

3-Bromopentadienylsilane: A New Reagent for the Introduction of a Functional Pentadienyl Unit with Fixed Configuration

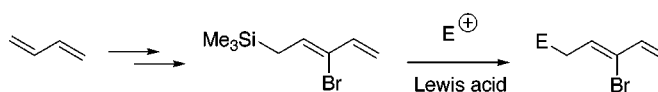
Maryline Roux, Maurice Santelli,* and Jean-Luc Parrain*

Laboratoire de Synthèse Organique associé au CNRS (ESA 6009),
Faculté des Sciences de Saint Jérôme, Avenue Escadrille Normandie-Niemen,
13397 Marseille Cedex 20, France

jl.parrain@lso.u-3mrs.fr

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ABSTRACT



The (*Z*)-1-trimethylsilyl-3-bromopenta-2,4-diene **3** was prepared through a sequence involving the reductive silylation of butadiene, dibromocarbene addition on the resulting disilane **1**, and thermolytic ring opening. With aldehydes, this new pentadienylsilane reacts exclusively via an S_E' pathway. In the presence of an alcohol or a carbamate under Lewis acid activation, **3** yields, respectively, bromopentadienyl ethers or bromopentadienyl-protected amines.

Over the last two decades, allylsilane reagents have proved to be efficient tools for the transfer of an allyl unit with a high tolerance for numerous functionalities both on the substrate and on the reagent.¹ While allylsilanes have received considerable attention, their homologous trimethylsilylpentadienes have only been little investigated from a synthetic point of view.² Trimethylsilylpentadiene (PDS)³ originally prepared by Seyferth et al. was found to react regioselectively in an S_E' fashion onto aldehydes, while reaction of the phenyl-substituted PDS with the acyliminium ion derived from glycidyl cation equivalent occurred via the S_E' pathway.⁴ Following our previous work describing the synthesis of β -allenylsilanes from allylsilanes via a sequence involving dibromocarbene addition and cyclopropylidene rearrangement,⁵ we planned to examine the synthesis and

subsequent reactivity of halo-substituted PDS. The halo-substituted PDS, which can be prepared from 1,4-bis-(trimethylsilyl)-but-2-ene **1**, would allow more flexibility in the 1,3-dienyl moiety construction.

Herein, we report the synthesis and the reactivity of a novel functional pentadienylsilane: 1-trimethylsilyl-3-bromopenta-2,4-diene **3** (BPDS). Disilane **1** was readily prepared from lithium, chlorotrimethylsilane, and butadiene in 65% yield as a 60/40 mixture of *Z* and *E* isomers.⁶ Treatment of **1** with bromoform and potassium *tert*-butoxide in pentane afforded a 60/40 mixture of *cis/trans* dibromocyclopropanes **2** via a the dibromocarbene addition reaction.⁷ It should be noted that under phase-transfer conditions⁸ **1** was left unchanged. This is likely due to steric reasons attributable to the difference of solvation of the reactive species (H₂O vs *t*-BuOH–pentane). Thermolysis of **2** under vacuum at 100

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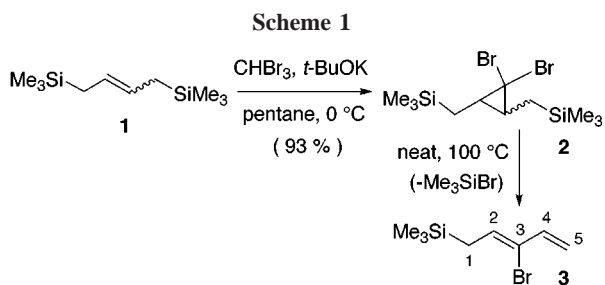
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(6) Weyenberg, D. R.; Toporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975.

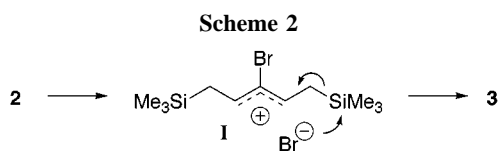
(7) Last, L. A.; Fretz, E. R.; Coates, R. M. *J. Org. Chem.* **1982**, *47*, 3211.

(8) Skatebol, L.; Abskharoun, G. A.; Greibrokk, T. *Tetrahedron Lett.* **1973**, 1367.

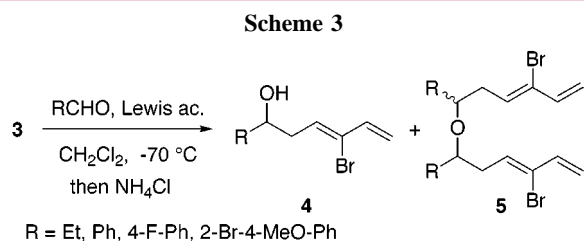
°C resulted in the ring cleavage rearrangement followed by elimination of trimethylsilyl bromide and led to (*Z*)-BPDS **3** in 75% yield (Scheme 1).



The (*Z*)-configuration of the trisubstituted double bond was assigned on the basis of an NMR NOESY experiment that exhibited a cross-peak between H2 and H5 and no cross-peak between H1 and H4 or H5. The electrocyclic ring opening of **2** produced the doubly silicon-stabilized intermediate cation **I** in which the more stable transoid configuration can explain the configuration of the double bond (Scheme 2).



Attention was next directed to the Lewis acid promoted addition reaction of **3** to aldehydes (Scheme 3).⁹ We first



surveyed various Lewis acids (SnCl₄, TiCl₄, BF₃·Et₂O, MgBr₂, TMSOTf) in the reaction of BPDS **3** with benzaldehyde in dichloromethane at -78 °C. Results are summarized in Table 1.

In the presence of 1.1 equiv of either SnCl₄ or TiCl₄, the reaction did not yield the expected homodienyl alcohols.

Instead, when SnCl₄ was employed, the starting materials were partially recovered after hydrolysis (entry 1), while with TiCl₄ (entry 2) numerous unidentified products were formed.

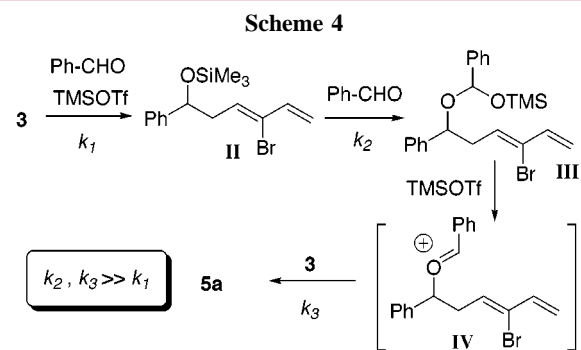
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Table 1. Lewis Acid Promoted Reaction of **3** with Aldehydes

entry	R	Lewis acid	4/5	yield (%)
1	Ph	SnCl ₄		
2	Ph	TiCl ₄		
3	Ph	MgBr ₂ ^a		
4	Ph	BF ₃ ·Et ₂ O	4a/5a (55/45)	55
5	Ph	TMSOTf	5a (0/100)	68
6	Et	TMSOTf	5b (0/100)	67
7	4-F-Ph	TMSOTf	5c (0/100)	51
9	2-Br-4-MeO-Ph	TMSOTf	5d (0/100)	51
10	2-Br-4-MeO-Ph	BF ₃ ·Et ₂ O	4d/5d (85/15)	60

^a 3-Bromopenta-1,3-diene was obtained as the sole product in 70% yield.

The use of MgBr₂ under identical conditions to the above led in 70% yield to the proteolysis product, 3-bromopenta-1,3-diene, with a clean (*Z*)-configuration of the double bond and the starting benzaldehyde (entry 3). With 1 equiv of BF₃·Et₂O, the reaction occurred in fair yield affording the expected homodienyl alcohol **4a** and ether **5a** as a 60/40 mixture of diastereoisomers.¹⁰ Surprisingly, the use of TMSOTf (10 mol %) gave only in 68% yield the ether **5a**. Other aldehydes tested under TMSOTf activation yielded the corresponding ethers **5** with poor diastereoselectivities (5–10% de). It should be noted that with 2-bromo-4-methoxybenzaldehyde (entry 10) the reaction could be driven in favor of **4d** provided BF₃·Et₂O was used.¹¹ The relative low kinetic reactivity of **3** toward aldehydes compared to oxocarbenium ions in the presence of BF₃·Et₂O or TMSOTf could explain the formation of ethers **5** instead of alcohols **4**.¹² In the TMSOTf-promoted reaction, a reasonable pathway is outlined in Scheme 4. Allylation reaction leads initially to



trimethylsilyl ether **II**, which rapidly reacts with a second equivalent of aldehyde giving the mixed silyl acetal **III**. This

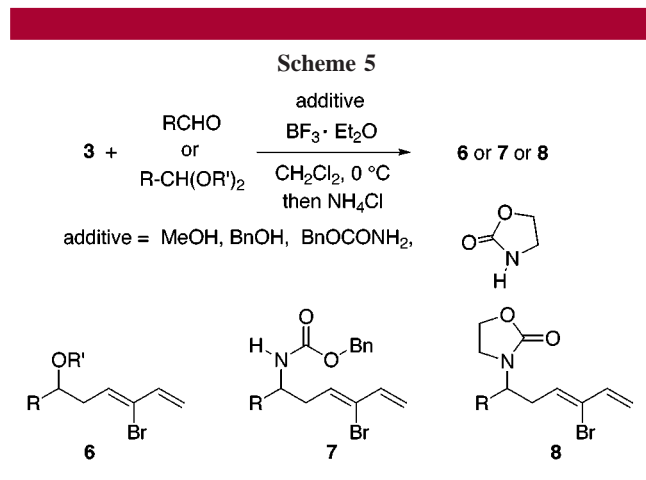
(10) Compared to simple pentadienylsilane, **3** exhibits similar trends in terms of reactivity (regioselective reaction with an S_E' fashion onto aldehydes).

(11) All the reactions were performed in dichloromethane at -70 °C for 2 h and then quenched with a saturated NH₄Cl solution.

(12) For a kinetic study of the reaction of aldehydes or carboxonium ions with allylsilanes, see: Mayr, H.; Gorath, G. *J. Am. Chem. Soc.* **1995**, *117*, 7862.

acetalization reaction under the Noyori conditions¹³ furnishes intermediary the oxocarbenium ion **IV**, which is trapped by **3**.¹⁴

Given the difference of reactivity of BPDS **3** toward aldehydes and oxocarbenium ions, we next investigated the possibility to carry the allylation reaction on an aldehyde in the presence of a second nucleophile such as a primary alcohol or a carbamate (Scheme 5, Table 2). First, we found



that reaction of **3** with acetals in the presence of 1 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ occurred via an exclusive S_{E}'' pathway and led to bromopentadienyl ethers (entries 1 and 2). Encouraged by this result, we studied the scope of the reaction using, in a one-pot process, methanol or benzyl alcohol. With 2 equiv of **3**, only the methyl ethers **6c–d** and the easily removable benzyl ethers **6e–g** were obtained in fair to good yields with a complete retention of configuration of the (*Z*)-double bond, which was established by NMR NOESY experiments. The first step, certainly a protodesilylation reaction¹⁵ with the alcohols, used yields the corresponding trimethylsilyl ethers that give from aldehydes the mixed trimethylsilyloxy acetals, the later giving, with the second equivalent of **3**, the diene ethers **6**. In contrast to a previously described method for the Sakurai–Hosomi allylation,¹⁴ it is not necessary to use silyl ethers; this slightly simplifies the procedure. Both free alcohols **4** and symmetrical ethers **5** were undetected excepted for the reaction of 2-bromo-4-methoxy-benzaldehyde where **4d** was obtained in 10% yield (entry 4).

Moreover, we also found that this method was not independent of the nature of the alcohol used. For example, attempts conducted with allyl alcohol were unsuccessful, while the use of *p*-methoxybenzyl alcohol gave only (*Z*)-3-bromo-6-(4-methoxyphenyl)hexa-1,3-diene.¹⁶ Finally, using the well-described procedure of Veenstra and Schmid,¹⁷

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(15) 3-bromopenta-1,3-diene was obtained as a nonpolar byproduct.

(16) Reaction of allyltrimethylsilane with *p*-methoxybenzyl alcohol was recently described. Kaur, G.; Kaushik, M.; Tehan, S. *Tetrahedron Lett.* **1997**, *38*, 2521.

(17) Veenstra, S. J.; Schmid, P. *Tetrahedron Lett.* **1997**, *38*, 997.

Table 2. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -Catalyzed Addition of BPDS **3**

entry	R-CHO or R-CH(OR') ₂	additive	6 , 7 or 8	Yield (%) ^a
1 ^e		-	6 a	75
2 ^e		-	6 b	48
3 ^d		MeOH	6 c	52
4 ^d		"	6 d	64
5 ^d		BnOH	6 e	70
6 ^d		"	6 f	79
7 ^d		"	6 g	56
8		BnOCONH ₂	7 a	52
9		"	7 b	59
10		"	7 c	56
11		"	7 d	58
12		"	7 e	41 ^b
13		"	7 f	27 ^c
14 ^d			8 a	66
15 ^d		"	8 b	57

^a Yields are of chromatographically pure material. ^b Obtained as 95/5 mixture of diastereoisomer (the relative stereochemistry of the major isomer was not determined); ^c Obtained in 2/1 mixture with **6b**. ^d 2 equiv of **3** was used to complete the reaction. ^e The reaction was performed at -78°C .

identical attempts conducted with benzylcarbamate or oxazolidinone led to protected homopentadienylamines **7a–f** and **8a,b**. As can be seen from the Table 2, both aliphatic or aromatic aldehydes react smoothly to give the desired adducts. Remarkably, the reaction with hydratropaldehyde and benzylcarbamate (entry 12) occurs in fair yield and with an excellent diastereoisomeric ratio (up to 95/5).

In conclusion, we have described a stereoselective approach to the synthesis of the non reported (*Z*)-bromopentadienylsilane starting from inexpensive materials. A modified version of the Sakurai reaction allowed an easy

access to functional bromo dienes with a total control of the stereochemistry of the trisubstituted double bond. Other potential uses of this reagent are in progress and will be reported in due course.

Acknowledgment. We thank the CNRS and MENRT for providing financial support.

Supporting Information Available: Typical experimental procedures, tabulated ^1H and ^{13}C NMR data for compounds **3–8**, and copies of ^1H , ^{13}C , and NOESY NMR spectra of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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