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INFLUENCE OF A SILYL GROUP ON AN ALLYLIC POSITION. A THEORETICAL APPROACH

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Abstract—Allylsilanes show in certain cases a behaviour towards electrophiles which is opposite to that of its carbon homologues. Theoretical calculations using Dewar's MINDO/3 method performed on 3-methyl 3-butenyl trimethylsilane and 2-methyl 2-butene show that geometrical optimization leads to a silicon-allylic carbon bond nearly parallel to the double bond π cloud, and both net atomic charges and HOMO coefficients indicate an inversion between these two substrates.

Allylsilanes are intermediates that have become increasingly more useful in organic synthesis. The silyl group exerts a strong influence on the ease and regioselectivity of their reactions. Thus they allow the realization of reactions hitherto unattainable in the hydrocarbon series.

In all cases examined, when the trimethylsilyl group has been substituted for the allylic hydrogen, its position in the molecule determines the course of the ensuing reaction entailing great regioselectivity. With an allylsilane, the regiospecificity observed is in certain cases opposite to that observed in the hydrocarbon series.

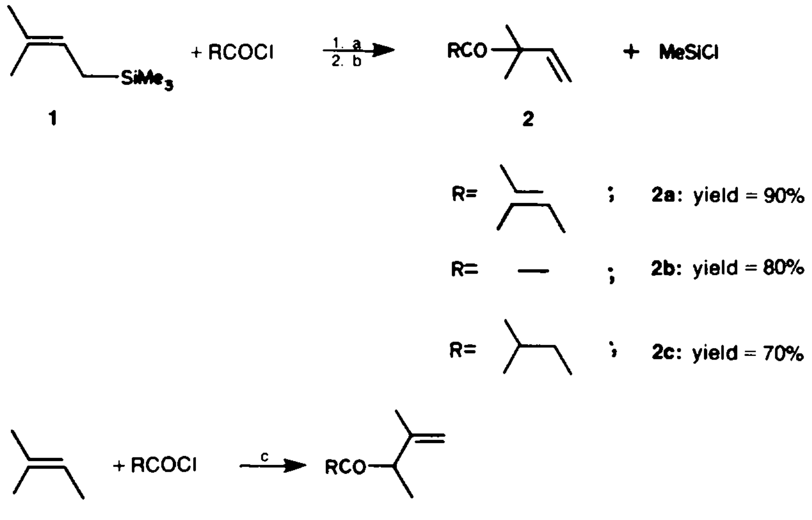
The inverted behaviour in the carbon-carbon double bond, caused by introduction of a trimethylsilyl group at an allylic position, has not yet received any theoretical support. The purpose of our work was to introduce an investigative approach by quantum chemistry methods.

RESULTS

We earlier proposed original methods of synthesis of allylic ketones[1,2] or homo-allylic alcohols[3,4] as a result of electrophiles (complexed acyl chlorides or carbonyls) reacting with allylsilanes.

We have shown that acylation of prenyltrimethylsilane[5a] gives a very different result compared with its hydrocarbon homologue, 2-methyl-2-butene[6] (Scheme 1).

We have also shown that chlorosulfonylisocyanate (CSI)[7] reacts with allylsilanes[5b] in a manner which leads selectively to the corresponding allylic nitrile. CSI and



a = $AlCl_3$; CH_2Cl_2; −60°C
b = H_2O; NH_4Cl; −30°C
c = 1) $SnCl_4$; 0°C; 2) H_2O

Scheme 1.

prenyltrimethylsilane react to give a product oppositely oriented to that which is obtained from the parent hydrocarbon.[7] The difference in behaviour between the two substrates is represented in Scheme 2.

The same reaction (acylation) effected upon 3,7-dimethyl-2-octenyltrimethyl-silane[8] is again an attack of the anti-Markovnikoff type, contrary in orientation to that usually encountered with carbon-only substrates (Scheme 3).

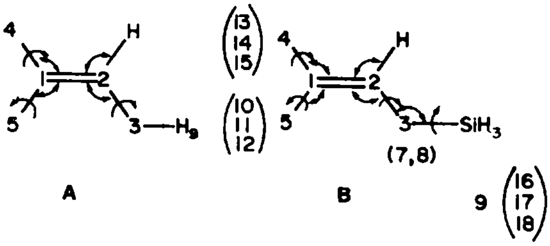
Such a reverse reactivity has been recently reported by Fleming[4] in his work with allylsilanes in the methylenecyclohexane series; their behaviour is again opposite to that observed during the reaction of for example, ethylidenecyclohexane and CSI.[16]

Our interest was in examining and providing theoretical support for the explanations of the inversion of orientation observed in the reaction of prenylsilane and its hydrocarbon homologue.

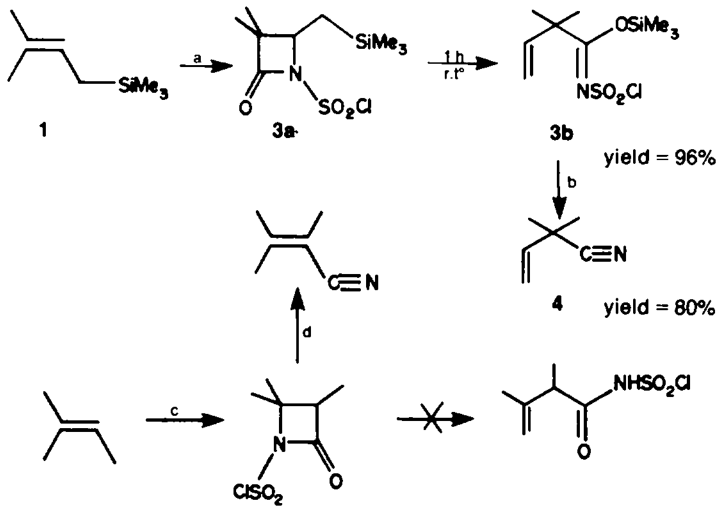
THEORETICAL APPROACH

This approach was undertaken by utilizing the MINDO/3[9] method of Dewar. He had already reported results, in the case of silylated derivatives, seemingly compatible with experimental results (notably their geometries and heats of dissociations).

The calculations were carried out on the compounds marked (A) and (B):



Only a partial optimisation was achieved due to a careful economization of calculation time. We took into account the angles <412, <512, <126, <123 and <239 as well as the angles dihedral to the rotations within the compounds, that is, the angle of the methyl groups, the SiH_3 and CH_2SiH_3 around the C–C and C–Si bonds.



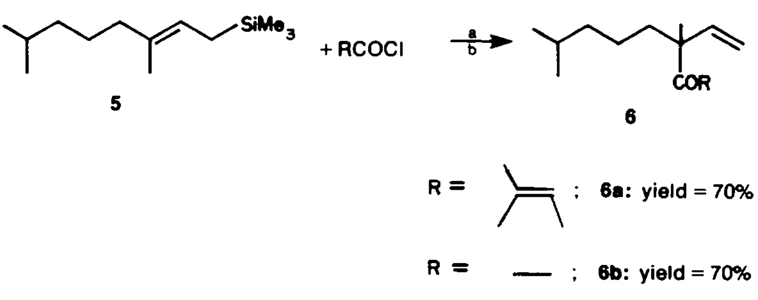
a: CSI; CCl_4; 0°C

b: 1) pyridine; Et_2O; 0°C – 2) H_2O

c: CSI; 30°C

d: DMF; 16–64 h; 60–80°C

Scheme 2.



a: $AlCl_3$; CH_2Cl_2; −60°C

b: NH_4Cl, H_2O; −30°C

Scheme 3.

The bond distances and angles which were not included in our optimization were accorded the values taken by Horn and Murell.[10] These values are shown in Table 1.

Similarly, we chose to examine theoretically the prenylsilane molecule instead of its trimethylsilylated homologue, for which one can assume[11,12] that the presence of methyl groups entails no modification of the original qualitative interpretation.

Table 2 summarizes the values obtained for the optimized angles of compound (B). From these values, it appears that the dihedral angle 1-2, 3-9 of this silylated compound takes on a value in the neighbourhood of 110°. The Si–CH_2 bond is nearly parallel to the ethylenic π electron cloud as shown in Scheme 4.

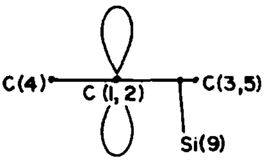
This in itself constitutes a positive argument in favour of a stabilizing interaction of the hyperconjugative type between the π double bond and the C–Si bond.

Such an interaction had already been postulated in derivatives of this type.[12].

A comparative study of the electronic densities at carbons 1 and 2 revealed the existence of inverse polarity along the double bonds between (A) and (B). This opposite behaviour is also reflected in the coefficient of the highest occupied molecular orbital (HOMO). Both these results are shown in Scheme 5.

Two possible mechanisms have been proposed for these reactions. The first hypothesis advances an attack of an ionized entity, an acylium ion,[13] or a dipolar intermediate leading to the formation of the β-lactam as postulated by Graf[7] in the case of the reaction of CSI.

The second possibility consists of a reaction scheme, more or less concerted: either a formal analog of an ene-reaction as in the case of acylation,[14] or a [π2s + π2a] cycloaddition which is symmetry—allowed by the Woodward–Hoffmann rules[15] in the case of CSI reactions.[16]

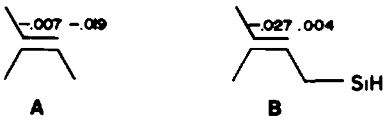


Atomic coordinates

	y	z
C_1	0.00	0.00
C_2	0.00	0.00
C_3	1.04	0.00
C_4	−1.28	0.00
C_5	1.22	0.00
Si_9	1.21	−1.54

B viewed down C = C(i.e. O_x)

Scheme 4.



Net atomic charges

HOMO coefficients

Scheme 5.

Table 1.

DISTANCES AND	ANGLES
d C-C = 1.488 Å	$\widehat{HCH}(CH_3)$ = 109°471
d C=C = 1.340 Å	$\widehat{HSiH}(SiH_3)$= 109°471
d C-Si = 1.856 Å	d C-H = 1.09 Å
d Si-H = 1.480 Å	
d C-H = 1.09 Å	

Table 2.

OPTIMIZED ANGLES IN (B) (DEGREES)			
214	120.6	1-2, 3-7	- 9.1
239	117.3	2-1, 5-10	154.0
123	135.7	2-1, 4-13	4.8
126	115.0	2-3, 9-16	-59.3
215	124.3		

During such a process, one can reasonably predict that the subsequent major interaction will occur between the sp_2 carbon which bears the largest coefficient in the olefin HOMO, and the atom which bears the largest coefficient in the CSI LUMO.

The latter has been normally assumed to be the central carbon atom.

Whichever be the mechanistic hypothesis retained, the theoretical calculations (taking into account the inversion between (A) and (B) at the charge, as well at the coefficient level) provide an element of validity to the behavioural modification of the two substrates envisaged.

Conclusion

This work has, first of all, confirmed and extended the interest in allylsilanes as organic synthons, synthons which permit for instance the introduction of mono- or di-isoprenoidic moieties.

Emphasis has then been placed on a quantum approach which clearly gives supportive evidence to this particular reactivity.

Further investigation into the way of approach of the two reactives is being undertaken in the form of a mechanism study of the electrophilic substitution of allylsilanes. Calculational results will allow us to choose between a concerted or a stepwise mechanism, with or without anchimeric assistance from silicon.

EXPERIMENTAL

Acylation reactions

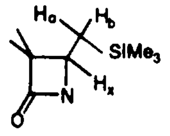
Acyl halide (55 mmol) in dichloromethane (10 ml) was added dropwise at low temperature (0°C in the case of acetyl chloride, or −20 to −40°C for senecioyl or isovaleroyl chloride) to a mixture of $AlCl_3$ (6.67 g, 50 mmol) and dichloromethane (50 ml) and stirred for 0.5–1 hr. The clear solution thus obtained was added dropwise (0.5 h) under stirring to the allylsilane (50 mmol in 100 ml of CH_2Cl_2) at −60°C. This solution was then stirred at −60° for 0.25 hr and poured into a mixture of ice and ammonium chloride previously cooled to −35°C. The layers were separated and the aqueous layer quickly extracted twice with ether (2 × 150 ml). The organic layer and ethereal extracts were collected and washed twice with a solution of sodium bicarbonate and with a saturated solution of ammonium chloride, dried (Na_2SO_4) and concentrated under vacuum to give the ketones which were isolated by distillation or purified by chromatography on a silica gel column.

2a, Artemisia ketone: IR: 3080, 1690, 1630, 1105, 1000, 920 cm^{-1}. ^{1}H NMR, δ(ppm), CCl_4: 1.13 (s, 6H, $2CH_3$–); 1.85 (d, 3H, allylic protons, J = 1.5 Hz); 2.08 (d, 3H, allylic protons, J = 1.5 Hz); 4.90 (m, 1H), 5.15 (m, 1H) ($=CH_2$); 5.90 (4 lines, 1H, –CH=); 6.13 (m, 1H, $-C\underline{H}=CMe_2$). **2b**, IR: 3060, 1700, 1625, 1120, 990, 910 cm^{-1}. ^{1}H NMR, δ(ppm) CCl_4: 1.07 (s, 6H, $2CH_3$–); 1.90 (s, 3H, CH_3–CO–); 4.85 (m, 1H), 5.10 (m, 1H) ($=CH_2$); 5.80 (4 lines, 1H, –CH=). **2c**, Dihydroartemisia ketone. IR: 3080, 1705, 1635 cm^{-1}. ^{1}H NMR, δ(ppm), CCl_4: 0.85 (d, 6H, $(C\underline{H}_3)_2CH$–, J = 6.5 Hz); 1.19 (s, 6H, 2Me); 1.80–2.40 (m, 3H, $-CO-C\underline{H}_2-$ and $-C\underline{H}{<}^{Me}_{Me}$); 4.95 (m, 1H), 5.17 (m, 1H) ($=CH_2$); 5.90 (m, 1H, –CH=). **6a**, IR: 3080, 1705, 1635 cm^{-1}. ^{1}H NMR, δ(ppm), CCl_4: 0.95 d, 6H, $(CH_3)_2CH$, J = 7 Hz; 1.20 (s, 3H, CH_3); 1.90 (d, 3H, CH_3–C= J = 1.5 Hz); 2.15 (d, 3H, CH_3–C=, J = 1.5 Hz); 5.00 (m, 1H), 5.20 (m, 1H) ($=CH_2$); 5.90 (m, 1H, –CH=); 6.20 (m, 1H, $-\underline{C}H=CMe_2$). **6b**, IR: 3100, 1715, 1640, 1000, 920 cm^{-1}. ^{1}H NMR, δ(ppm) 1.12 (d, 6H, $(C\underline{H}_3)_2CH$–); 1.42 (s, 3H, CH_3); 1.25–2.00 (m, 7, aliphatic $-CH_2-$ and $Me_2C\underline{H}$–); 2.25 (s, 3H, CH_3–CO–); 5.15 (m, 1H), 5.26 (m, 1H) (ethylenic protons), 6.04 (m, 1H, –CH=).

Cyanation reaction

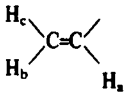
CSI (4.8 g, 34 mmol) was added dropwise at 0°C to a solution of prenyltrimethylsilane **1** (4.95 g, 35 mmol) in CCl_4 (10 ml). **3a** was obtained in CCl_4. IR: 1815 (C=O); 1410, 1175 (SO_2); 1250, 845, 755 cm^{-1} ($SiMe_3$). ^{1}H NMR δ(ppm) O internal reference (s, 9H, $SiMe_3$); 1.2 (s, 3H, Me) 1.3 (s, 3H, Me–); 4.0 (dd, 1H, H_x)

$J_{ax} = 4$ Hz
$J_{bx} = 11$ Hz



The solution was then allowed to come back to room temp. evaporated under vacuum to give **3b** (9.26 g, 96% yield) as a viscous pale yellow liquid.

3b, IR: 3080 ($C=CH_2$); 1640 (C=C); 1540 (C=N), 1370, 1170–1190 (SO_2); 1255, 845 ($SiMe_3$). ^{1}H NMR δ(ppm), 0.48 (s, 9H, $SiMe_3$); 1.32 (s, 6H, 2Me).



m corresponding to H_a : 5.8
H_b : 5.2
H_c : 5.1

$J_{ab} = 9$ Hz, $J_{ac} = 17$ Hz, $J_{bc} = 1.0$ Hz.

3b was then diluted in a 30 cm^3 ether solution. Pyridine (3 g, 38 mmol) was then added dropwise at 0°C on this solution. The pyridine–SO_3 complex which precipitated was filtered off and washed twice with ether. The ethereal layers were collected, washed twice with aqueous NH_4Cl at 0°C and dried over $MgSO_4$. Ether was evaporated under vacuum and **4** (2.5 g, 77% yield) purified by chromatography on silicagel. **4**: IR 3080 ($C=CH_2$); 2240 (C≡N); 1640 (C=C); 990, 930 cm^{-1} ($CH=CH_2$).

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