have synthesized the new isomeric compounds Ia-c which contain two furazanyldiazenoxide units.



Ia

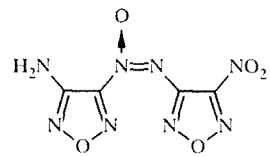


Ib



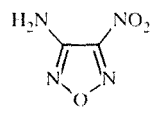
Ic

In stage 1, a mixture of 10 mmole 3-(aminofurazanyl-ONN-azoxy)-4-nitrofurazane (II) and 5 mmole aminonitrofurazane (III) suspended in 56 ml conc. HCl was oxidized by the addition of 350 ml 0.3 N $KMnO_4$ solution (1 h, 50-60°C) and then kept at this temperature for 2 h. Extraction with chloroform gave a mixture which was chromatographed on a silica gel column ($CHCl_3$ eluent) to give 0.7 mmole 3-(nitrofurazanyl-ONN-azoxy)-4-(nitrofurazanylazo)furazane (IV), 3.8 mmole azobis(nitrofurazanyl-NNO-azoxy)furazane (V), mp 98°C, and 2.3 mmole dinitroazofurazne (VI). The yield of compound IV, necessary for the second step, was not increased by changing the mole ratio of amines II and III nor by changing the order of mixing the reagents.

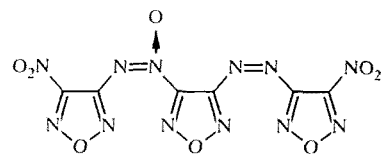


II

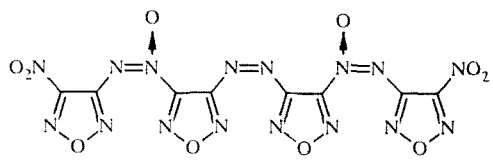
+



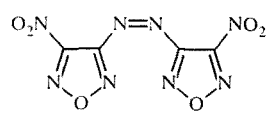
III



IV



V



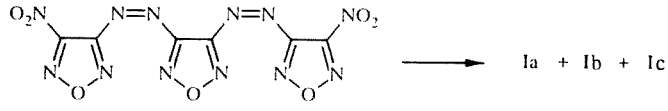
VI

N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 714-715, May, 1994. Original article submitted April 11, 1994.

0009-3122/94/3005-0629$12.50

In the second stage 0.8 mmole of furazane IV was oxidized with a mixture of 15 ml 104% oleum and 0.39 mmole ammonium persulfate at 80-90°C for 90 min. The products extracted with chloroform were separated on a silica gel column (1:1 benzene – hexane as eluent) to give 2.8 mmole bis(nitrofurazanyl-NNO-azoxy)furazane Ia and 1.0 mmole 3-(nitrofurazanyl-NNO-azoxy)-4-(nitrofurazanyl-ONN-azoxy)furazane, Ib.

The third isomer — bis(nitrofurazanyl-ONN-azoxy)furazane Ic — was obtained by oxidizing 1 mmole nitrofurazanyl-azofurazane VII with a mixture of 9 ml 20% oleum and 40 mmole ammonium persulfate at 70-80°C for 3 h. Compound Ic (0.14 mmole) was isolated from the mixture of isomers Ia, Ib and Ic (6:4:3, 0.63 mmole) by chromatography on silica gel.



VII

The structures of all the new synthetic compounds were established by elemental analysis, mass spectrometry, and IR and ^{13}C and ^{14}N NMR spectroscopy. Details of the syntheses, including that of some of the starting materials, will be given in a forthcoming paper.

Compound Ia, $C_6N_{12}O_9$. mp 85°C. IR spectrum, cm^{-1}: 1580 s, 1505 s, 1490 s, 1350 s, 1295 m, 1150 s, 1029 s, 940 m, 880 m, 810 s.

Compound Ib, $C_6N_{12}O_9$. Oil. IR spectrum, cm^{-1}: 1580 s, 1510 s, 1350 s, 1300 w, 1215 m, 1160 s, 1130 m, 1032 s, 980 w, 940 m, 820 s.

Compound Ic, $C_6N_{12}O_9$. mp 115°C. IR Spectrum, cm^{-1}: 1591 s, 1563, 1511 s, 1482 s, 1445 w, 1365 m, 1310 w, 1211 m, 1149 m, 1038 m, 855 s.

Compound IV, $C_6N_{12}O_8$. mp 70°C. IR Spectrum, cm^{-1}: 1580 s, 1530 w, 1500 m, 1350 s, 1180 m, 1020 s, 930 w, 820 s.

Compound VI, $C_4N_8O_6$. mp 56°C. IR Spectrum, cm^{-1}: 1583 s, 1545 s, 1452 w, 1430 w, 1355 s, 1200 m, 1185 s, 1050 m, 1035 s, 920 m, 870 s.

Compound VII. $C_6N_{12}O_7$. Oil. IR Spectrum, cm^{-1} (CCl_4): 1580 s, 1350 s, 1245 w, 1180 m, 1040 m, 830 s.

REFERENCES

1. V. O. Kulagina, T. S. Novikova, T. M. Mel'nikova and L. I. Khmelnitskii, Khim. Geterotsikl. Soedin., No. 5, 716 (1994).