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Novel alkynyl(phenyl)iodonium salts: nitrofurazanylate as a counterion

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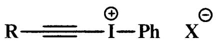
Abstract—Alkynyl(phenyl)iodonium nitrofurazanylates **6**–**9** were prepared by reaction of 3-hydroxy-4-nitrofurazan **4** with iodosylbenzene and terminal acetylenes. © 2001 Elsevier Science Ltd. All rights reserved.

Hypervalent organoiodine compounds are versatile synthons whose preparative routes are well documented.[1] Among known alkynyl(aryl)iodonium salts **1**, the compounds with oxy anions (typically, $X=CF_3CO_2^-$, TsO^-, $CF_3SO_3^-$) have been the most widely studied.[2] To our knowledge, no related derivatives have been reported in which a phenolate anion has been used as a counterion.



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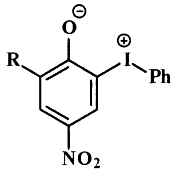

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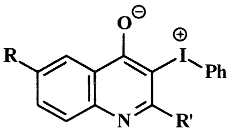

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Nevertheless, a few examples of iodonium inner salts such as **2** and **3**, incorporating phenolate anionic centers, have been prepared by reaction of [bis(acyloxy)iodo]arenes with nitrophenols[3] and hydroxy derivatives of six-membered heterocycles,[4] respectively. Introduction of the iodine(III) moiety *ortho* to the hydroxy group was invariably observed. Use of hydroxy derivatives lacking electron-withdrawing groups was unsatisfactory because the precursors were oxidized to quinones.

We reasoned that preparation of an analog of compound **1** incorporating a phenolate anion would be aided by (i) high acidity; (ii) inability of the anion to undergo ring-chain tautomerism; (iii) resistance of the anion to oxidation. 3-Hydroxyfurazans[5] are ideally suited to these requirements and we therefore, chose as the starting point for our investigation, 3-hydroxy-4-nitrofurazan **4**.[6]

We were delighted to observe that reaction of iodosylbenzene with **4** and phenylacetylene in CH_2Cl_2 under a dry atmosphere proceeded smoothly to give the desired alkynyl(phenyl)iodonium nitrofurazanylate **6** in 62% yield. In the experiment, a mixture of PhIO (50 mmol) and **4** (50 mmol) in CH_2Cl_2 (20 mL) was stirred at rt for 2 h, and to resulting solution PhC≡CH (55 mmol) was added at 0°C and then stirred for 12 h at room temperature. The mixture was filtered and concentrated, and the resulting oil was triturated with hexane (20 mL), ether (2×15 mL), and cooled CH_3CN (2 mL), under dry conditions. The white solid **6** was identified by spectroscopic data and elemental analyses.[7]

In an analogous manner, *p*-diethynylbenzene, 3-ethynyl-4-methylfurazan, and *tert*-butylacetylene were converted to salts **7**, **8**, and **9** in 51, 73, and 29% yields, respectively.

The pathway which we propose for the reaction involves initial formation of the highly reactive [hydroxy(nitrofurazanoxy)iodo]benzene **5** which attacks the corresponding acetylene.

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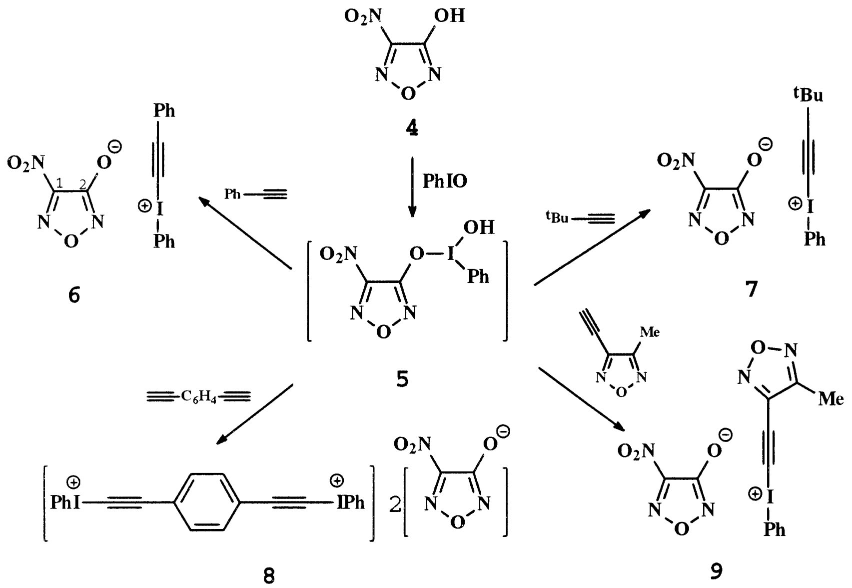

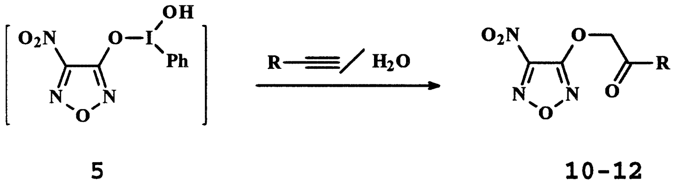

10 (R = Ph), **11** (R = 3-methylfurazan-4-yl), **12** (R = *tert*-Bu)

In contrast to these results, we have found that when the same reagents were reacted in CH_2Cl_2 in the presence of moisture, α-ketoethers[8] were obtained instead of the anticipated iodonium salts. Typically, an equimolar mixture of PhIO, compound **4**, and a terminal acetylene was stirred at 0°C for 2 h and for 5 h at 20°C under standard conditions. The mixture was concentrated in vacuo and separated by flash chromatography (pentane→CH_2Cl_2), giving α-ketoethers **10**–**12** in 65–75% yield.

The same α-ketoethers **10**–**12** were prepared from salts **6**, **7**, and **9** in similar yields by refluxing in chloroform.[9]

In conclusion, a variety of substituted alkynyl(phenyl)iodonium nitrofurazanylates can be efficiently synthesized by the reaction of 3-hydroxy-4-nitrofurazan with iodosylbenzene and terminal acetylenes. The method represents the first example of the successful preparation of iodonium salts incorporating a heterocyclic phenolate anion as the counterion. The preparation of α-ketoethers from these iodonium salts illustrates the high synthetic potential of the reagents for the introduction of the furazanoxy moiety into organic molecules.

Current efforts in this laboratory are focused on the further applications of this methodology towards the formation of complicated furazan derivatives.

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7. For **6**: mp 189–192°C (dec.). Anal. calcd for $C_{16}H_{10}N_3O_4$-C, 44.16, H, 2.32, N, 9.66, I, 29.16. Found: C, 43.83, H, 2.60, N, 9.80, I, 30.01; IR (KBr): 3100, 2155, 1600, 1550, 1480, 1390, 1370, 1305, 1200, 1040, 1000, 805, 740, 725 cm^{-1}; ^{13}C NMR (acetone-d_6,): 118.1 (C_β), 128.5, 130.0, 130.4, 132.9, 133.2, 136.8, 136.9, 153.7 (*C*1), 157.6 (*C*2), 161.3. For **7**: mp 114–116°C (dec.). For **8**: mp 232–236°C (dec.). For **9**: mp 123–125°C (dec.). Compounds **10**–**12** are oils. All products **7**–**12** gave correct results for mass spectroscopy and/or elemental analysis and exhibited anticipated IR and NMR characteristics.
8. The α-ketoether **10**, for example, may be isolated as a byproduct from the organic solvent during preparation of salt **6**.
9. The sodium nitrofurazanylate[6a] is analogous to picrate as a nucleophile. It may be noted here that our attempts to make α-ketoether **10** by the alkylation of sodium nitrofurazanylate with bromoacetophenone failed. This clearly illustrates the importance of the iodonium salts in furazanoxy derivative synthesis.