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A Novel Synthesis of Pyrazolo[3,4-*c*]furazan Derivatives

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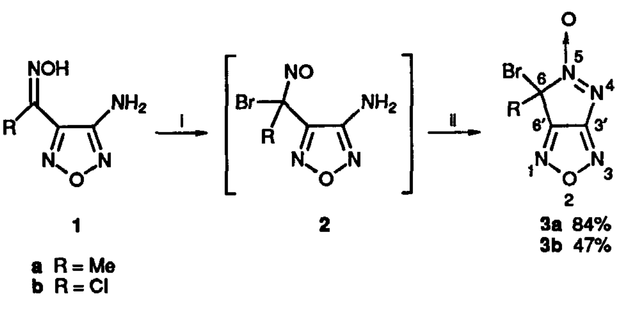
The first derivatives of pyrazolo[3,4-*c*]furazan *N*-oxide have been synthesized from the corresponding 3-amino-4-(hydroxyiminomethyl)furazan by treatment with bromine followed by DBI.

Pyrazolo[3,4-*c*]furazan derivatives are known to have been synthesized either by oxidation of 4-nitroso-5-aminopyrazoles with hypochlorites,[1,2] or by dehydration of 4,5-dihydroxyiminopyrazolines, *e.g.* with acetic anhydride;[2] namely, the titled bicycles are prepared from pyrazole intermediates.

This work describes the synthesis of the above bicyclic system starting from furazan precursors. We have found that treatment of 3-amino-4-hydroxyiminomethyfurazan derivatives **1** with bromine in the presence of base in inert solvent affords nitrosobromide **2**, which interacts with dibromoisocyanurate (DBI)[3] without purification to form the *N*-oxide of bicycle **3**[†] as oils, Scheme 1. Reaction of **1** with DBI also affords **3** in decreased yields (5–8%), but considerable amounts of by-product impede the isolation of the product.



Scheme 1 *Reagents and conditions*: i, Br$_2$, pyridine, CH$_2$Cl$_2$, room temperature, 0.5 h; ii, DBI, CH$_2$Cl$_2$, room temperature

Bicyclic systems **3** were purified by chromatography. The structure proposed for these compounds was consistent with the data obtained from their microanalysis, IR, MS and ^{1}H, ^{14}N and ^{13}C NMR spectra.[‡] Assignment of C-6 and C-6′ NMR signals for **3a** was proved by selective polarization transfer[4] from methyl protons: $^2J(CH_3–C6) = 5.4$ Hz $^3J(CH_3–C6') = 3.7$ Hz. The broadening of the C-6′ signal was caused by a ^{14}N–^{13}C coupling interaction. There is one narrow signal ($\Delta\nu_{1/2} = 40$ Hz) for the nitrogen of the *N*-oxide group and two broad peaks ($\Delta\nu_{1/2} > 600$ Hz) for the N-1, N-3 and N-4 atoms in the ^{14}N NMR spectrum. Polarization transfer CH$_3$–^{15}N is observed on N–5 [$^3J(CH_3–{}^{15}N5) = 2.8$ Hz] and N-1 [$^4J(CH_3–N1) < 0.5$ Hz]. An N-4 signal was not observed, probably as it was broadened *via* ^{14}N5–^{15}N4 coupling.

To conclude, this simple method for the preparation of *N*-oxide fused pyrazole derivatives is likely to find use in the synthesis of different substances not mentioned in this report.

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References

1 E. Mohr, *J. Prakt. Chem.*, 1908, **79**, 1.
2 R. C. Bertelson, K. D. Glanz and D. B. McQuain, *J. Heterocycl. Chem.*, 1969, **6**, 317.
3 In the last few years, DBI has been extensively used for linear azoxy compound synthesis: S. G. Zlotin, M. V. Sharashkina, Yu. A. Strelenko and O. A. Luk'yanov, *Mendeleev Commun.*, 1991, 49 and references cited therein.
4 K. R. R. Pachler and P. L. Wessels, *J. Magn. Reson*, 1973, **12**, 337.

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[†] Compound **3b** is rather unstable while **3a** is kept for a long time without decomposition.

[‡] Selected spectroscopic data for **3a**: IR (KBr) ν/cm^{-1} 1585, 1505, 1440, 1400, 1380, 1280, 1210, 1095, 1020, 915, 895, 830, 800, 740; ^{1}H NMR (CDCl$_3$) δ 2.44; ^{13}C NMR (CDCl$_3$) δ 26.98 (CH$_3$), 77.73 (C6), 151 (C6′), 162.73 (C3′); ^{14}N NMR (CDCl$_3$) δ 18 (N1, N3), −4.8 (N5), −77 (N4); ^{15}N NMR (CDCl$_3$) δ 28.44 (N1), 6.38 (N3), −4.74 (N5), −76.27 (N4); MS *m*/*z* 220, 218 (M$^+$), 176, 174 (M$^+$ − N$_2$O), 162, 160 (M$^+$ − N$_2$ − NO), 146, 144 (M$^+$ − N$_2$O − NO). For **3b** ^{14}N NMR (CDCl$_3$) δ −11.2 (N5).