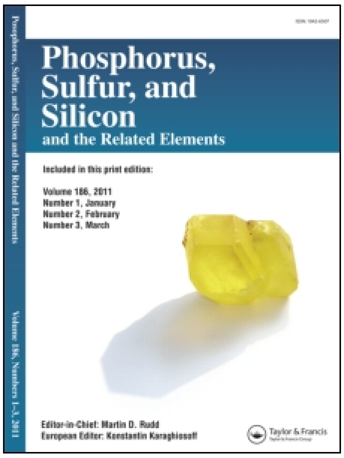

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Chemistry Prospects of new Sugar-Derived Vinyl Sulfones

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CHEMISTRY PROSPECTS OF NEW SUGAR-DERIVED VINYL SULFONES

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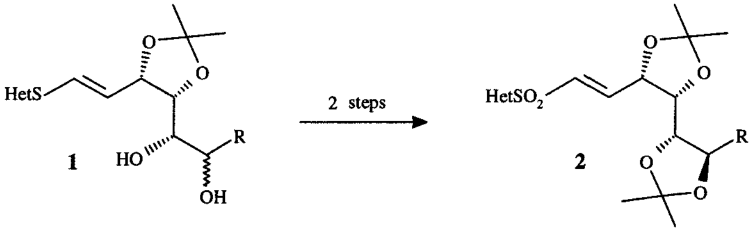
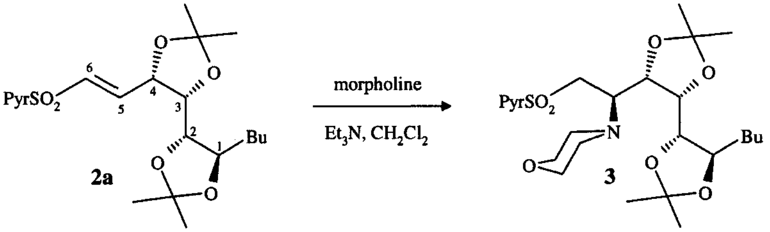
Abstract Major aspects of the reactivity potential of sugar-derived vinyl sulfones of type **2** were explored, including conjugate addition, desulfonylation, vinylic deprotonation, allylic transposition and dipole cycloaddition.

The synthetic versatility offered by vinyl sulfones is universally recognized.[1] However, the study of the chemical behaviour of a vinyl sulfone system attached to a chiral polyoxygenated appendage has never been undertaken.

A Grob-type heterolytic fragmentation process[2] applied to aza-heterocycle / thiosugar hybrid structures[3] affords (E)-configurated chiral vinylsulfides of type **1**, which can readily be converted into the corresponding vinyl sulfones **2** :



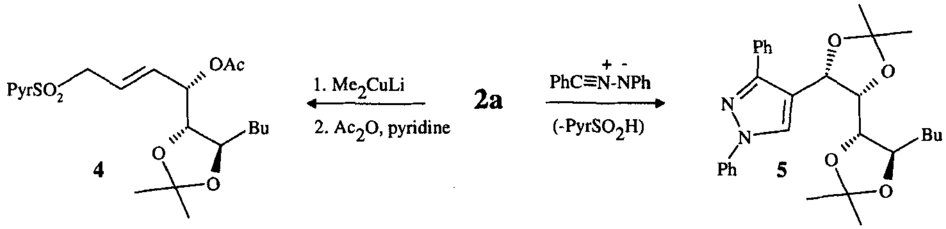
Such compounds were generally shown to conform to the reactivity rules established for simple vinyl sulfones : they can notably behave as versatile Michael acceptors towards miscellaneous nucleophilic species, e.g. the hydride anion,[4] amines,[5] thiols[6] or some organometallic reagents[7]. Most of the conjugate additions studied were shown to be highly stereoselective. As an example,[8] vinyl sulfone **2a** (Het = 2-pyridyl, R = n-butyl) reacted with morpholine[9] to produce the adduct **3** in 80% yield with a *de* exceeding 94%:



Many more diverse transformations of compounds **2** were carried out, including sodium dithionite reductive desulfonylation[10] or alkyllithium-induced vinylic α-deprotonation.[11]

Even more striking examples of the versatile chemical behaviour of our sugar-derived vinyl sulfones are given with the following cases :

- reductive elimination provoked by an organocopper reagent,[12] leading to the transposed allylic sulfone **4**
- dipole cycloaddition of diphenyl nitrilimine,[13] which results (after 2-pyridylsulfinic acid elimination) in the chiral chain-substituted pyrazolic system **5**



In addition, intramolecular cyclizations of the title compounds were performed and were shown to yield 2,5-disubstituted chiral tetrahydrofurans under high diastereoisomeric control.[14]

This short preview of several selected reactivity features of sugar-derived vinyl sulfones claims to be demonstrative of their broad synthetic scope, which is currently under investigation in our laboratory.

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8) Selected data for **2a** : syrup, $[\alpha]_D$ +27° (*c 1.0*, $CHCl_3$); MS: *m/z* M+1 = 426; ^1H-NMR ($CDCl_3$) : 0.91 (t, 3H, J_{vic} 7.0, Bu), 1.23, 1.33, 1.37, 1.52 (4s, 12H, 4 Me), 1.30 à 1.60 (m, 6H, Bu), 3.48 (dd, 1H, $J_{2,1}$ 8.0 Hz, $J_{2,3}$ 1.9 Hz, H-2), 3.90 (m, 1H, H-1), 4.25 (dd, 1H, $J_{3,4}$ 7.1 Hz, H-3), 4.90 (ft, 1H, $J_{4,5}$ 5.6 Hz, H-4), 6.91 (d, 1H, $J_{6,5}$ 15.2 Hz, H-6), 7.19 (dd, 1H, H-5), 7.52 (dd, 1H, $J_{5\pi,4\pi}$ 7,7 Hz, $J_{5\pi,6\pi}$ 4,4 Hz, H-5π), 7.94 (ft, 1H, $J_{4\pi,3\pi}$ 7.7 Hz, H-4π), 8.08 (d, 1H, H-3π), 8.73 (d, 1H, H-6π).
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