



Synthesis and transformation of 1,2-dioxines linked to aromatic systems.

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Sara J. Krivickas

B.Sc. (Hons)



Department of Chemistry

The University of Adelaide

South Australia

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Abstract

γ -Hydroxy enones have been overlooked in the past due to their transient nature, sensitivity towards acidic and basic conditions, and tendency to undergo rearrangement. A large portion of the previously reported reactions of γ -hydroxy enones have involved the formation of furans, however *cis* and *trans* γ -hydroxy enones have been shown recently by the *Taylor* group to be important intermediates in the formation of cyclopropanes, γ -lactones and aromatic dihydrofurans.

Chapter 2 focuses on the synthesis of a series of phenanthro- and indole-1,2-dioxines and subsequent treatment with stabilised phosphorus ylides. It was proposed this would result in the generation of dihydrophenanthrofurans (**196 / 197**) and dihydrofuroindoles (**199 / 200**). The phenanthro-1,2-dioxines were found to undergo furanisation in a similar manner to the previously reported naphtho-1,2-dioxines (**184**). The indole-1,2-dioxines however were found to be too sensitive to allow reaction with phosphorus ylides.

The phenanthro- and naphtho-1,2-dioxines (**194 / 184**) were treated with stabilised malonate nucleophiles to afford a range of novel *bis*-fused lactones in good yield and high diastereoselectivity. The mechanism of this reaction was explored as discussed in Chapter 3.

Chapter 4 presents the synthesis of *bis*-1,2-dioxines (**264**) and their reaction with nucleophiles, to create *bis*-cyclopropanes and *bis*- γ -lactones in good yields and high diastereoselectivity. The control of stereoselectivity by the use of bulky ylides and LiBr was investigated and the results discussed. Intermediates of the cycloaddition of singlet oxygen to the *bis*-dienes (**278**) were

utilised to prepare novel unsymmetrical *bis*-cyclopropanes and compounds containing both γ -lactone and cyclopropyl moieties.

Declaration

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university or other tertiary institution. To the best of my knowledge it contains no material published or written by another person, except where due reference has been made.

I give my consent to this copy of my thesis being available for loan and photocopying when deposited in the University Library

Sara J. Krivickas

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Abbreviations

1-Dimensional	1-D
2-Dimensional	2-D
Accurate mass calculated	Acc. Mass. Calc.
Analysis Calculated	Anal. Calc.
2,2'-azobisisobutyronitrile	AIBN
<i>N,N</i> -bis(salicylidene)ethylenediaminocobalt (II)	Co(SALEN) ₂
1,4-Diazabicyclo[2.2.]octane	DABCO
Diastereomeric excess	de
Di-isobutylaluminium hydride	DIBAL-H
Dimethoxy ethane	DME
Enantiomeric excess	ee
Ethyl acetate	EtOAc
Infrared	IR
<i>iso</i> -propane (1-methylpropane)	Pr ⁱ
Mass to charge ratio	<i>m/z</i>
Nuclear magnetic resonance	NMR
Rotational overhauser enhancement spectroscopy	ROESY
sulfoxide, piperidine and carbonyl	SPAC
<i>tert</i> -Butyl (2,2-dimethylpropane)	Bu ^t
Tetrahydrofuran	THF
Thin layer chromatography	TLC
Triethylamine	TEA
triphenyl phosphine	TPP
triphenyl phosphine oxide	TPPO