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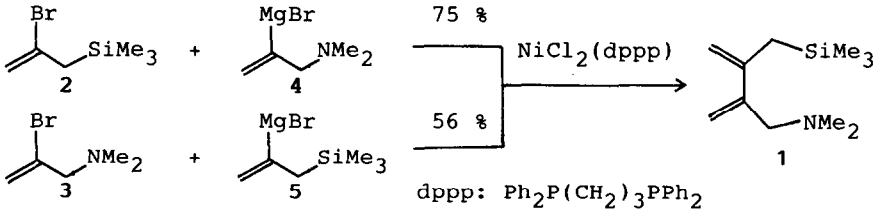
2-DIMETHYLAMINOMETHYL-3-TRIMETHYLSILYLMETHYL-1,3-BUTADIENE AS 2,2'-BIALLYL DIRADICAL SYNTHON. A NEW AND FACILE ENTRY TO 1,2-DIMETHYLENECYCLOHEXANES, AND [6.6] AND [6.7] RING SYSTEMS[1]

Akira Hosomi*†, Ken Otaka§, and Hideki Sakurai*§
Faculty of Pharmaceutical Sciences, Nagasaki University, Nagasaki 852† and
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980§
Japan

Summary: The title compound, prepared readily by the cross-coupling reaction of β-bromoallyltrimethylsilane and the Grignard reagent from β-bromoallyldimethylamine, is an effective reagent as 2,2'-biallyl diradical synthon to give [6.6] and [6.7] ring systems by tandem cycloaddition reactions. 1,2-Dimethylenecyclohexanes can also be isolated in good yield.

Allylsilanes have been recognized as versatile synthons of reactive intermediates such as regio-controlled allyl anions.[2] We have previously reported that the isoprenylsilane is a useful reagent both for the nucleophilic isoprenylation as an allylsilane and for the Diels-Alder reaction as a highly regioselective 1,3-diene.[3] We report herein a convenient preparation and tandem cycloaddition reactions of 2-dimethylaminomethyl-3-trimethylsilylmethyl-1,3-butadiene (**1**) that serves formally as a 2,2'-biallyl synthon.[4]

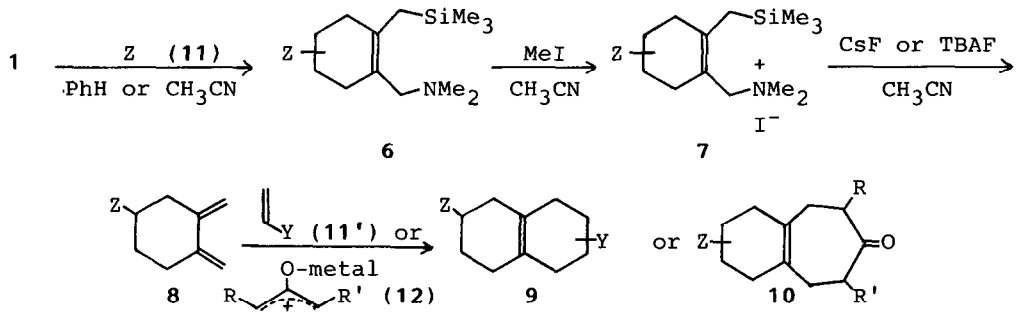
The requisite 1,3-diene **1**[5] can be prepared conveniently by the nickel-catalyzed cross-coupling reaction[6] of (2-bromo-2-propenyl)trimethylsilane (**2**)[7] and the Grignard reagent **4** from (2-bromo-2-propenyl)dimethylamine (**3**). (eq. 1) Similarly, combination of the bromide **3** and the Grignard reagent **5** from **2** is



(1)

considered to be another favorable access to **1**.

Tandem cycloaddition reactions of **1** provide a novel and interesting route to [6.6] and [6.7] ring systems, the whole sequences being shown below.



Preparation of octalines **9** can be attained readily in a stepwise manner, the products **6**-**9** being isolated cleanly at any step. Indeed **1** reveals high reactivity toward a variety of dienophiles (**11**) bearing electron-withdrawing groups to give efficiently the corresponding stable cycloadducts **6** as a regioisomeric mixture in good yield. The structure of **6** involving an allylsilane moiety is clear from complete spectral analyses. After the cycloadducts **6** are quaternized with methyl iodide, treatment of a system containing ammonium salts **7** that are also isolable, with cesium fluoride or tetra-n-butylammonium fluoride (TBAF) even at temperature lower than 25 °C provides smoothly 1,2-dimethylenecyclohexanes **8** by the conjugate 1,4-elimination.[8] **8**, otherwise hard to prepare, can be either isolated cleanly or, without isolation, trapped conveniently with second dienophiles (**11'**) to afford octalines **9** in excellent yield. The results are illustrated in Table I.

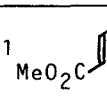
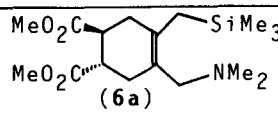
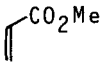
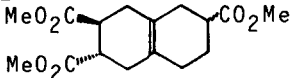
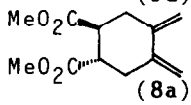
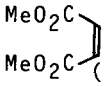
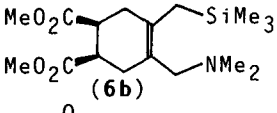
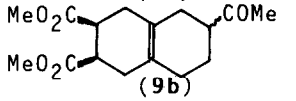
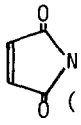
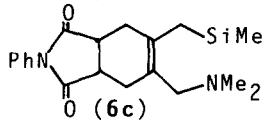
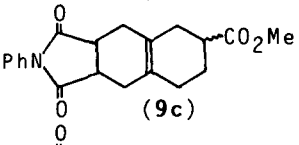
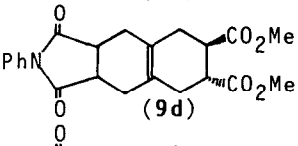
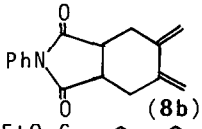
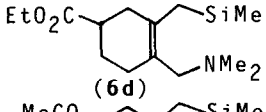
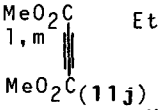
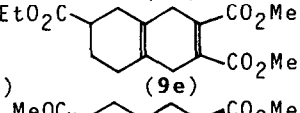
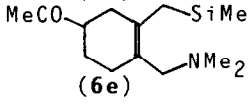
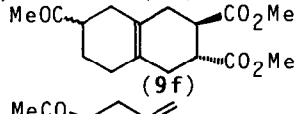
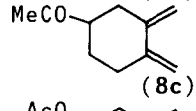
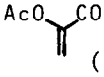
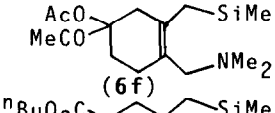
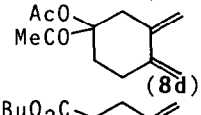
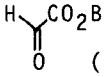
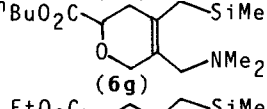
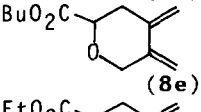
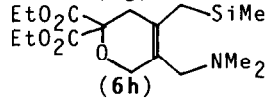
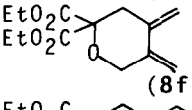
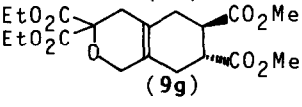
It should be pointed out that 1,2-dimethylenecyclohexanes **8** are expedient reagents for the cycloaddition reactions as highly reactive dienes, presumably due to the rigid s-cis structure. In fact, tetracyclic derivatives **9h** and **9i** that may be important key intermediates for synthesis of anthracycline antibiotics, are obtained by the tandem Diels-Alder reaction of **1** and methyl vinyl ketone (**11e**) or methyl α-acetoxyvinyl ketone (**11f**) as the first dienophile and naphthoquinone (**11k**) as the second one, although **11k** does not work sufficiently as the first one. (eq. 2) Moreover the [3 + 4] cycloaddition of **8** and 2-oxyallyl cations **12**[9] proceeds very smoothly to give the corresponding [6.7] ring compounds **10**. (eq. 3 and 4)

Reactions of **1** with heterodienophiles **11g** and **11h** are also observed to afford the cycloadducts **6g** and **6h** in 90 and 73% yield, which are similarly converted to 1,2-dimethylene-4-oxocyclohexanes **8e** and **8f** quantitatively by treatment with fluoride ion after quaternization. Cycloaddition of **8f**, in situ generated from **6h**, to dimethyl fumarate (**11a**) affords the corresponding bicyclic compound **9g** in 76% yield.

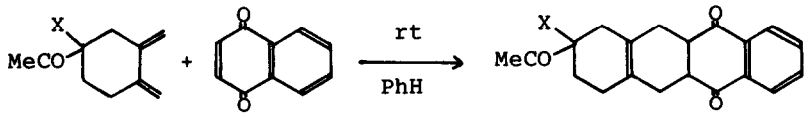
It is noteworthy to state that **6**-**9** can be prepared by the "one pot" operation without isolation of each product during all sequences. Apparently the overall yields are improved considerably rather than those in the stepwise manner. In this case acetonitrile is utilized conveniently as a solvent in the reactions.

The present reaction in which **1** is regarded as a novel 2,2'-biallyl

Table I. Tandem Diels-Alder Reactions of 1

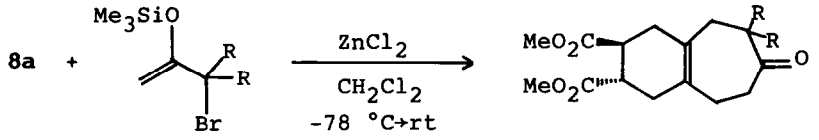
Entry	First Dienophile	Product (6)[a,b] (% Yield)	Second Dienophile	Product (8) or (9)[b,c,d] (% Yield)
1	 (11a)	 (6a) (86)	 (11i)	 (9a) (85)[e,f]
2	11a			 (8a) (75)[g] (80)[g,h] (97)[i]
3	 (11b)	 (6b) (71)	11e	 (9b) (66)[e,j]
4	 (11c)	 (6c) (85)	11i	 (9c) (66)[e,k]
5	11c		11a	 (9d) (74)[g]
6	11c			 (8b) (63)[g]
7	 (11d)	 (6d) (74)[l,m]	 (11j)	 (9e) (91)
8	 (11e)	 (6e) (82)[l,n]	11a	 (9f) (80)[e,o]
9	11e			 (8c) (73)[g]
10	 (11f)	 (6f) (70)[o]		 (8d) (82)
11	 (11g)	 (6g) (90)[l,p]		 (8e) (94)
12	O=C(CO$_2$Et)$_2$ (11h)	 (6h) (73)[l,q]		 (8f) (91)
13			11a	 (9g) (76)

a) Reactions were conducted in PhH or CH_3CN at room or reflux temperature. b) Products were usually purified and isolated by TLC. c) **6** was treated with MeI and then CsF. d) Conversion of **6** to **9** was conducted in CH_3CN without isolation of **7** and **8**, otherwise noted. e) A stereoisomeric mixture. f) 1.1 : 1. g) The final product was obtained by "one pot" operation through all sequences. h) TBAF was used. i) The ammonium salt **7** and CsF were used for desilylation. j) 1.4 : 1. k) 3.7 : 1. l) A regioisomeric mixture. m) 2.4 : 1. n) 2.7 : 1. o) 1.2 : 1. p) 3.7 :1. q) 3.1 :1.



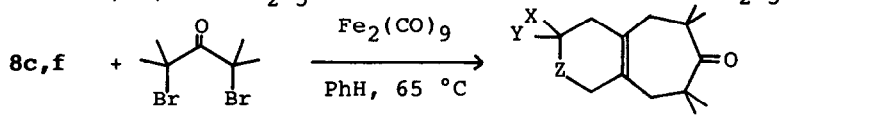
8c, X = H **11k** **9h**, X = H, 85 %
d, X = OAc **i**, X = OAc, 80 %

(2)



13a, R = Me **10a**, R = Me, 96 %
b, R,R = $(CH_2)_5$ **b**, R,R = $(CH_2)_5$, 66 %

(3)



10c, X=H; Y=COMe; Z=CH_2, 71 %
d, X=Y=CO_2Et; Z=O, 47 %

(4)

synthon constitutes a convenient and interesting entry to [6.6] and [6.7] ring systems which are important intermediates to a variety of cyclic naturally occurring products. Octalines **9** may be further converted to [5.7] ring compounds such as perhydroazulenones.[10]

Acknowledgment: We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

References and Notes

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