

Carbonium Ion Rearrangements in the Norbornyl Series Controlled by a Silyl Group†

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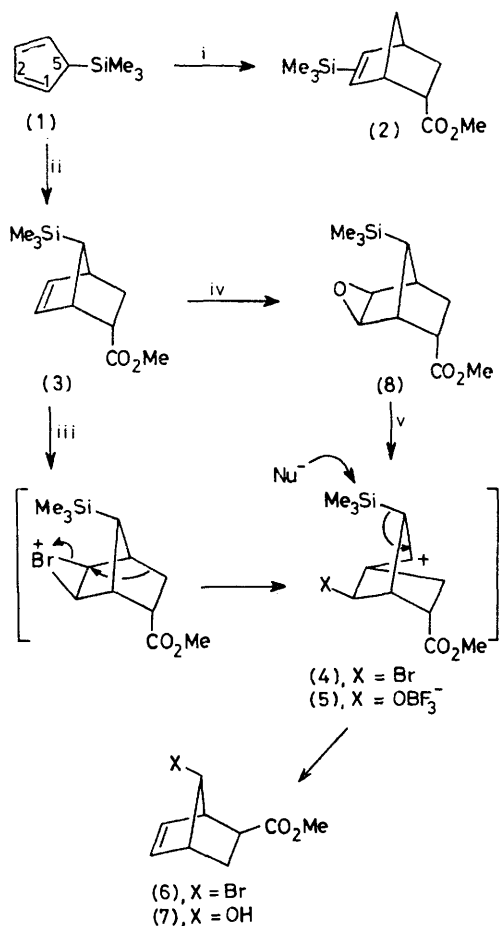
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Summary Methyl 7-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-carboxylate (**3**) and its epoxide (**8**) rearrange on treatment with bromine or boron trifluoride, respectively, to give 7-functionalised norbornenes (**6**) or (**7**).

† Reprints of this paper will not be available.

THE synthesis of 7-substituted norbornenes can be a problem, because the obvious route, the Diels-Alder reaction of a 5-substituted cyclopentadiene with a dienophile, is not always clean; usually, the 5-substituted cyclopentadiene rapidly gives mixtures of the 1- and 2-substituted isomers, which then react with the dienophile. However, trimethylsilylcyclopentadiene is unusual in that the 5-substituted isomer (**1**) is the major isomer at equilibrium, and, hence, 7-substituted norbornenes are major products, at least with reactive dienophiles.¹ We now report how the presence of the 7-silyl group encourages carbonium ion rearrangements in the norbornyl system so that 7-functionalised norbornenes are the products. The rearrangements are encouraged and the outcome controlled in much the same way as the rearrangement of diphenylphosphinoyl² and phenylthio groups,³ which we have already reported.

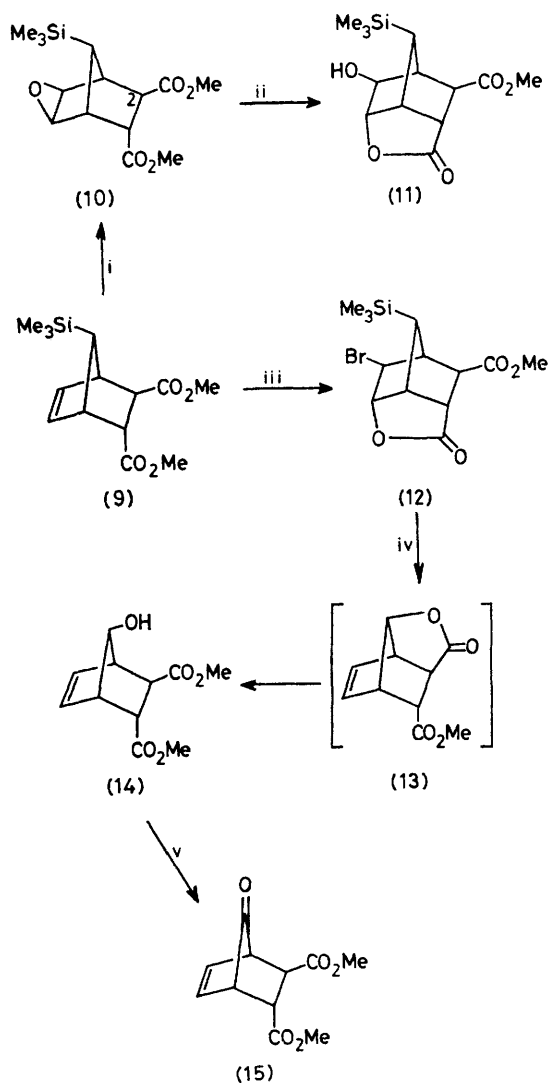
Methyl acrylate is not a reactive enough dienophile to give directly the 7-silylated norbornene (**3**), but gives instead the products (**2**) from reactions with the least abundant, but most reactive, silylated cyclopentadiene.⁴ There is, incidentally, little regioselectivity in this reaction. In the presence of boron trifluoride, however, the major adduct (51%) is the 7-substituted isomer (**3**). On treatment with bromine in methanol, this compound rearranges (Scheme 1) to give the 7-bromonorbornene (**6**) (74%).



SCHEME 1. Reagents: i, $\text{CH}_2=\text{CHCO}_2\text{Me}$; ii, $\text{CH}_2=\text{CHCO}_2\text{Me}-\text{BF}_3\cdot\text{OEt}_2$; iii, Br_2-MeOH ; iv, $\text{CF}_3\text{CO}_3\text{H}$; v, $\text{BF}_3\cdot\text{OEt}_2$

Similarly, the epoxide (**8**) rearranges in the presence of boron trifluoride to the 7-hydroxynorbornene (**7**) (67%). In both cases, the silyl group encourages rearrangement, because the cations (**4**) and (**5**) are stabilised by the neighbouring C-Si bond,⁵ and the outcome is controlled by the ready loss of the silyl group.⁶

Dimethyl fumarate is a reactive enough dienophile to give directly the adduct (**9**) (79%). However, the epoxide (**10**) did not rearrange on treatment with boron trifluoride, and a lactone (**11**) was formed instead,⁷ a type of reaction which represented only a very minor pathway (3%) in the case of the epoxide (**8**). Presumably, the presence of a methoxycarbonyl group on C-2 of (**10**) makes C-2 reluctant to migrate. Similarly, bromination of (**9**) gave the lactone (**12**) (53%); again this was only a minor pathway (12%) in the case of (**3**). However, the bromide (**12**) does rearrange



SCHEME 2. Reagents: i, $\text{CF}_3\text{CO}_3\text{H}$; ii, $\text{BF}_3\cdot\text{OEt}_2$; iii, Br_2-MeOH ; iv, $\text{AgNO}_3-\text{MeOH}$; v, $(\text{CF}_3\text{CO})_2\text{O}-\text{Me}_2\text{SO}$.

(Scheme 2) when its solvolysis in methanol is catalysed by silver ion. The isolated product, the alcohol (**14**) (98%), is presumably formed by methanolysis of an intermediate lactone (**13**). The corresponding compound to (**12**) without

a silyl group does not rearrange under these conditions. The overall yield of the alcohol (**14**) from dimethyl fumarate is 47% when the intermediates are not purified.

This approach to the synthesis of 7-functionalised norbornenes is a promising one, since bromo and especially hydroxy groups are versatile substituents. For example, we were able to oxidise the alcohol (**14**) to the ketone (**15**) (90%), a compound we had already made by an inferior but

more obvious route as part of a projected total synthesis.⁷ We have, however, been unable to induce the rearrangement of (**3**) with carbon electrophiles, like chlorosulphonyl isocyanate and acetyl fluoroborate;⁸ phenylsulphenyl chloride and phenylselenyl bromide induce rearrangement in (**3**) to the extent of only 22 and 20%, respectively.

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