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ORGANOSILANES:

Synthesis and reactivity directed towards annulations

A thesis presented to the University of Auckland for the degree of

Doctor of Philosophy

by

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APPENDIX: Crystallographic data
Ruthenium-catalysed coupling of alkenes (principally vinylsilanes) with the ortho C-H bond of a wide range of monocyclic, bicyclic and tricyclic aromatic ketones led to a high yield of ortho-alkylated adducts. A methoxy substituent located para to the directing carbonyl moiety had an activating effect while an ortho methoxy resulted in severe inhibition of the coupling reaction and methoxy cleavage was observed. However, an ortho TBDMS ether allowed the C-H/olefin coupling to proceed quantitatively, which was attributed to inhibition of catalyst quenching by preventing chelate formation.

With a view to cyclopentaannulation, the adducts from the C-H/olefin coupling containing a ArCH₂CH₂SiMe₃ side chain were functionalised by radical bromination leading to a 1,2-dibromo compound which was converted into a COCH₃ by elimination and hydrolysis. An analogous sequence, when applied to a more complex substrate, gave products resulting from bromination and/or elimination at a different benzylic site. Attempted intramolecular aldol reactions of a 1,4-dicarbonyl compound failed and resulted instead in skeletal rearrangement. The carbon-silicon bond in ArCH₂CH₂SiMe₃ could be converted into a silanol (RSiMe₂OH) when treated with aluminium chloride, but attempts to oxidise the C-Si bond (to give an alcohol) in this compound were unsuccessful.

Silicon-carbon bond oxidation in adducts containing a ArCH₂CH₂Si(OR)₃Me side chain gave an ArCH₂CH₂OH fragment provided that a proximal ketone was converted to an alcohol prior to the oxidation to avoid unwanted Baeyer-Villiger reaction. The resultant 1,5-diols could not be oxidised directly to a 1,5-dicarbonyl compound, but were converted into a mono alcohol by ionic hydrogenation and subsequent deprotection in excellent overall yield. Successive benzylic and primary alcohol oxidation provided the required 1,5-dicarbonyl functionality, but this enone aldehyde was not suitable for cyclopentaannulation. Attempts to synthesise an alternative substrate (a keto aldehyde) via protection of the primary alcohol followed by benzylic oxidation were unsuccessful, but could be achieved by conjugate reduction of the enone. The ensuing pinacol coupling failed.

The quassinoid ring system was accessed by functional group interconversion to yield a 8-keto ester, which underwent latonisation using SmI₂.
Coupling of alkynylsilanes with the ortho C-H bond of various aromatic ketones proceeded in high yield under ruthenium catalysis and resulted in the introduction of a vinyl group predominantly of E configuration. In contrast, the aromatic ketone 1-acetylnaphthalene, underwent cyclopentaannulation in a one-pot sequence under analogous conditions, which was confirmed by X-ray crystallographic analysis. This was proposed to occur via β-silyl migration as a key step. Attempts to synthesise an alkynylsilane bearing alkoxy substituents failed and gave only a dialkyne, which underwent ruthenium-mediated C-H bond insertion cleanly. The resultant alkenylalkynylsilanes could not be oxidised to an aldehyde.

Trimethyl orthoformate-promoted intramolecular cyclisation of the ortho vinylated aromatic ketones resulted in cyclopentaannulation in high yield. The newly formed 5-membered ring was confirmed by an X-ray structure of a diterpenoid analogue. Mono or tricyclic substrates produced benzofulvenes in high yield when the ketone was exocyclic, while a naphthalene derivative resulted in the isolation of methanol adducts. A diterpenoid containing a dihydrofuranyl ring could be synthesised via intramolecular Hg(II) cyclisation of an alcohol and a proximal alkene.
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