

REGIOSPECIFIC ALLYLATION OF ACETALS WITH ALLYLSILANES CATALYZED  
 BY IODOTRIMETHYLSILANE. SYNTHESIS OF HOMOALLYLEthers<sup>1</sup>

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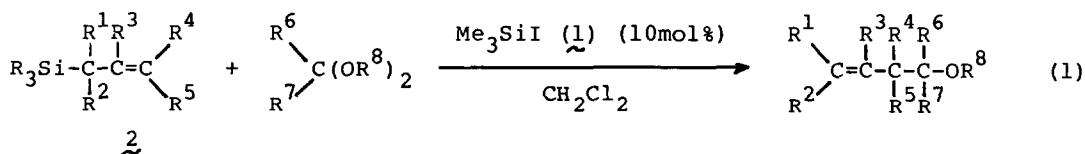
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Summary: Allylation of acetals with allylsilanes is catalyzed by iodotrimethylsilane to give the corresponding homoallyl ethers, with regiospecific transposition of the allyl group.

In previous papers,<sup>2,3</sup> we have described a convenient *in situ* method of preparing iodotrimethylsilane (1) from hexamethyldisilane and iodine with some applications. We also have reported in a series of papers the use of allylsilanes (2) for regiospecific allylation of carbonyl compounds, acetals, and acid chlorides.<sup>4</sup> In these reactions, an equivalent amount of a Lewis acid, usually titanium tetrachloride, is used for the activator, but sometimes the use of a large amount of a Lewis acid can be a drawback of the reaction.

In this paper, we report that the regiospecific allylation reaction of acetals with allylsilane can be catalyzed very smoothly by iodotrimethylsilane.<sup>5</sup> Although applications of a stoichiometric amount of iodotrimethylsilane to a variety of reactions have been recorded in organic synthetic chemistry,<sup>6</sup> the present study is, as far as we know, the first example of using a catalytic amount of iodotrimethylsilane. We have found that an amount of less than 10 mol% of iodotrimethylsilane (1) is enough to catalyze the reaction. The results are listed in Table 1.

Since it is known that iodotrimethylsilane can be generated *in situ* by the reaction of allyltrimethylsilane and iodine,<sup>6</sup> the present reaction can be effected by a catalytic amount of iodine with a slight excess amount of allyltrimethylsilane. The present reaction has following features and advantages, in addition to generality of the reaction, mildness of reaction conditions, high yields of products, and easy manipulation of the conversion.



(1) The allyl transfer was completely accompanied by a regiospecific

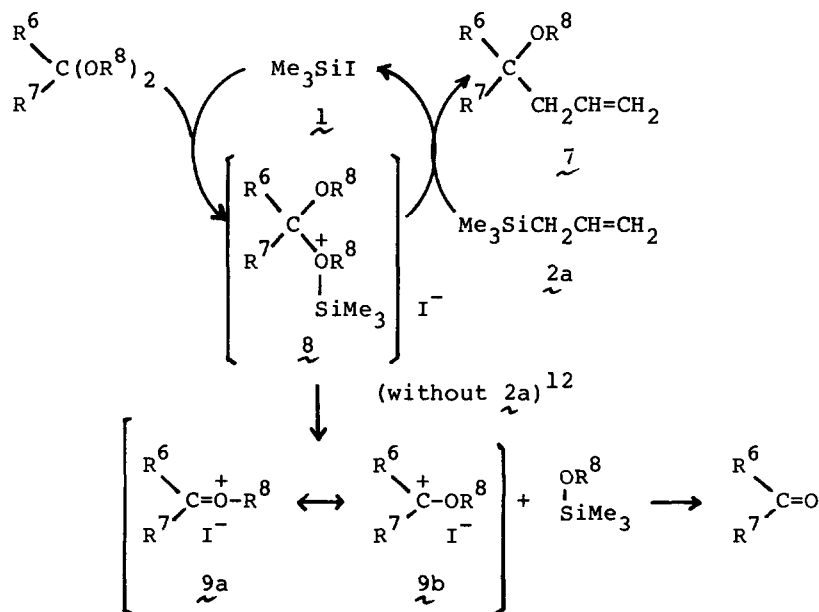
Table 1. Allylation of acetals with allylsilanes (2) catalyzed by iodotrimethylsilane (1)<sup>a</sup>.

Entry	Allylsilane	Acetal	Conditions	Products(%yield) <sup>b</sup>
1	Me <sub>3</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> (2a)	Me <sub>2</sub> C(OMe) <sub>2</sub>	-78°, 2h then -50°, 1.5h	Me <sub>2</sub> CCH <sub>2</sub> CH=CH <sub>2</sub> OMe (83)
2	2a	PhCH(OMe) <sub>2</sub> (3)	-78°, 8h	PhCHCH <sub>2</sub> CH=CH <sub>2</sub> OMe (6) (81)
3	2a	Ph(CH <sub>2</sub> ) <sub>2</sub> CH(OMe) <sub>2</sub>	-78°, 6h	Ph(CH <sub>2</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH=CH <sub>2</sub> OMe (95)
4	2a	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(OMe) <sub>2</sub> (4)	-78°, 1h then -20°, 2h	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHCH <sub>2</sub> CH=CH <sub>2</sub> OMe (65)
5	2a	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(OMe) <sub>2</sub> (5)	-78°, 25min then -30°, 2h	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHCH <sub>2</sub> CH=CH <sub>2</sub> OMe (70)
6	2a	PhCH=CHCH(OMe) <sub>2</sub>	-78°, 1h then -30°, 7h	PhCH=CHCHCH <sub>2</sub> CH=CH <sub>2</sub> OMe (84)
7	2a	PhCH=CHCH(OEt) <sub>2</sub>	-78°, 1h; -60°, 1h then rt, 0.5h	PhCH=CHCHCH <sub>2</sub> CH=CH <sub>2</sub> OEt (91)
8	Me <sub>3</sub> SiCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> (2b)	3	-78°, 1h; -60°, 1h then rt, 0.5h	PhCHCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> OMe (78)
9	2b	4	-78°, 25min then -30°, 2.5h	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub> OMe (69)
10	i-PrMe <sub>2</sub> SiCH <sub>2</sub> CH=CH <sub>2</sub> (2c)	3	-78°, 1h	6 (70)
11	Me <sub>3</sub> SiCH(CH <sub>3</sub> )CH=CH <sub>2</sub> (2d)	3	-40°, 0.5h	PhCHCH <sub>2</sub> CH=CHCH <sub>3</sub> OMe (85)
12	i-PrMe <sub>2</sub> SiCH <sub>2</sub> CH=CHCH <sub>3</sub> (2e)	3	-40°, 1.5h then 0°, 3h	PhCHCH(CH <sub>3</sub> )CH=CH <sub>2</sub> OMe (82)
13	Me <sub>3</sub> SiCH <sub>2</sub> C(CH=CH <sub>2</sub> )=CH <sub>2</sub> (2f)	5	-78°, 40min then -40°, 3h	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHCH <sub>2</sub> C(CH=CH <sub>2</sub> )=CH <sub>2</sub> OMe (90)
14	Me <sub>3</sub> SiCH <sub>2</sub> CH=CHCH=CH <sub>2</sub> (2g)	3	-78°, 50min	PhCHCH <sub>2</sub> CH=CHCH=CH <sub>2</sub> OMe (88)
15	Me <sub>3</sub> SiCH <sub>2</sub> C≡CSiMe <sub>3</sub> (2h)	3	-78°, 1h then -50°, 1h	PhCHC(SiMe <sub>3</sub> )=C=CH <sub>2</sub> OMe (82)

<sup>a</sup> All reactions were carried out in dichloromethane in the presence of 10 mol% iodotrimethylsilane. <sup>b</sup> Yields after isolation.

transposition in the allylic group as shown in the examples. (Entry 11 and 12) (2) With  $\alpha,\beta$ -unsaturated acetals (Entry 6 and 7), only monoallylation occurred regioselectively at the acetal carbon. No diallylation product was observed, while the reactions activated by a Lewis acid gave diallylated products.<sup>7</sup> (3) Increasing steric hindrance around the silicon and/or the  $\alpha$  and  $\gamma$ -carbon atoms of the allyl group retarded the reaction. Thus, allyltriethylsilane, ( $\alpha,\alpha$ -dimethylallyl)- and ( $\gamma,\gamma$ -dimethylallyl)trimethylsilane as well as crotyl(*t*-butyldimethyl)silane did not enter the reaction, and crotyl(*i*-propyldimethyl)silane (2e) underwent the reaction with benzaldehydedimethyl acetal more slowly than allyl(*i*-propyldimethyl)silane (2c). (4) Carbonyl compounds such as aldehydes and ketones did not react with allylsilanes catalyzed by 1, although similar reactions promoted by a Lewis acid occurred very rapidly.<sup>8</sup> Orthoformates, esters and ethers including benzyl and allyl ethers did not enter the reaction. (5) Functionalized allylic silanes may be effective for the allylation catalyzed by 1. Thus, the reaction of 2-trimethylsilylmethyl-1,3-butadiene (2f) with isovaleraldehyde dimethylacetal gave ipenol methyl ether in excellent yield (Entry 13).<sup>9</sup> 2,4-Pentadienylsilane (2g) and propargylsilane (2h) afforded the corresponding pentadienylation product<sup>10</sup> and allenic product (Entry 15), respectively. (6) The overall conversion of the reaction is rather similar to the recently reported reaction with trimethylsilyl trifluoromethanesulfonate.<sup>11</sup>

Although the mechanism of the reaction has not been elucidated, the results can be rationalized by scheme 1, in which the initial formation of an oxonium ion (8)<sup>12</sup> takes place at low temperature. The facts found in the reaction suggest



Scheme 1. A catalytic cycle of the allylation.

that the intermediate (8) may be subjected to the bimolecular nucleophilic displacement by the allylsilane (2). When the allylsilane (2) is absent, 8 may be converted to 9 to give the corresponding ketone as is seen in the literature.<sup>13</sup>

Typical procedures are as follows:<sup>14</sup> A) In a 30 ml two-necked flask fitted with a condenser, a dropping funnel and a magnetic-stirr bar, iodine (51 mg, 0.2 mmol) and dichloromethane (2 ml) were placed and then allyltrimethylsilane (274 mg, 2.4 mmol) was added and stirred for 50 min at room temperature. Benzaldehyde dimethylacetal (314 mg, 2 mmol) was added to the mixture cooled to -78° with a Dry Ice-methanol bath. After stirring for 8 h, the solvent was removed and the residue was subjected to TLC. Pure 4-methoxy-4-phenyl-1-butene (262 mg, 81% yield) was obtained. B) In the same 30 ml two-necked flask, a mixture of an allylsilane (2.2 mmol), an acetal (2 mmol) and dichloromethane (2 ml) was placed and cooled to -78°. Iodotrimethylsilane (0.2 mmol), freshly prepared from hexamethyldisilane and iodine, was added by means of a syringe. The mixture was worked up in the same manner. This procedure was used for the allylation with allylsilanes other than allyltrimethylsilane.

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#### References and Notes

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