

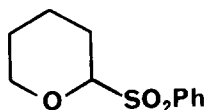
PREPARATION AND REACTIONS OF 2-BENZENESULPHONYLTETRAHYDROPYRAN

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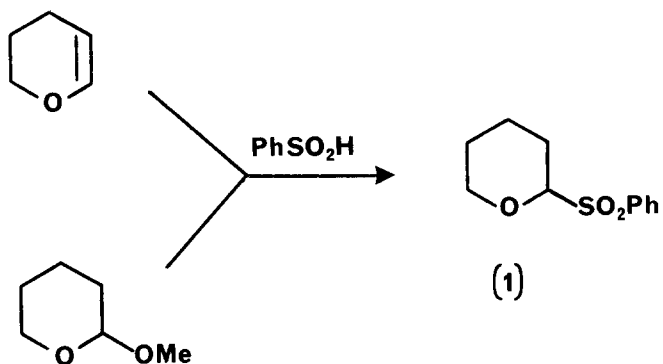
Summary: The anion derived from 2-benzenesulphonyltetrahydropyran (1) reacts with various electrophiles to give alkylated or acylated products some of which are useful precursors for spiroketal synthesis.

Methods for forming carbon-carbon bonds at the 2-position of cyclic ethers are currently of importance in synthesis.¹ Our recent observation that 2-diphenylphosphinoxy cyclic ethers undergo the Wittig-Horner reaction with aldehydes or lactols is one solution to this problem.² These results, however, prompted the idea that similar 2-benzenesulphonyl derivatives might provide an alternative and potentially more flexible approach. Here we report preliminary observations upon the use of the anion derived from 2-benzenesulphonyl-tetrahydropyran (1).

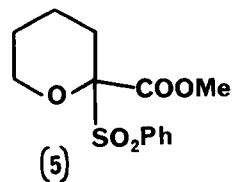
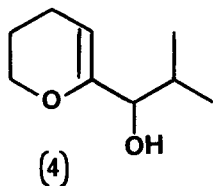
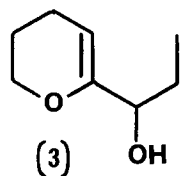
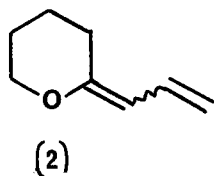


(1)

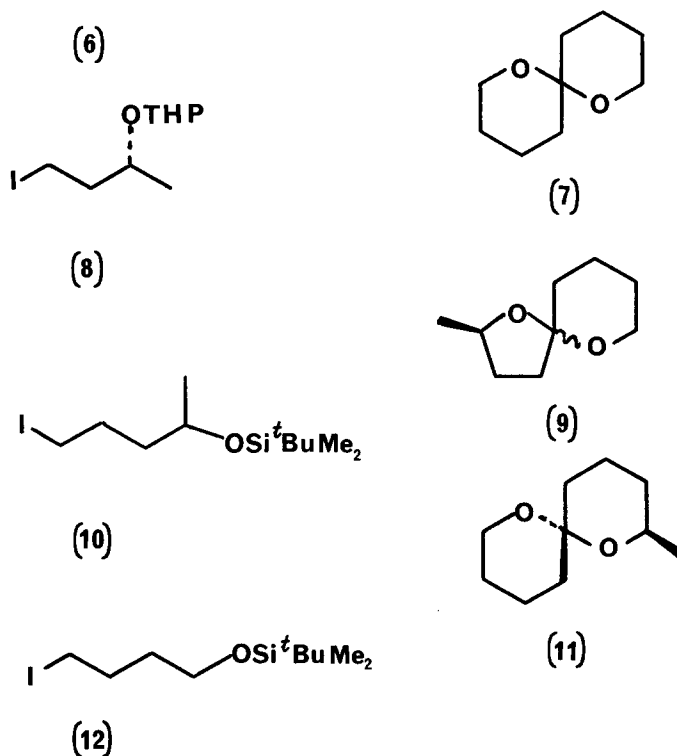
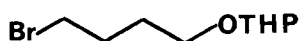
The crystalline and easily handled sulphone (1) was obtained by reaction of either 3,4-dihydro-2H-pyran or 2-methoxytetrahydropyran with benzenesulphonic acid. During this last process the reaction rate was noticeably enhanced by the addition of calcium chloride.



Deprotonation of (1) was readily achieved using one equivalent of *n*-butyllithium at -78°C in tetrahydrofuran. The resulting anion was subsequently reacted with a variety of electrophilic species. For example with allylbromide the volatile exocyclic diene (2) was obtained in 55% yield; directly upon work-up with saturated ammonium chloride, there being no need to eliminate benzenesulphonic acid in a separate step. Similarly reaction of the anion with aldehydes such as acrolein or iso-butyraldehyde afforded (3) and (4) in 76% and 77% yields respectively again by simultaneous loss of benzenesulphonic acid. Reaction with methylchloroformate produced the acylated derivative (5) (81%).



Application of the chemistry to the preparation of spiroketals is also possible. Reactions of the anion from (1) with the bromide (6) affords an intermediate which on protic work-up with camphor sulphonic acid gave the naturally occurring spiroketal pheromone (7) previously isolated from *Dacus oleae*.³ In a similar way reaction of the optically active iodide (8) provides the natural product (9)⁴ (79%) in its optically pure form ($[\alpha]^{20} - 12.1^\circ$). Alkylation of the anion with (10) gave the spiroketal (11) (47%) after protonation. The anion from (1) also reacts with the dimethyl *t*-butylsilyl protected iodide (12) to give (7) (52%) on acidic work-up.



Reactions of anions α to both oxygen and the phenylsulphonyl group have so far found limited use in the literature.⁵ We believe these new results will promote further applications in a variety of useful transformations.

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Footnotes.

All new compounds were fully characterised by spectroscopic microanalytical and/or accurate mass data.

Later reactions showed that the addition of camphor sulphonic acid was not necessary owing to the concomitant formation of phenylsulphinic acid during the neutralisation of reaction mixture.

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