HIGHLY REGIOSELECTIVE DIELS-ALDER REACTIONS OF
2-TRIMETHYLSILYLMETHYL- AND 2-TRIMETHYLSTANNYLMETHYL-1,3-BUTADIENE[1]

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Summary: 2-Trimethylsilylmethyl and 2-trimethylstannylmethyl-1,3-butadiene undergo facile cycloaddition with dienophiles, and show high regioselectivity with unsymmetrical dienophiles.

We have recently reported that 2-trimethylsilylmethyl-1,3-butadiene (1b) is a useful reagent for the isoprenylation,[2] where the reaction of (1b) proceeds as a substituted allylsilane.[3] We report here that (1b) and the corresponding stannane (1c)[4] are good dienes for the Diels-Alder reaction with various reactive dienophiles.

The thermal reaction of 2-trimethylsilylmethyl-1,3-butadiene (1b) and 2-trimethylstannylmethyl-1,3-butadiene (1c) with symmetrical dienophiles proceeds smoothly with a stereospecific mode to afford pure cycloadducts. (eq. 1)
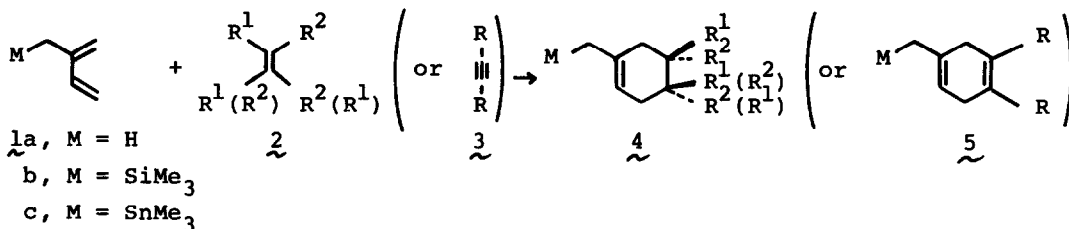
The stereospecificity of the present reaction as a Diels-Alder reaction[5] may be demonstrated by the stereochemical outcomes in the reactions of 1b with dimethyl maleate and with dimethyl fumarate, in which only one respective stereoisomer was obtained from each isomeric ester. The results are summerized in Table 1. The diene 1b is considerably more reactive than its 1-substituted isomer (1d). (entry 6)

The reaction of 1 with unsymmetrical dienophiles, as listed in Table 2, is of special interest in relation to the regioselectivity in the reaction.
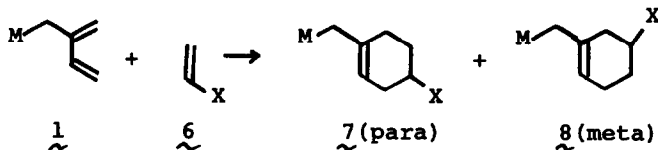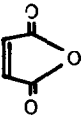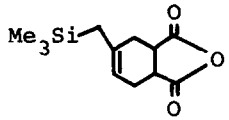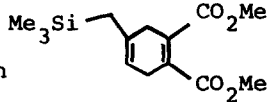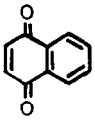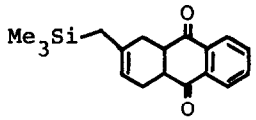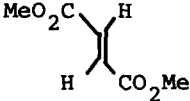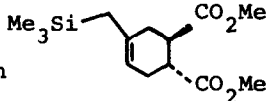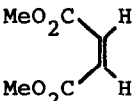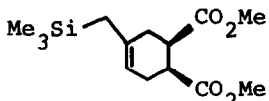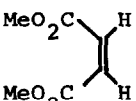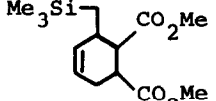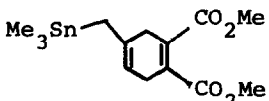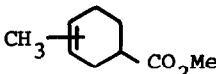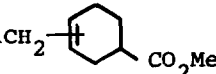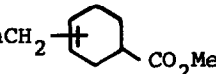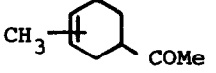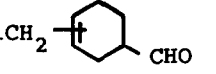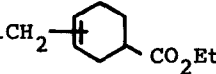
Table 1.   Diels-Alder reactions of trimethylsilylmethyl and trimethyl-
stannylmethyl-substituted dienes with symmetrical dienophiles.

Entry	1,3-Diene	Dienophile	Condition	Adduct(% yield)[a]
1	1b	(maleic anhydride)	Et$_2$O rt, 20 h	Me$_3$Si-adduct (100)
2	1b	MeO$_2$CC≡CCO$_2$Me	CH$_2$Cl$_2$ reflux, 16.5 h	Me$_3$Si-adduct, CO$_2$Me / CO$_2$Me (96)
3	1b	(1,4-naphthoquinone)	Benzene reflux, 17 h	Me$_3$Si-adduct (88)
4	1b	MeO$_2$C\H / H\CO$_2$Me	Benzene reflux, 108.5 h	Me$_3$Si-adduct, CO$_2$Me / CO$_2$Me (79)
5	1b	MeO$_2$C\H / MeO$_2$C\H	Xylene 180°, 64.5 h	Me$_3$Si-adduct, CO$_2$Me / CO$_2$Me (79)
6	Me$_3$Si (1d)	MeO$_2$C\H / MeO$_2$C\H	Xylene 180°, 122h	Me$_3$Si-adduct, CO$_2$Me / CO$_2$Me (42)
7	1c	MeO$_2$CC≡CCO$_2$Me	CH$_2$Cl$_2$ reflux, 15 h	Me$_3$Sn-adduct, CO$_2$Me / CO$_2$Me (94)

[a] Yields after isolation by TLC or GLC.

It is very interesting to note that higher para/meta ratios are observed
for both 1b and 1c than for isoprene.[6] The Diels-Alder reaction of isoprene with
an unsymmetrical dienophile with an electron-withdrawing group gave predominantly
a para isomer, the para/meta ratio being around 70/30 at 120°C. Since it has
been found that the ratio does not change in the temperature range from 25°C to
200°C,[6a,b] we can compare the data with those of 1b and 1c. With methyl acrylate,
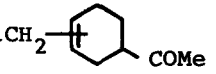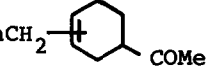the ratio increases to 84/16 for 1b and to 91/9 for 1c. Almost the same trend
can be observed for methyl vinyl ketone. Based on the HOMO-LUMO interaction in
the Diels-Alder reaction,[7] the result can be explained in terms of the extensive
σ(M-C)-π conjugation for 1b and 1c that raises the HOMO of the dienes with

Table 2.   Regioselectivity in the Diels-Alder reaction of 1,3-dienes
            with unsymmetrical dienophiles

Entry	1,3-Diene	Dienophile	Reaction Condition[a] time/h (Temp/°C)	Product(% yield)[b]	Ratio of Para:meta[c]
1	1a	$CH_2=CHCO_2Me$	46 (80) / 6 (120)[d,e]	CH_3—⬡—CO_2Me (11) (83)	70 : 30
2	1b	$CH_2=CHCO_2Me$	46 (80)	Me_3SiCH_2—⬡—CO_2Me (58)	84 : 16
3	1c	$CH_2=CHCO_2Me$	39 (80)	Me_3SnCH_2—⬡—CO_2Me (73)	91 : 9
4[f]	1a	$CH_2=CHCOMe$	15 (120)[e]	CH_3—⬡—$COMe$	71 : 29
5	1b	$CH_2=CHCOMe$	36 (80)	Me_3SiCH_2—⬡—$COMe$ (83)	83 : 17
6	1c	$CH_2=CHCOMe$	69 (80)	Me_3SnCH_2—⬡—$COMe$ (94)	92 : 8
7	1b	$CH_2=CHCHO$	34 (80)	Me_3SiCH_2—⬡—CHO (69)	97 : 3
8	1b	$CH_2=CHCO_2Et$	46 (80)	Me_3SiCH_2—⬡—CO_2Et (63)	82 : 18

[a] Reactions were carried out in benzene, unless otherwise stated. [b] Yield after isolation by TLC. [c] Determined by GLC. [d] ref. 6b. [e] in toluene. [f] Ref. 6c.

increasing coefficients of atomic orbitals at the 1-position of the HOMO. Higher para/meta ratio of 1c is thus reasonable because of the stronger σ-π conjugation effect exerted by the Sn-C than by the Si-C bond.[8]

Finally, cycloadducts of the reaction themselves are functionalized allyl-silanes so that the regiospecific introduction of proton or other electrophiles can be anticipated,[3] as indeed it is the case as follows.

All new compounds obtained in this work gave correct elemental analyses and satisfactory spectral data.
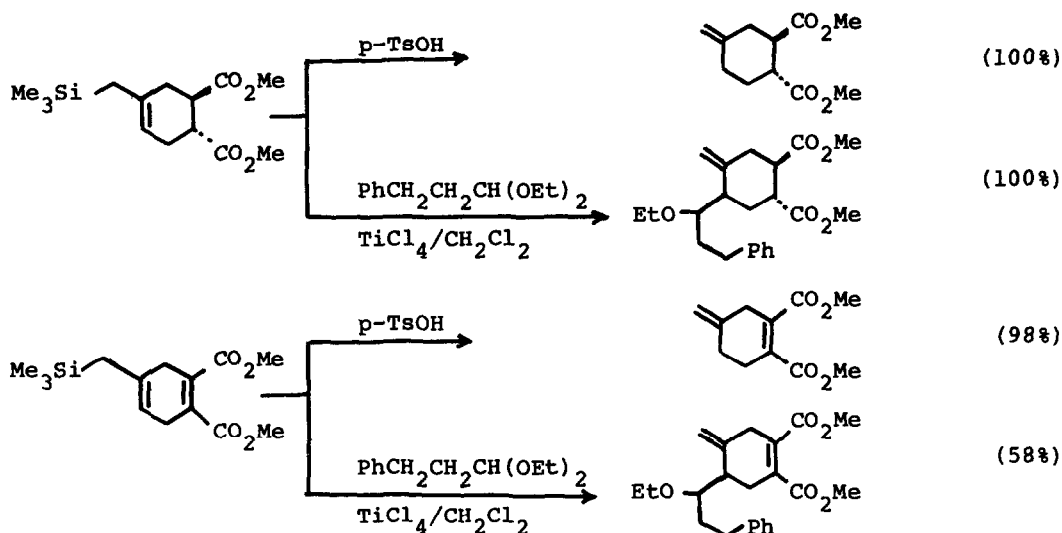
References and Notes

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3. A. Hosomi, H. Hashimoto, H. Kobayashi, and H. Sakurai, Chem. Lett., 245 (1979), and references cited therein.

4. 2-Trimethylstannylmethyl-1,3-butadiene ($\underset{\sim}{1}$c) was prepared from the Grignard reagent of chloromethyltrimethylstannane (8.53 g, 0.04 mol) and chloroprene (5.31 g, 0.06 mol) in the presence of a catalytic amount of dichlorobis(diphenylphosphino)propanenickel (II) (87 mg, 0.16 mmol) by the procedure employed for the preparation of the corresponding silyl derivative $\underset{\sim}{1}$b.[2] An oil; 7.0 g (0.03 mol, 75 % yield); bp 77-78°C/40 mmHg. NMR (CCl$_4$) δ 0.07 (9H, s), 1.89 (2H, d, J = 1.0 Hz), 4.65-5.20 (4H, m), 6.33 (1H, dd, J = 10.0 and 17.4 Hz); ν_{max} (neat) 3080, 1625, 1590, 985, 960, 900 cm^{-1}; λ_{max} (hexane) 239.5 nm (ε = 1.0 x 10^4)

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