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2-TRIMETHYLSILYLETHYL-1,3-BUTADIENE AS A SYNTHETIC EQUIVALENT OF PARENT CROSS-CONJUGATED HEXATRIENE, 3-METHYLENE-1,4-PENTADIENE[1]

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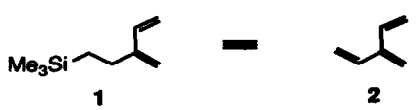
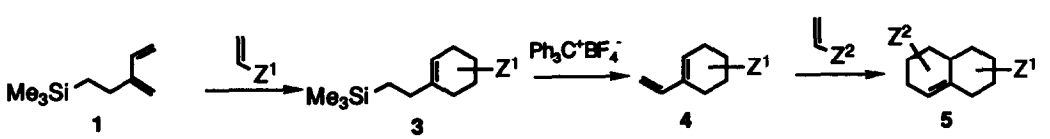
Summary: 2-Trimethylsilylethyl-1,3-butadiene, readily prepared by the cross-coupling reaction of the Grignard reagent of 3-bromo-3-butenyltrimethylsilane with vinyl bromide catalyzed by a nickel-phosphine complex, works as a synthetic equivalent to 3-methylene-1,4-pentadiene (parent [3]dendralene) by the consecutive Diels-Alder reactions.

Much attention has been recently directed to consecutive cycloaddition which may be one of the most useful and convenient route to linear and nonlinear polycyclic hydrocarbons,[2] important biologically active materials.[3] Recently we have reported that 2-aminomethyl-3-silylmethyl-1,3-butadiene reacts with two dienophiles *via* consecutive cycloaddition-1,4-elimination-cycloaddition, giving octahydronaphthalenes and related linear polycycles of the structures in which 2,3,6,7-substitution pattern is substantially involved, and that this works as synthetic equivalents of 2,2'-biallyl diradical and zwitterion.[4] In an extension of the study on the synthetic application of organosilicon compounds to organic synthesis,[5] we now report that 2-trimethylsilylethyl-1,3-butadiene (**1**), the title compound, is a synthetic equivalent to parent cross-conjugated hexatriene (**2**, [3]dendralene), unstable and otherwise inaccessible,[6] by the consecutive cycloaddition-1,2-elimination-cycloaddition (Scheme 1). This reagent works as an active 1,3-diene, affording the corresponding octahydronaphthalenes (**5**) of the structures, in which the eventual "elbow bend" is implicit in the 3,4,6,7-substitution pattern.





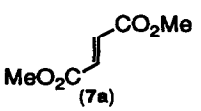
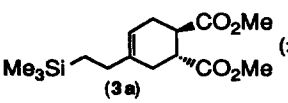
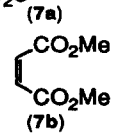
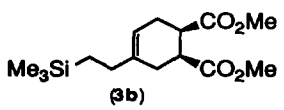
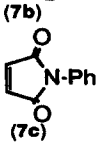
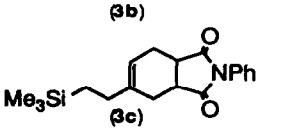
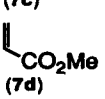
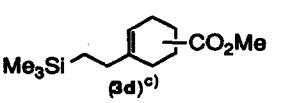
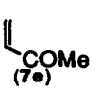
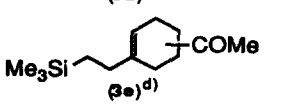
Scheme 1

The title compound (1) can be readily prepared starting from chloromethyltrimethylsilane and 2,3-dibromopropene by two steps. 3-Bromo-3-butenyltrimethylsilane (2), prepared by the coupling reaction of trimethylsilylmethylmagnesium chloride (6) with 2,3-dibromo-2-propene in excellent yield, reacted with vinyl bromide by the Grignard cross-coupling reaction catalyzed by dichloro[1,3-bis(diphenylphosphino)propane]nickel [Ni(dppp)Cl_2][7] to give the desired 1 in overall 78% yield (Scheme 2).[8]

Scheme 2

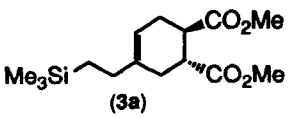
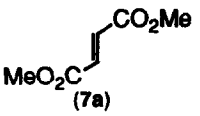
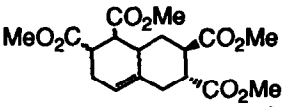
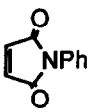
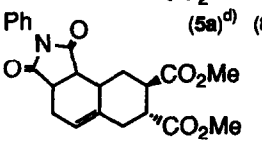
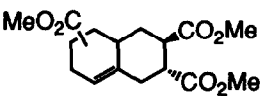
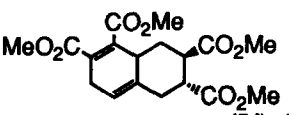
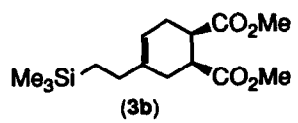
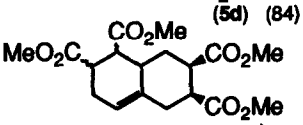
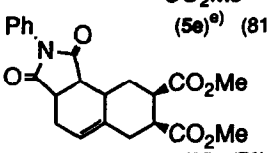
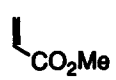
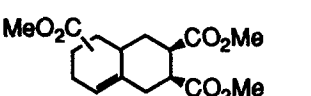
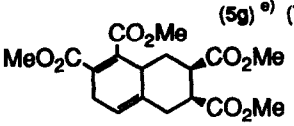
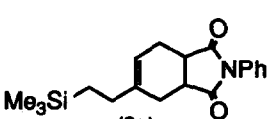
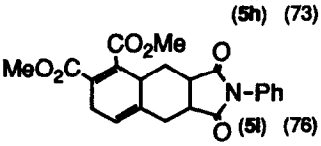
The 1,3-diene (1), thus obtained, reacted smoothly with various dienophiles (7) such as dimethyl fumarate (7a), dimethyl maleate (7b), N-phenylmaleimide (7c), methyl acrylate (7d), and methyl vinyl ketone (7e) in a neat condition at 130°C or in toluene at reflux to afford the corresponding cycloadduct (3) in high yield (Table 1). The reaction with dimethyl fumarate and dimethyl maleate proceeded in a stereospecific mode. In the case of unsymmetrical dienophiles such as methyl acrylate, a mixture of regioisomers (1,3- and 1,4-substitutions) was obtained in a ratio of 27 : 73, almost similarly to the results with isoprene.[9] In these cases, the effect of the TMS group was not sufficiently large, in contrast to isoprenylsilane (2-trimetylsilylmethyl-1,3-buta-diene), in which a considerably efficient regio-control due to σ,π-conjugation[10] was realized.[5]

Table 1. Cycloaddition of 1

Entry	Dienophile[a]	Products (3) (yield / %)[b]
1	 (7a)	 (3a) (>99)
2	 (7b)	 (3b) (85)
3	 (7c)	 (3c) (82)
4	 (7d)	 (3d)[c] (85)
5	 (7e)	 (3e)[d] (81)

a) All reactions were carried out in a sealed tube at 130 °C for 24 h. b) Yield after isolation by TLC. c) Meta: para=27:73 by NMR determination. d) The isomer ratio was not determined.

Table 2. Consecutive 1,2-Elimination and Cycloaddition of 3

Entry	Cycloadduct (3)[a]	Dienophile (7)[b]	Products (5) (yield / %)[c]
1	 (3a)	 (7a)	 (5a)[d] (81)
2	3a	 (7c)	 (5b) (75)
3	3a	 (7d)	 (5c)[e] (80)
4	3a	$MeO_2C-C\equiv C-CO_2Me$ (7f)	 (5d) (84)
5	 (3b)	7a	 (5e)[e] (81)
6	3b	7c	 (5f) (79)
7	3b	 (7d)	 (5g)[e] (71)
8	3b	7f	 (5h) (73)
9	 (3c)	7f	 (5i) (76)

a) A solution of $Ph_3C^+BF_4^-$ (1eq) in acetonitrile (3mL) was used . The reaction was carried out at room temperature for 5 h. b) The diene (4), obtained by treatment of 3 with $Ph_3C^+BF_4^-$, was used to the next cycloaddition reaction without further purification. The reaction was carried out in toluene at reflux for 36 h. c) Overall yield from the first adduct (3) after isolation by TLC. d) A ca.2:1 mixture of stereoisomers. e) The ratios of regio- and/or stereoisomers were not determined.

When the reaction of **3** with triphenylmethyl tetrafluoroborate ($Ph_3C^+BF_4^-$) was carried out in CH_3CN with stirring at room temperature, the yellow color of the solution gradually faded into colorless and it was found that vinylcyclohexene derivative (**4**) was formed. After the disappearance of **3** was confirmed by GLC, **4** was isolated by TLC from the reaction mixture. Apparently hydride abstraction took place selectively and efficiently at the β-position of the TMS group of the first cycloadduct (**3**), giving to a β-silyl carbocation which was stabilized due to σ,π-conjugation.[10] Vinylcyclohexenes (**4**), thus obtained, were allowed to react with a second dienophile to afford [6.6]-membered ring products (**5**) in high yield whose substituent pattern differed much from that of the products derived from 2,2'-biallyl diradiacal synthon, previously reported.[4] More conveniently, *in situ* generated **4**, without isolation, was subjected to react with a second dienophile, after the solvent was changed from CH_3CN to toluene (Scheme 1, Table 2). With dimethyl acetylenedicarboxylate (**7f**), non-aromatized cycloadducts were obtained conveniently.

The synthetic utility of the present reagent is shown by the readily available starting material, easy manipulation of the conversion, mild reaction conditions, and a new access to the nonlinear "elbow bend" in the ring system. Although the present consecutive Diels-Alder procedure proceeds in modest overall yield, this methodology provides valuable synthetic intermediates which are essentially otherwise inaccessible. The elaboration of these intermediates and the exploration of other strategies for the preparation of nonlinear polycyclic hydrocarbons are the subjects of further study.

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References and Notes

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8. Bp. 67°C (30 mmHg). ^1H NMR ($CDCl_3$, 60 MHz) δ 0.00 (s, 6H), 0.70 (m, 2H), 2.20 (m, 2H), 5.03 (m, 2H), 5.11 (bs, 1H), 5.29 (bs, 1H), 6.39 (dd, J=10.7, 17.6Hz, 1H); IR (CCl_4) ν_{max} 3095, 3045, 3010, 1595, 1250 cm^{-1}; MS m/z 154 (M^+, 10), 139 (19), 124 (5), 111 (8), 73 (100).
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