

Hypervalent Organoiodine Chemistry: a New Synthesis of β -Methylene Cyclic Ethers

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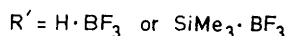
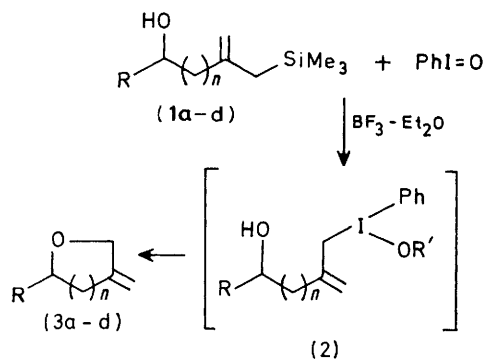
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The allylsilanes (**1**), containing suitably-substituted hydroxy-groups, on treatment with iodosylbenzene in the presence of $\text{BF}_3\text{-Et}_2\text{O}$ in an ether solvent, give 5- or 6-membered β -methylene cyclic ethers (**3**) in good yields, presumably *via* the highly reactive allylaryliodonium intermediates (**2**).

Hypervalent organoiodine compounds have been shown to be useful mild oxidizing reagents,¹ and diaryliodonium salts are synthetically important owing to their reactivity with a variety of nucleophiles.² However the synthetic utility of the promising alkylaryliodonium intermediate is not well known because of their thermodynamic instability.³ We report a new synthesis of the β -methylene cyclic ether (**3**) *via* the probable reactive alkylaryliodonium intermediate (**2**), itself derived from the reaction between the allylsilane (**1**) and iodosylbenzene in the presence of $\text{BF}_3\text{-Et}_2\text{O}$ as shown in Scheme 1.

Allylsilane normally acts as the equivalent of an allyl anion and will transfer the allyl group to various electrophiles in the presence of a Lewis acid.⁴ Therefore, the umpolung type of reactivity for the allylsilyl group of (**1**) must be achieved for the conversion of (**1**) into the cyclic ether (**3**).⁵

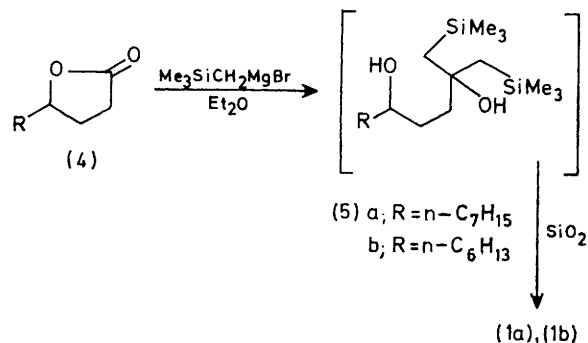


- a; $n = 2$, $\text{R} = n\text{-C}_7\text{H}_{15}$
 b; $n = 2$, $\text{R} = n\text{-C}_6\text{H}_{13}$
 c; $n = 1$, $\text{R} = \text{Ph}[\text{CH}_2]_2$
 d; $n = 1$, $\text{R} = \text{CH}_2=\text{CH}[\text{CH}_2]_8$

Scheme 1

The allylsilanes (**1a—d**) were prepared as follows. Treatment of the commercially available γ -lactones (**4a**) and (**4b**) with trimethylsilylmethylmagnesium chloride (4 mol. equiv.) in refluxing ether for 2 h followed by treatment of the product with silica gel in chloroform yielded the allylsilanes (**1a**) and (**1b**) in 41 and 45% yields, respectively, *via* the 1,3-disilanes (**5a**) and (**5b**) (Scheme 2). The alcohols (**6a**) and (**6b**), obtained by the Grignard reaction of the corresponding aldehydes with 2-methylprop-2-enyl-magnesium chloride underwent disilylation⁶ (Bu^nLi -tetramethylethylenediamine-hexane and then Me_3SiCl) to give (**7a**) and (**7b**), whose selective protodesilylation (10% H_2SO_4 -tetrahydrofuran) afforded the allylsilanes (**1c**) and (**1d**) in 57 and 46% yields, respectively.

The allylsilane (**1a**), on treatment with iodosylbenzene (1 mol. equiv.) and $\text{BF}_3\text{-Et}_2\text{O}$ (2 mol. equiv.) in ether at -20°C



Scheme 2

- (6a); $\text{R}^1 = \text{Ph}[\text{CH}_2]_2$, $\text{R}^2 = \text{H}$
 (6b); $\text{R}^1 = \text{CH}_2=\text{CH}[\text{CH}_2]_8$, $\text{R}^2 = \text{H}$
 (7a); $\text{R}^1 = \text{Ph}[\text{CH}_2]_2$, $\text{R}^2 = \text{SiMe}_3$
 (7b); $\text{R}^1 = \text{CH}_2=\text{CH}[\text{CH}_2]_8$, $\text{R}^2 = \text{SiMe}_3$

Table 1. Intramolecular cyclisation of allylsilane (**1**) using iodosylbenzene and $\text{BF}_3\text{-Et}_2\text{O}$.

(1)	Solvent	Conditions	Product (% yield) ^a
(a)	Et_2O	-20°C , 2 h and then 0°C , 1 h	(3a) (58)
(b)	dioxan	r.t., ^b 2 h	(3b) (65)
(c)	glyme	0°C , 1.5 h	(3c) (52)
(c)	dioxan	r.t., 3 h	(3c) (68)
(d)	dioxan	r.t., 4 h	(3d) (40)

^a Yield refers to pure isolated compound. ^b r.t. = room temperature.

for 2 h and then 0°C for 2 h, afforded the 6-membered β -methylene cyclic ether (**3a**) in 58% yield after chromatographic purification (SiO_2).[†] In a similar manner, intramolecular cyclisations of (**1c**) and (**1d**) gave the 5-membered cyclic ethers (**3c**) and (**3d**). The results are shown in Table 1. The use of ether solvents proved better than the use of dichloromethane or n-hexane. The formation of iodobenzene in the cyclisation reaction was usually observed.

The first step of the intramolecular cyclisation is probably the nucleophilic attack of an allylsilyl group of (**1**) on iodosyl-

benzene, activated by $\text{BF}_3\text{-Et}_2\text{O}$, to produce a highly reactive allylphenyliodonium salt (**2**); the latter can now act as an allyl cation equivalent. The successive intramolecular nucleophilic attack of the suitably-substituted hydroxy-group on the iodonium group produces the cyclic ether (**3**).

Kliegman⁷ reported the displacement reaction of the trimethylsilyl group in allyltrimethylsilane by methanol in the presence of palladium(II) acetate. However, the yield of allyl methyl ether was only 5%. We have established the umpolung type of reactivity for the allylsilyl group by using a hypervalent organoiodine compound; the yield of the cyclisation product (**3**) was good.

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[†] Selected spectroscopic data: (**3**) ^1H n.m.r. (CDCl_3) δ 0.7–2.5 (19H), 3.1–3.5 (1H, m), 3.94, 4.16 (each 1H, AB type, J 12.5 Hz), and 4.75 (2H, s); mass spectrum m/z 196 (M^+ , 4%), 126(6), 97(100), 69(31), and 67(37).