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An efficient synthesis of hydroxyfurazans

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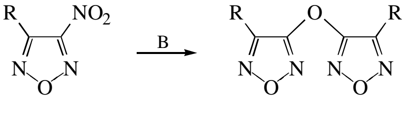
The nitro group on the furazan ring is found to undergo a facile regioselective displacement by a hydroxy group on treatment with the solid crystal hydrate of inorganic bases in dry acetonitrile; this straightforward reaction affords the hydroxyfurazans in high yields.

In connection with a project directed at the investigation of the nucleophilic reactions of nitrofurazans **1**,[1,2] we have studied the reactivity of **1** with solid anhydrous bases in dry conditions resulting in ether bond formation and giving difurazanyl ether derivatives **2** (Scheme 1).[3–6] The yields of **2** were generally very good. A major limitation of this method is that the reaction is successful only with highly electron-withdrawing groups (R).



1 **2**

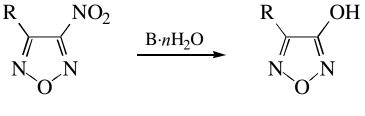
Scheme 1 *Reagents and conditions*: MeCN, 80 °C, B = MX or M_2Y (M = Li, Na, K; X = NO_2, OAc, CN, HCO_3; Y = CO_3, HPO_4).

This unusual reaction pathway was identified, and a mechanism for the transformation proposed.[3]

We now report the surprising finding that a similar reaction between certain nitrofurazans **1** and the solid crystal hydrate of inorganic bases in dry acetonitrile can be used to synthesize hydroxyfurazan **3**[†] in high yield, with no significant difurazanyl ether derivatives (Scheme 2).

When nitrofurazan **1a–d** (0.01 mol) was stirred with a suspension of the crystal hydrate (0.01–0.02 mol) in MeCN (15 ml), the reaction was completed as a rule in less than 2 h at 75–80 °C, and the corresponding hydroxyfurazan **3a–d** emerged as the only reaction product. The results obtained are summarised in Table 1.

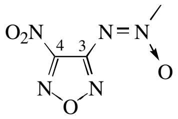
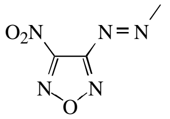
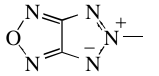
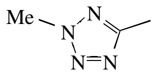
On the other hand, the inclusion of 3% water in the MeCN reaction medium halved the yields of the hydroxyfurazans. This set of by-products was observed under the experimental conditions. It should be noted that low yields of hydroxyfurazans previously obtained from the corresponding nitrofurazans and aqueous alkali in organic solvents were also dependent on by-product formation.[6,7] For example, reaction between 3,4-dinitrofurazan **1a** and aqueous alkali in acetone proceeded *via* nonselective attack at each carbon to produce a mixture of mono and dihydroxy derivatives.



1a–d **3a–d**

Scheme 2 *Reagents and conditions*: MeCN, 75–80 °C.

Table 1 Reaction of 3-R-4-nitrofurazan with the solid crystal hydrate of inorganic bases B·nH_2O in dry acetonitrile.

Entry	R	B·nH_2O	Reaction time/min	Yield (%)
1	NO_2	$Na_2CO_3 \cdot 10H_2O$	45	**3a**, 98
2		$Na_2B_2O_7 \cdot 10H_2O$	60	**3a**, 86
3		$Na_2CO_3 \cdot 10H_2O$	10	**3b**, 57
4		$Na_2CO_3 \cdot 10H_2O$	25	**3c**, 70
5		NaOAc·3H_2O	35	**3d**, 87
6	CN	$Na_2CO_3 \cdot 10H_2O$	60	**3e**, 91
7		NaOAc·3H_2O	200	**3e**, 93
8		$Ba(OH)_2 \cdot 8H_2O$	65	**3f**, 79
9		CsF·1.5H_2O	120	**3f**, 73

The selectivity observed in the reaction is most likely a consequence of the incorporation of the intermediate hydroxyfurazan salt into the crystal lattice of the starting crystal hydrate, which prevents them from further transformation.

In conclusion, a novel, simple and efficient method for the synthesis of hydroxyfurazans has been developed. Hydroxyfurazans with such reactive groups as nitro, cyano and azoxy are now readily accessible.

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[†] The compounds **3a**,[3,7] **3c**,[6,7] **3d**[7] and **3e**[3,7] corresponded in all respects with the compounds described earlier. New compounds gave satisfactory combustion analyses and accurate mass measurements. Some selected data for **3b**: mp 107–108 °C; ^{13}C NMR ([$^2H_6$]acetone) δ: 149.8 (C-3), 152.4 (C-2), 157.0 (C-4, C–NO_2), 158.4 (C-1, C–OH); ^{14}N NMR ([$^2H_6$]acetone) δ: –36.3 (NO_2, $\nu_{1/2} = 10$ Hz), –60.8 (N_2O, $\nu_{1/2} = 40$ Hz); IR, (ν/cm^{-1}): 3120–2790, 1580, 1495, 1425, 1345, 1245, 1180, 1120, 1090, 1020, 925; MS, *m/z*: 185 ($M^+ - N_2 - NO$). For **3f**: mp 158–159 °C; IR, (ν/cm^{-1}): 3080–2850, 1630, 1575, 1400, 1300, 1265–1175, 1073, 1055, 1000, 910; MS, *m/z*: 168 (M^+), 140 ($M^+ - N_2$), 110 ($M^+ - N_2 - NO$).

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