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The Reactivity of 3-bromo-2-trimethylsilyl-1-propene towards electrophiles
A short synthesis of 2-substituted-4-trimethylsilylfurans

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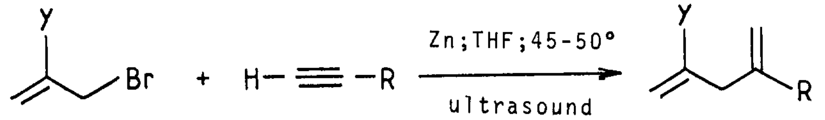
Summary - *3-bromo-2-trimethylsilyl-1-propene* 1c *reacts with various electrophiles (aldehydes, a ketone, nitriles, terminal alkynes) in the presence of zinc to give functionnalized vinylsilanes. A three steps synthesis of 2-substituted-4-trimethylsilylfurans from* 1c *and a nitrile is described. Opening of epoxysilanes with cuprates gave an easy access to α-trimethylsilylalcohols.*

We have recently reported[1] that the functionnalized bromides 1a and 1b added regioselectively to terminal alkynes in the presence of zinc to give the dienes 2a and 2b. We have now extended this reaction to the 3-bromo-2-trimethylsilyl-1-propene 1c (see scheme 1 and table). The reagent 1c was easily available from 2-trimethylsilyl-2-propen-1-ol[2] through bromination[3] with N-bromosuccinimide, methyl sulfide[4] in methylene chloride (2.5hr at 0° ; 63-67%). Allylic anions generated from 1c have found little use in organic synthesis[5]. This led us to examine the reactivity of other electrophiles like ketones, aldehydes and nitriles[6] with bromide 1c in the presence of zinc. All these electrophiles reacted as expected under our Barbier conditions[1,7] (see the experimental part) to furnish the products listed in the table. As noted earlier[1] the introduction of an oxygen atom at the α or β position to the triple bond enhanced the yield of the reaction. Benzaldehyde, acetophenone and even enolisable aldehydes like hexanal or 2-phenylpropionaldehyde gave in good yield the addition products. Aliphatic and aromatic nitriles led after acidic hydrolysis to β,γ-unsaturated ketones[8]. The use of a substituted allylic bromide eg. a mixture of 1-bromo-2-trimethylsilyl-2 butene and 3-bromo-2-trimethylsilyl-1-butene[9] gave regiospecifically the ketone resulting from attack of the more

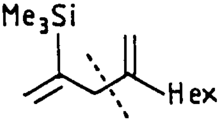
Scheme 1 -



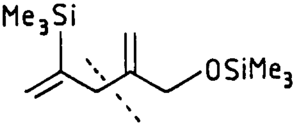
1a : Y = COOR
1b : Y = PO(OR)$_2$
1c : Y = SiMe$_3$

2a : Y = COOR
2b : Y = PO(OR)$_2$
2c : Y = SiMe$_3$

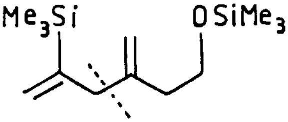
Table - Products obtained by the reaction of bromide 1c with alkynes, aldehydes, a ketone, and nitriles, in the presence of zinc at 45-50° in THF.



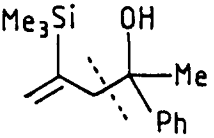
(50%) [a]



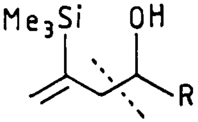
(60%)



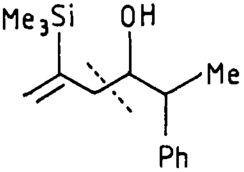
(60%)



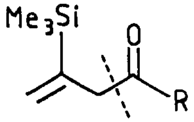
(78%)



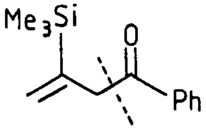
R = phenyl : (79%)
R = pentyl : (75-78%)



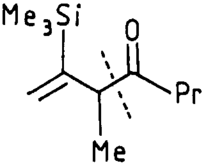
(78%)



R = propyl : (80%)
R = heptyl : (82%)
R = pentyl : (82%)
R = cyclohexyl : (74%)



(61%)



(54%)

a/ All quoted yields correspond to distilled or flash chromatographically purified materials. All spectroscopic data (IR, ^{1}H-NMR and ^{13}C-NMR) are compatible with the structures shown in the *formulae*. Newly formed bonds are indicated by dotted lines.

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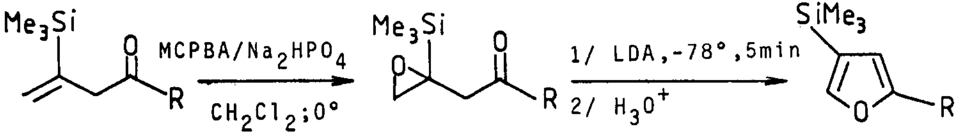
substituted allylic carbon atom in 54% yield (see table). The synthesized enones 3 could be transformed in two steps into 2-substituted-4-trimethylsilylfurans[10] (see scheme 2).

Scheme 2 -



3/ molecular sieves 12h

3

4a:73% 4b:79%
4c:78% 4d:72%

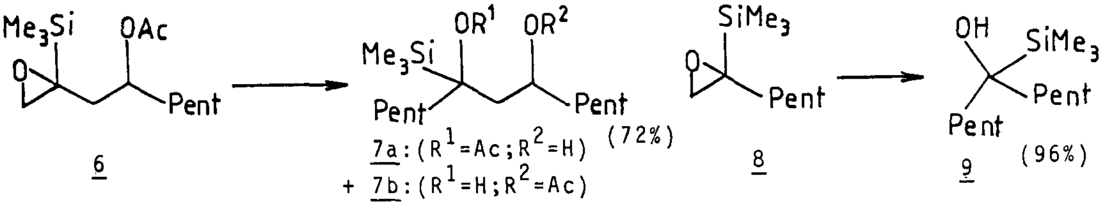
5a:71% 5b:72%
5c:82% 5d:81%

a : R = pentyl ; b : R - heptyl ; c : R = cyclohexyl ; d : R = phenyl.

Treatment of the enones 3a-d with an excess of m-chloroperbenzoic acid (MCPBA) (3.35eq.) in dry methylene chloride buffered with Na_2HPO_4[11] (16-19hr, 0°) led to the epoxysilanes 4a-d (70-79%) which were then added to a LDA (1eq.) solution in THF at -78°[12]. After 5 min, the reaction mixture was hydrolysed with a NH_4Cl solution, extracted with hexane, washed with a NaCl solution, dried and evaporated. The crude product was dissolved into ether and stirred 12hr over molecular sieves to give the furans 5a-d in 71-82% yields.

We were surprised[13] to find that epoxysilane[14] 6 was opened by lithium dibutylcuprate (2eq.,-35°,0,5hr) to give a mixture of the acetates 7a and 7b (72%) (see scheme 3). This regioselective attack seems to be general : epoxysilane[11] 8 reacted with 2eq. of lithium dibutylcuprate in ether (-25°, 24h) to give, in virtually quantitative yield, alcohol 9 (see scheme 3).

Scheme 3 -



Typical procedure -

A 100ml flask is charged under nitrogen with 2g (30.6 mmol) of zinc (purity : 99.999%), 1g of finely crushed glass[15],≈1g (5.3 mmol) of 1,2-dibromoethane and 3 ml of dry THF. This mixture is shortly boiled to start the formation of $ZnBr_2$. After 15 min, 16-18 mmol of the electrophile dissolved in 1ml THF is added and the flask is immersed in a common laboratory cleaner[16] (48kHz ; 30 W) filled with warm water (55°). If the electrophile is an aldehyde, a ketone or a nitrile, only half of it is added first, the other half is slowly added together with the solution of bromide 1c (12.8 mmol in 9 ml THF) over 15 min at 45-50°. After 15-30 min (VPC control) at 40-45°, the reaction mixture is cooled at 0° and 10 ml of aq. NH_4Cl solution and 20 ml of ether are added. If the electrophile is a nitrile, hydrolysis is performed by addition of 20 ml of 0.2NHCl , stirring for 5 min and addition of 20 ml of aq.NaCl, 40 ml of ether and 20 ml of CH_2Cl_2. After filtration, the aq. layer is extracted with 2 x 20 ml of an ether/CH_2Cl_2 mixture (3:1). The organic layer is washed first with 10 ml of 0.2N HCl (VPC control indicates complete hydrolysis of the intermediate imine), then with a NaCl solution and dried over $MgSO_4$. Distillation or flash-chromatography furnishes the analytically pure products listed in the table.

Acknowledgements -

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