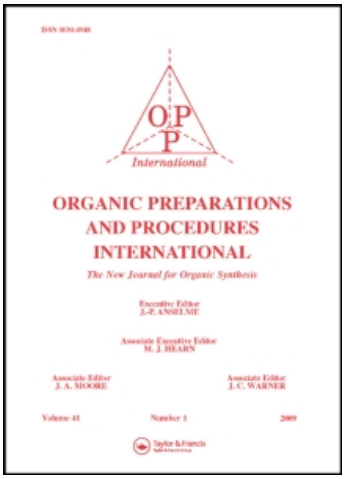

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HEPTAFLUOROISOPROPOXIDE ION IN AROMATIC SUBSTITUTION

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diacetal dinitrate, **2**, as well as work on the identification of process impurities is greatly appreciated. Our thanks to Ms. Barbara Baughman for assistance in the preparation of this manuscript.

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3. The procedure given here is essentially that of Somayaji *et al* (ref 1).

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HEPTAFLUOROISOPROPOXIDE ION IN AROMATIC SUBSTITUTION

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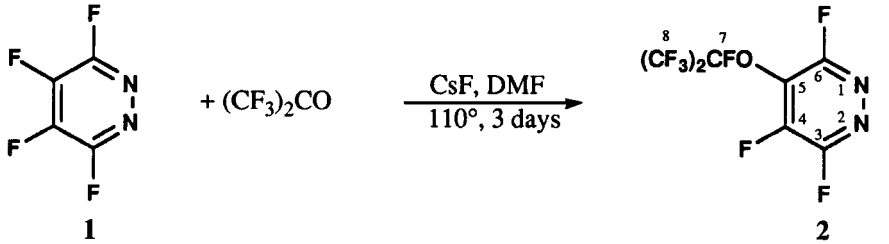
As an activated perfluoro heteroaromatic, tetrafluoropyridazine (**1**) undergoes nucleophilic displacement reactions to form a variety of mono- and polysubstituted products. In early work, this precursor was reported to most easily substitute fluorine atoms at C-4 and C-5.[1] However, subsequent studies indicate that substituent orientations on the final products are more complex, citing the importance of both kinetic and thermodynamic control.[2] Kinetically favored C-4 and C-5 products are formed in the reaction of trifluoromethane thiolate ion with **1**.[3] We report here a similar reaction where substitution is accomplished utilizing a fluorinated alkoxide ion.

Hexafluoroacetone was found to react with tetrafluoropyridazine (**1**) in the presence of



1 **2**

cesium fluoride to trap the labile heptafluoroisopropoxy group forming the previously unreported, stable 3,4,6-trifluoro-5-(heptafluoroisopropoxy)pyridazine (**2**). The heptafluoroisopropoxide ion is generated *via* reversible addition of fluoride ion to hexafluoroacetone in DMF. The use of this ion in synthesis is rather difficult since it is a very weak nucleophile and highly dissociated at elevated temperatures.[4] Nevertheless, this ion displaced fluorine in the activated heterocycle **1** to form the kinetically favored product **2**. It is significant that the relatively unstable heptafluoroisopropoxy group can be trapped in an aromatic system although it appears to be reversibly displaced by fluoride ion. The presence of a disubstituted product in the reaction mixture was also established by glc-ms; however, this compound could not be satisfactorily isolated by preparative glc for further analysis.

The synthesis of the new pyridazine **2** suggests that this procedure may provide a convenient route for introducing perfluoroalkoxy moieties directly into aromatic systems.

EXPERIMENTAL SECTION

The NMR spectrum was determined on a Bruker MSL 500 spectrometer using $CDCl_3$ as a solvent with a CCl_3F internal standard and the mass spectrum was measured with a Finnigan MAT 8200 spectrometer at 70 eV.

3,4,6-Trifluoro-5-(heptafluoroisopropoxy)pyridazine (2).- Tetrafluoropyridazine (3.2g, 21mmol) and dimethylformamide (16 ml) were introduced into a high vacuum, heavy walled 100 ml Pyrex cylindrical flask equipped with a Teflon™ stopcock and containing cesium fluoride (1 g) which had been rigorously dried by heating under a dynamic vacuum. The vessel was cooled to -196° in liquid nitrogen and evacuated, after which hexafluoroacetone (42 mmol) was condensed into the vessel. Upon warming to ambient temperature, the vessel was wrapped with heating tape in order to maintain a temperature of 105-110° and placed on a mechanical shaker for three days. Following this, unreacted hexafluoroacetone was released into a well ventilated hood and 1 M aqueous HCl (65 ml) was added to the reaction vessel to form a two-phase mixture. The lower organic layer was shown by analytical glc to contain 31% of 3,4,6-trifluoro-5-(heptafluoroisopropoxy)pyridazine (**2**) and 21% of disubstituted product. The monosubstituted compound (**2**) was isolated by preparative glc (chromosorb G with 5% QF-1) and characterized.

MS: m/z (rel. intensity) M^+ 318(30); $C_4F_3N_2^+$ 133 (70); $C_4F_3N^+$ 119(20); $C_4F_3^+$ 105(95); $C_3F_3^+$ 93(25); $C_2F_2N^+$ 76(50); CF_3^+ 69(100).

^{19}F NMR: δ F_8 -80.3 (d, J_{F8F7} 3 Hz), F_6 -85.1 (m), F_3 -91.6 (dd, J_{F6F3} 32.2 Hz. J_{F3F4} 24.5 Hz), F_4 -133.5 (m), F_7 -139.5 (m).

Anal. Calcd for $C_7F_{10}N_2O$: F, 59.74. Found: 59.80

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SYNTHESIS OF 5-HYDROXYMETHYL-I,4-DIOXAN-2-ONE

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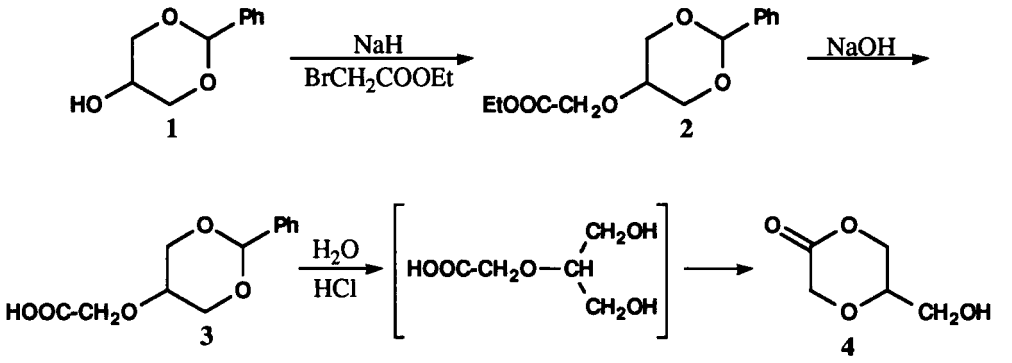
1,4-Dioxan-2-one derivatives find application in several fields, e.g. polymers,1 corrosion inhibitors,[2] biomaterials.[3,4] Due to the additional functionality, 5-hydroxymethyl-1,4-dioxan-2-one (**4**) may be regarded as a useful intermediate. However, in spite of the simplicity of its structure, this compound is still unreported. Its synthesis is described here.



The 1,3-protected glycerol **1** was reacted with ethyl bromoacetate in the presence of sodium hydride to give ester **2**. Alkaline hydrolysis of the latter provided the corresponding acid **3**. This compound was submitted to acidic hydrolysis and subsequent distillation *in vacuo*. Redistillation of