Ring Expansion Route to Cyclopentenes *via* Regiospecific 1,2-Vinyl Migration

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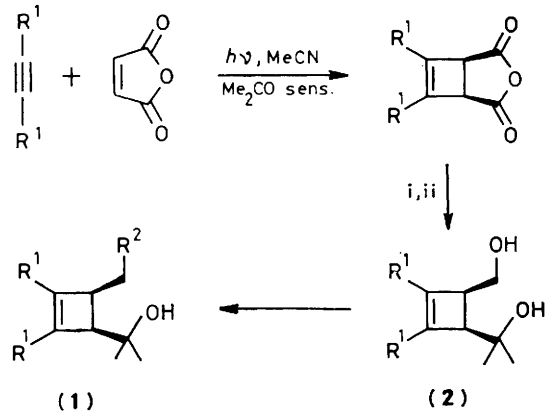
Cyclobut-2-enylmethyl cations undergo regiospecific and highly stereoselective ring expansions *via* 1,2-vinyl shifts to produce 4-chlorocyclopentenes.

Ring expansions *via* 1,2-alkyl shifts are well established organic reactions,[1] but their usefulness in modern synthetic operations is limited by a number of factors. Amongst the most critical is the requirement that the migration involved in ring expansion be highly selective, *i.e.* where applicable, only one ring residue should migrate, and new bonds should be made stereoselectively. We describe a general route to cyclopentenes which depends upon a highly regio- and stereo-selective ring expansion of substituted cyclobut-2-enylmethyl systems.[2]

The cyclobutene precursors (**1**) are made by standard methods, involving alkyne [2 + 2]photocycloaddition to maleic anhydride,[3] followed by controlled reduction and methylation of the photoadducts to give the diols (**2**) (Scheme 1). Subsequent protection or removal of the primary alcoholic function in (**2**) leads to a range of cyclobutenes (**1**) bearing a tertiary alcohol group. When these alcohols are converted into the corresponding chlorides,[4] and the chlorides treated with zinc chloride, formation of 4-chlorocyclopentenes (**3**)† in yields of 48—70 % is observed. The notable feature of the ring expansion is that only 1,2-vinyl migration is detected, *i.e.* there are no 3-chlorocyclopentene products.



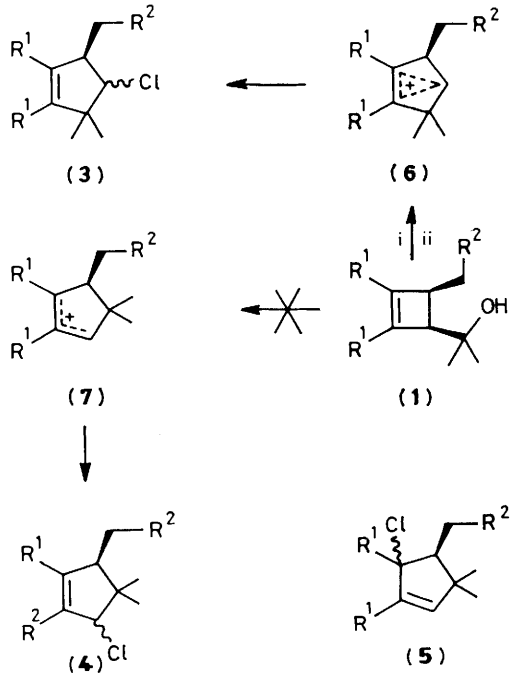
(**1**) (**2**)

Scheme 1. R^1 = Et or Ph; R^2 = H, OMe, or OCOPh. *Reagents:* i, $NaBH_4$ (1.05 mol. equiv.); ii, MeLi (4 mol. equiv.).

A typical procedure involves treatment of an alcohol (**1**) with 1.3 mol. equiv. of phosphorus pentachloride, in the presence of calcium carbonate (1 mol. equiv.), in chloroform as solvent.† The resultant chlorides are not wholly stable to purification procedures, and conversion into the cyclopentenes (**3**) is best achieved after the chlorides have been characterised spectroscopically. Anhydrous zinc chloride (1.5 mol. equiv., suspended in dichloromethane or carbon tetrachloride) has been found to effect conversion into (**3**) within a few minutes at room temperature, or at ice-bath temperature. A simpler alternative procedure involves one-pot conversion of the alcohols (**1**) into the chlorides (**3**) by stirring the former with a mixture of phosphorus pentachloride (1.3 mol. equiv.), zinc chloride (1.5 mol. equiv.), and calcium carbonate (1 mol. equiv.) at 22 °C for 1 h.

The chromatographically purified products show no hydroxy or alkene stretching i.r. absorptions, and are readily assigned structures (**3**) on the basis of their ^1H and ^{13}C n.m.r. spectra, in which the absorptions due to the –CHCl and $-CMe_2$ groups are of particular relevance. For example, for the chloride (**3**, R^1 = Ph, R^2 = H) the –CHCl group shows δ (^1H) 3.77 (d, *J* 9 Hz) and δ (^{13}C) 75.77 (d) p.p.m., while the $-CMe_2$

† Satisfactory analytical and spectroscopic data have been obtained for all the alcohols (**1**) and the chlorides (**3**).



Scheme 2. R^1 = Et or Ph; R^2 = H, OMe, or OCOPh. *Reagents:* i, PCl_5, $CaCO_3$; ii, $ZnCl_2$.

group shows δ (^{1}H) 1.07 (s) and 1.13 (s), and δ (^{13}C) 21.13 (q) and 25.80 (q) p.p.m. These data allow elimination of other reasonable structures, notably those of the 3-chlorocyclopentenes (**4**) or (**5**) (Scheme 2).

The stereochemistry of these ring-expansion reactions is also of interest, since the products (**3**) are normally formed as one diastereoisomer only, with *trans*-geometry. Exceptions are the ester and ether in the series (**1**, R^1 = Ph) in which both diastereoisomers are detected, but the *cis*-isomer is predominant. This combination of regiospecificity with high stereoselectivity makes the ring expansion route to doubly functionalised five-membered rings an attractive synthetic option.[5]

The origins of these selectivities may be related to the stability of cyclopent-3-enyl carbocations.[6] Thus the regiochemistry would seem to depend upon a continuous stabilisation, by the cyclobutene double bond, of charge development in the ring as 1,2-vinyl migration leads to the carbocation (**6**). Although the isomeric cyclopent-2-enyl (allylic) carbocation (**7**) would also appear to be an attractive intermediate, its formation is possibly relatively disfavoured because the type of stabilisation described above, for (**6**), cannot be achieved readily. This is apparent from molecular models, which indicate that the π-bond in (**1**) would only stabilise developing charge on the ring late in the migration step leading to (**7**), and hence to (**4**) or (**5**).

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