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Promotion effect of hypervalent iodine compounds on the reactions of 3-hydroxy-4-nitrofurazan with cycloalkenes

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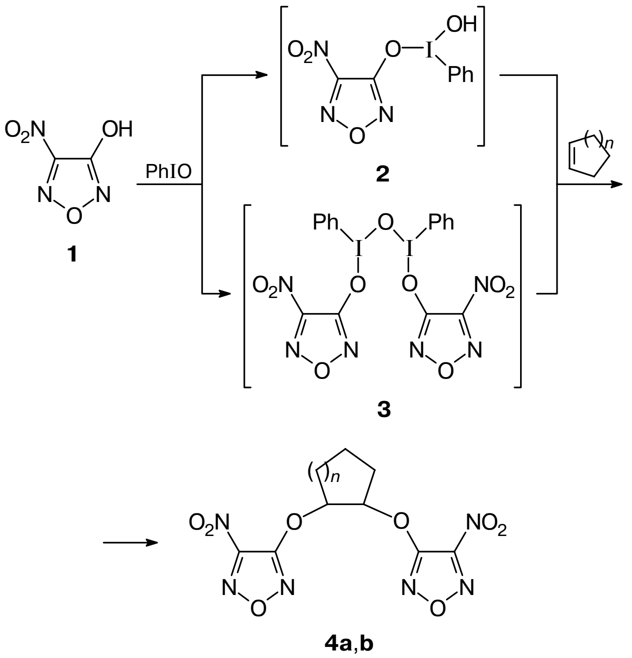
It is known[1,2] that 4-nitrofurazan-3-olate anion exhibits no nucleophilic properties and reacts, like picrate anion, only with very strong nucleofuges. 3-Alkoxy(phenoxy)-4-nitrofurazans can be obtained either by replacing the nitro group in 3,4-dinitrofurazan under the action of the corresponding alkoxides or phenoxides[3—5] or by oxidizing the amino group in the corresponding aminofurazans into a nitro group.[6,7]

Studies on the functionalization of olefins promoted by hypervalent iodine derivatives[8] have shown that such weak nucleophiles as $CF_3CO_2^-$, TsO^-, $CF_3SO_3^-$, and ClO_4^- can add to olefins. It is worth noting that different nitrophenols and hydroxy derivatives of heterocycles react with hypervalent iodine compounds differently.[8]

It was shown recently[9] that 4-nitrofurazan-3-olate anion is a perfect counterion to alkynyliodonium cations. In continuation of these investigations, we performed reaction of 3-hydroxy-4-nitrofurazan (**1**) with iodosylbenzene and found that an adduct of type **2** or **3** was formed. The addition of the latter to cyclopentene or cyclohexene yielded the corresponding 1,2-bis(4-nitrofurazan-3-yloxy)cycloalkanes **4a**,**b** (Scheme 1).

Scheme 1



n = 1 (**a**), 2 (**b**)

Melting points were determined on a Koffler stage. Natural-isotope ^1H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13, 75.7, and 21.5 MHz, respectively) in $CDCl_3$ (with nitromethane as the external standard for the ^{14}N NMR spectra). Mass spectra were obtained with Varian MAT CH-6 and Varian MAT CH-111 instruments (70 eV). IR spectra were recorded on a Specord IR-75 spectrometer. The course of the reaction was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates.

A solution of compound **1** (2 g, 0.015 mol) in anhydrous CH_2Cl_2 (~30 mL) was added at 0 °C to a suspension of PhIO (3.3 g, 0.015 mol) in the same solvent (~20 mL) in an atmosphere of argon. After stirring at 20 °C for 1 h, the reaction mixture became homogeneous. Cyclohexene (1.5 g, 0.018 mol) was added, and stirring was continued for 24 h in the absence of moisture. The reaction mixture was washed with water, filtered through a thin layer of silica gel, and concentrated *in vacuo*. Column chromatography of the residue (silica gel 40/100, light petroleum—CH_2Cl_2, 10 : 1) gave 1,2-bis(4-nitrofurazan-3-yloxy)cyclohexane **4b** as colorless crystals, yield 52%, m.p. 95.5—96.5 °C. MS (EI, 70 eV), *m/z*: 342 $[M]^+$, 296 $[M - NO_2]^+$, 266 $[M - NO_2 - NO]^+$, 250 $[M - 2\,NO_2]^+$. IR (KBr), ν/cm^{-1}: 2944, 1604, 1544, 1494, 1368, 1208, 1040, 1000, 920, 832. ^1H NMR, δ: 1.55 (br.m, 6 H, $CH_2C\underline{H}_2CH_2$, $C\underline{H}_{eq}CHO$); 2.37 (br.d, 2 H, $C\underline{H}_{ax}CHO$); 4.75 (br.dd, 2 H, CHO). ^{13}C NMR, δ: 21.5 ($CH_2\underline{C}H_2CH_2$); 27.5 ($\underline{C}H_2CHO$); 83.3 (CHO); 153.8 (C(4′)); 157.0 (C(3′)). ^{14}N NMR, δ: −41.2 (NO_2).

Cyclopentene reacts analogously to give 1,2-bis(3-nitrofurazan-4-yloxy)cyclopentane **4a** as colorless crystals, yield 32%, m.p. 107—108 °C.

It should be noted that compound **1** reacts with cyclohexene also in the presence of (diacetoxy-λ^3-iodanyl)benzene $PhI(OAc)_2$. However, the yield of compound **4b** is no higher than 10%. According to GL/MS data, a complex mixture of the reaction products contains 1,2-diacetoxycyclohexane (*m/z* 200 $[M]^+$) and 1-acetoxy-2-(4-nitrofurazan-3-yloxy)cyclohexane (*m/z* 271 $[M]^+$).

It is known[8] that trifluoromethanesulfonate and perchlorate anions react stereospecifically with cyclohexene in the presence of hypervalent iodine derivatives to form

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cis-adducts. The ^1H and ^{13}C NMR spectra of compounds **4a**,**b** recorded at ~20 °C and at −20 °C contain broadened signals, which precludes any conclusion about the stereospecificity of the reaction of furazan **1** with cycloalkenes. This broadening is probably due to the interaction between the closely spaced bulky nitrofurazanyl substituents rotating freely about the C—O bond.

Thus, it was shown for the first time that hypervalent iodine derivatives promote the addition of the non-nucleophilic 4-nitrofurazan-3-olate anion to cycloalkenes.

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