Addition of Some Unsymmetrical Electrophilic Reagents to Cyclic αβ-Unsaturated Silanes

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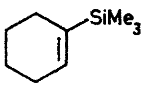
Summary Additions of some iodine based electrophilic reagents to 1-trimethylsilylcyclohexene (**1**), and its 4-t-butyl derivative, occur with high regio- and stereo-selectivity to give adducts in which iodine is attached to C-1 (**2** and **5**): these adducts have been transformed into a number of functionalised silanes.

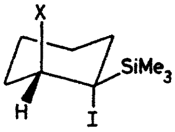
The chemistry of $\alpha\beta$-unsaturated silanes has recently been fairly extensively investigated[1,2] particularly from the point of view of electrophilic attack at the carbon atom bonded to silicon with subsequent or concomitant de-silylation,[2] and several synthetically useful processes have been developed. We report here the addition of some iodine based electrophilic reagents[3] (formally IX) to 1-trimethylsilylcyclohexene (**1**) and a conformationally biassed analogue.

Thus treatment of (**1**) with (a) I_2–MeOH–sulpholan gave (**2a**; 77%), (b) I_2–LiN_3–$CHCl_3$–sulpholan gave (**2b**; 80%), and (c) I_2–LiSCN–$CHCl_3$–sulpholan gave (**2c**; 65%). The constitution of the adducts (**2a**—**c**) follows from i.r. and n.m.r. data (particularly band width of the signal ascribable to C-2-H) and from the chemical evidence that treatment with 1,5-diazabicyclo[5.4.0]undec-5-ene in benzene under reflux in each case gave a high yield of the allylically functionalised vinyl silanes (**3a**), (**3b**), and (**3c**), respectively.

The high regioselectivity seems to be most conveniently interpreted in terms of an intermediate iodonium ion (**4**) which undergoes nucleophilic attack (diaxial opening) at the carbon atom not bonded to silicon. This orientation contrasts with the mode of opening postulated for the corresponding protonated epoxide,[4] where attack is at the carbon bonded to silicon. To our knowledge this is the first example of such a clear dichotomy, and indeed a parallel between the two processes is often drawn.[5] Possibly the transition state for the iodonium ion opening has relatively high carbonium ion character and can benefit from the well known ability of silicon to stabilise a β-carbonium ion.[6] Other evidence in favour of the latter suggestion is provided by formation of the isothiocyanate (**2c**). Addition to cyclohexene under the same conditions gives predominantly *trans*-1-iodocyclohexyl thiocyanate.[7]

Addition to 4-t-butyl-1-trimethylsilylcyclohexene gave in high yield the adduct (**5a**) (from I_2–MeOH) and (**5b**) (from I_2–LiN_3). The high selectivity with this conformationally biassed substrate is explicable in terms of reversible formation of diastereoisomeric iodonium ions[8] *via* attack from either side of the olefin, followed by product determining nucleophilic attack (diaxial opening) *trans*- to t-butyl involving (**6**) only.


(**1**)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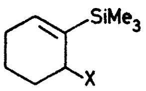
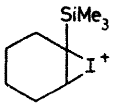
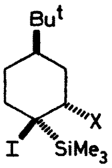
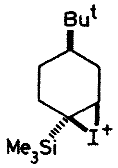
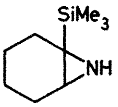
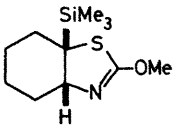

(**3**)


(**4**)


(**5**)


(**6**)


(**7**)


(**8**)

a; X = OMe
b; X = N_3
c; X = NCS

d; X = NH_2
e; X = NHMe
f; X = NH·CS·OMe

The adducts (**2a**—**c**) and (**5a**,**b**), as indicated above, provide convenient synthetic precursors to a variety of novel allylically substituted vinyl silanes *via* elimination. Further transformations, which show some of the potentialities of the adducts, have been effected leading to: (**3d**) [$LiAlH_4$ reduction of (**3b**)]; (**3e**) [$LiAlH_4$ reduction of (**3c**)]; and (**3f**) [treatment of (**3c**) with KOH–MeOH]. We have also shown that reduction of (**2b**) with $LiAlH_4$ gave the aziridine (**7**) and treatment of (**2c**) with KOH–MeOH, gave the thiazole (**8**).

(*Received*, 15*th December* 1978; *Com.* 1331.)

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