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CYCLOADDITION REACTIONS OF 2-TRIBUTYLSTANNYL-1,3-BUTADIENE

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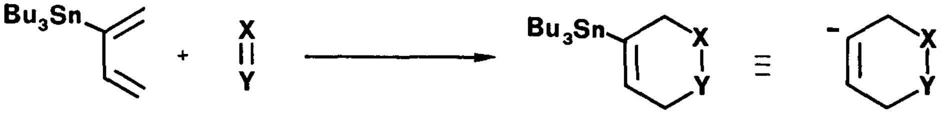
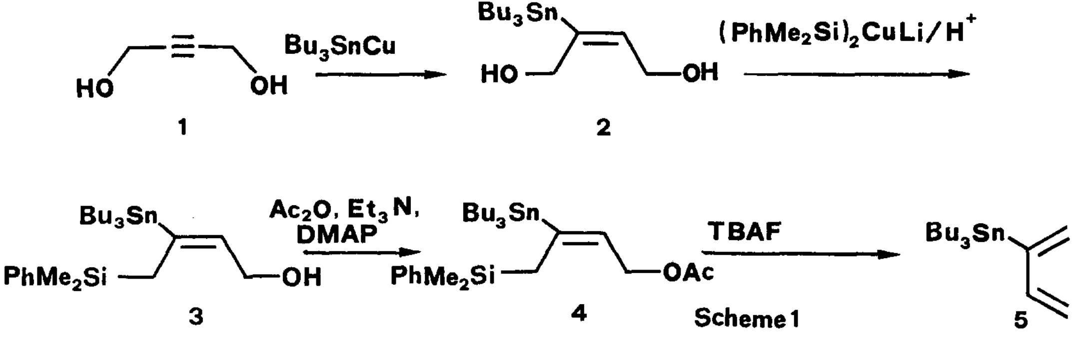
Summary. An extensive study on the reactivity of 2-tributylstannyl-1,3-butadiene with dienophiles is reported. The presence of a Lewis acid seems to be crucial in the regiochemical control of the cycloaddition. One example of further functionalisation of the adduct through its C-Sn bond is also reported.

In the big family of heterosubstituted dienes employed in Diels Alder reactions[1], little attention has been devoted to organostannyl derivatives[2]. For example ,since its first preparation by Aufdermarch[3], 2-stannylbutadiene has been sparely used in synthesis and his efficacy as diene in Diels Alder reactions has never been properly investigated[4].
In relation with a recent report of a simple synthesis of 2-tributylstannyl-1,3-butadiene **5** [5], we decided to study its reactivity with activated dienophiles. The goal was to realise a simple method for a regiocontrolled preparation of differently substituted stannylcyclohexenes from which cyclohexene-anions could be generated by tin-lithium exchange, and thus we now report our first promising results of this study.

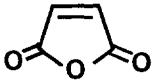
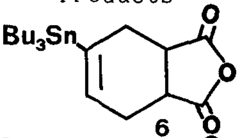
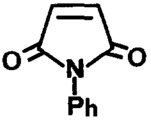
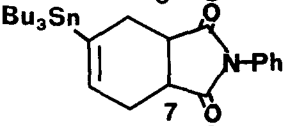
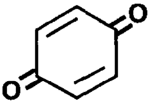
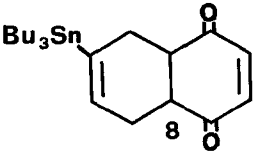
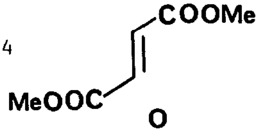
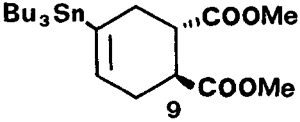
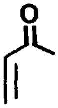
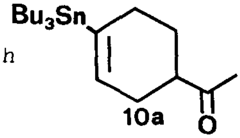
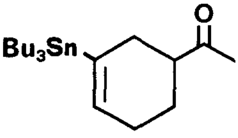
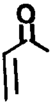
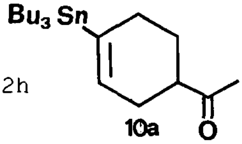
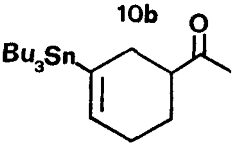
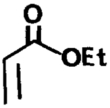
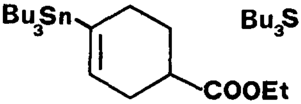
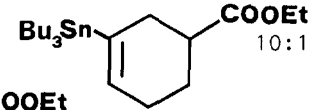
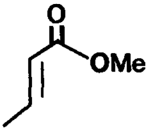
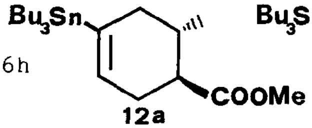
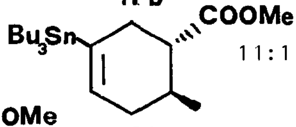
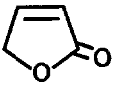
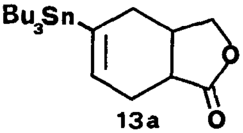
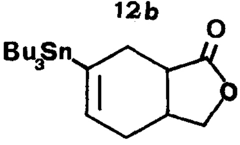


2-Tributylstannyl-1,3-butadiene **5** could be easily prepared in appreciable yields (65 % overall) from 2-butyn-1,4-diol **1** as reported in Scheme 1[5].



Scheme 1

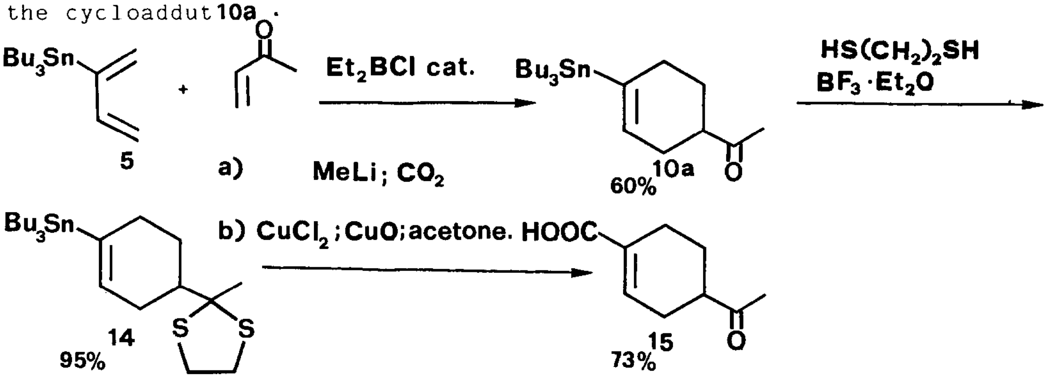
Table 1. Reaction of **5** with dienophiles.

Entry	Dienophile	Conditions[a]	Products[b]	a : b ratio	% Yields
1		C_6H_6,reflux,2h	 **6**		75
2		neat,100°C,3h	 **7**		80
3		neat,110°C,3h	 **8**		67
4		neat,100°C,8h	 **9**		69
5		C_6H_6,reflux,12h	 **10a**  **10b**	3:1	50
6		Et_2BCl 10%, $C_2H_4Cl_2$,r.t.,12h	 **10a**  **10b**	18:1	69
7		Et_2AlCl 15%, CH_2Cl_2,r.t.10h	 **11 a**  **11 b**	10:1	72
8		Et_2BCl 10%, $C_2H_4Cl_2$,r.t.,36h	 **12a**  **12b**	11:1	60
9		Et_2BCl 20%, $C_2H_4Cl_2$, reflux ,6h.	 **13a**  **13 b**	9:1	33

a) All the reactions' conducted with a diene:dienophile ratio of 1-1.2:1 .

b) Ratio of regioisomers determined by GLC and ^1H NMR analyses.All products were isolated by PTLC or flash chromatography and fully characterized.

Cycloadditions of **5** with common dienophiles are summarised in Table 1. Pure adducts of symmetrical dienophiles (Entries 1-4 in Table 1) were readily obtainable by termic reactions in sealed tubes at 110-125°C without solvent. As predictable on the ground of the previously observed behaviour of 2-silylbutadienes[7-8], the stannyl mojety exhibits only weak directing effects in reactions of **5** with unsymmetrical olefins (Entry 5 in Table 1). Regioselectivity and yields are increased in presence of Lewis acids[9]. We tested the reaction between **5** and methylvinylketone with different Diels Alder catalysts to find the better conditions of cycloaddition, and results are reported in Table 2. Higher yields were obtained with weak acids but generally the regioselectivity was low.Strongest acids gave better selectivity but yields were depressed by polymerisation of the reagents. The best compromise seems to be use of 10-20 % of Et_2AlCl or Et_2BCl in chlorinated solvents, and this conditions were succesfully employed with all the other dienophiles investigated (Entries 6-9 in Table 1).
The big potentiality of 2-tributylstannyl-1,3-butadiene (**5**) in synthesis is illustrated by the following example which reports the preparation of the limonene analogous[11] **15** [12] through the functionalisation of the C-Sn bond of the cycloaddut**10a** .



References and notes

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3. G.Aufdermarch, J.Org.Chem., 28, 1994, (1964).
4. To our knoledge the only reports of 2-stannyl-1,3-butadienes doesn't concern cycloaddition reactions.See for example : J.C. Cochron, A.J.Lensink, J.G.Noltes, Organometallics, 2, 1099, (1983). H.J.Reich, K.E.Yelm, I.L.Reich, J.Org.Chem., 49, 3438, (1984).
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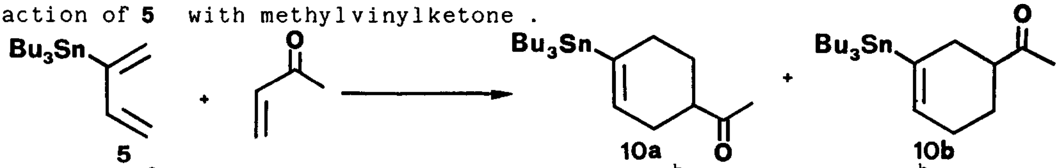
Table 2. Study on the effect of Lewis acids on the regioselectivity of the reaction of **5** with methylvinylketone .



Lewis acid[a]	Conditions	% Yield[b]	10a :10bratio[b]
$TiCl_4$	CH_2Cl_2, from -78°C to 0°C	31	40 : 1
$ZnBr_2$	CH_2Cl_2, from -78°C to r.t.	30	30 : 1
$BF_3.Et_2O$	CH_2Cl_2, from 0°C to r.t.	40	35 : 1
Et_2AlCl	CH_2Cl_2/hexane r.t.	75	16 : 1
Et_2BCl	$C_2H_4Cl_2$,r.t.	69	18 : 1
Me_2SnCl_2	$CHCl_3$, reflux	60	3 : 1
$Rh(PPh_3)Cl_2$	Toluene,reflux	55	15 : 1

a)Lewis acids employed in 10-30 % molar. b) Yields of isolated products. c)After isolation of pure isomers**10a** and**10b** by PTLC (el. Hexane/Et.Ac 5/1) and attribution of the structures by ^1H NMR[10], ratios were determined by CLG analyses of the crude.

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8. I.Fleming, A.Percival J.C.S.Chem.Comm., 278, (1978).

9. P.Lazlo, J.Lucchetti L'actualite' Chimie, Oct.1984, 42.

10. **10a** $\delta(CDCl_3)$: 0.9-1.7 (29H, m, Bu_3Sn and CH_2), 2.1 (2H, m, CH_2-CSn), 2.2 (3H, s, CH_3), 2.3 (2H, m,CH_2-CHCO, broad doublet after irradiation at 5.9 ppm), 2.5 (1H, m, CHCO), 5.9 (1H, m, CH=).
ν_{max} (film) 1750 (CO) , 1645 (C=C)cm^{-1}. m/z , 376 (M^+),165 (base).
10b $\delta(CDCl_3)$: 0.9-1.7 (29H, m, Bu_3Sn and CH_2), 2.1 (3H, s, CH_3), 2.2 (2H, m, CH_2CH=, triplet like signal after irradiation at 5.8 ppm), 2.4 (3H, m, CH_2CSn and CHCO), 5.8 (1H, m, CH=).
ν_{max} (film) 1750 (CO) , 1635 (C=C) cm^{-1}. m/z ,376 (M^+), 165 (base).

11. T.Mandai, Y.Horayuki, M.Toshio, F.Harno, K.Hiroshi, M.Kowada, J.Otera Chem.Lett., 1057, (1980).

12. **15** $\delta(CDCl_3/DMSO-d_6)$: 2.20 (3H, s, CH_3), 1.8-2.6 (7H, m,), 6.9 (1H, m, CH=), 9.9 (1H, b, OH).
ν_{max} ($CHCl_3$) 3200-2900 (OH), 1740 (CO), 1690 (CO), 1635 (C=C)cm^{-1}.
m/z 168 (M^+), 69 (base).

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