Palladium-catalysed Dimerization–Double Stannation of 1,3-Dienes using Hexamethyldistannane

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Hexamethyldistannane **1a** reacts with 1,3-dienes **2** highly regio- and stereo-selectively in the presence of a catalytic amount of bis(dibenzylideneacetone)palladium to afford dimerization–double-stannation adducts **3** in high yields.

The activation of σ-bonds between group 14 atoms such as Si–Si, Si–Sn, Sn–Sn and Ge–Ge by transition metal catalysts and subsequent insertions of unsaturated compounds (alkynes, dienes, alkenes) are of current interest.[1] We have recently published details of the 1,4-silylstannation of 1,3-dienes using organosilylstannane ($R_3SiSnR^1{}_3$) in the presence of a platinum catalyst.[2] Here, we report the palladium-catalysed regio- and stereo-selective dimerization–double-stannation of 1,3-dienes using hexamethyldistannane **1a**. In the presence of a palladium catalyst, **1a** has been utilized in

Table 1 Dimerization–double stannation of 1,3-dienes using hexamethyldistannane[a]

Entry	Diene	Product	Time/h	*T*/°C	Yield (%)[b]
1	**2a**	**3a**	<0.05	0	89 (78)
2	**2a**	**3a**	<0.05	−30	85
3	**2b**	**3b**	5	Room temp.	75 (62)
4[c]	**2b**	**3b**	17	Room temp.	0
5[d]	**2b**	**3b**	27	Room temp.	13
6[e]	**2b**	**3b**	20	Room temp.	5
7	**2c**	**3c**	4	50	(40)

[a] **1a** (0.50 mmol), **2** (2.0 mmol), $Pd(dba)_2$ (0.025 mmol), toluene or benzene (2.0 ml). [b] By GLC. The numbers in parentheses show isolated yields by Kugelrohr distillation. [c] $Pd(PPh_3)_4$ (0.025 mmol) as catalyst precursor. [d] $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ (0.025 mmol) as catalyst precursor. [e] $PdCl_2(PhCN)_2$ (0.025 mmol) as catalyst precursor.

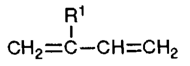
double stannation of alkynes.[3] However, there has been no precedent for the reaction of organodistannanes **1** with 1,3-dienes.

The results are listed in Table 1. The reaction of **1a** with 4 equiv. of buta-1,3-diene **2a** in the presence of a catalytic amount (5 mol% based on **1a**) of $Pd(dba)_2$ (dba = dibenzylideneacetone) in toluene at 0 °C affords a single dimerization–double-stannation product (**3a**; *E,E*-1,4 adduct)[†] exclusively, in high yield (entry 1). The reaction is almost instantaneous even at −30 °C (entry 2). The dimerization–double-stannation products **3** in the present study are all new compounds, which possess two versatile allylic stannane functionalities.[4] The reaction is not limited to **2a**. Isoprene **2b** also reacts with **1a** to give **3b** in high yield (entry 3). The reaction proceeds with high regio- and stereo-selectivities (head to head; *E,E*-1,4 adduct), and no other isomers are detected by GLC or ^{13}C NMR.

The nature of the catalyst precursor affects the reaction highly, $Pd(dba)_2$, naked Pd^0 complex, was found to be the most effective precursor. Other palladium complexes such as $Pd(PPh_3)_4$,[‡] $Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ and $PdCl_2(PhCN)_2$ (entries 4–6) as well as $Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2$ and $Pd(dba)_2$ + $4PBu_3$ showed no or only low catalytic activity.

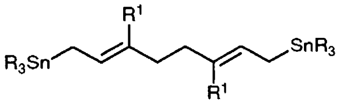
R_3SnSnR_3

1a; R = Me
b; R = Bu

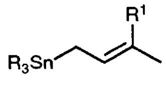


$CH_2{=}\overset{R^1}{\overset{|}{C}}{-}CH{=}CH_2$

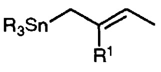
2a; R^1 = H
b; R^1 = Me
c; R^1 = $OSiMe_3$



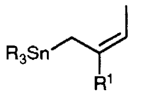
3a; R = Me, R^1 = H
b; R = Me, R^1 = Me
c; R = Me, R^1 = $OSiMe_3$



4 ; R = Bu, R^1 = H
5a; R = Bu, R^1 = Me



5b; R = Bu, R^1 = Me



6; R = Bu, R^1 = H
7; R = Bu, R^1 = Me

In the reaction, Me_3SiO-functionality on diene is tolerated. Thus, a highly regio- and stereo-selective reaction also proceeds with **2c** to give **3c** as a single isomer (entry 7), where the stereochemistry has been confirmed unambiguously by NOE difference spectrum.[†] However, with other 1,3-dienes such as penta-1,3-diene, 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene, no reactions occur and **1a** remains intact. 2-Phenylbuta-1,3-diene did not afford **3**; the steric effect seems to affect the reaction significantly.

Steric bulk of **1** also influences the reaction dramatically. Instead of the dimerization–double stannation, formal hydrostannation of 1,3-diene proceeds, when hexabutyldistannane **1b** is employed in place of **1a** under similar reaction conditions: **1b** (1 equiv.), **2** (4 equiv.), $Pd(dba)_2$ (0.05 equiv.) at room temp. in benzene. Allylic stannanes **4** (in 78% isolated yield, 1.56 equiv.) and **5** (in 78% total isolated yield, 1.55 equiv.; **5a** : **5b** = 7 : 3) are obtained by the reaction of **1b** with **2a** and **2b**, respectively. In both cases the corresponding (*Z*)-isomers **6** and **7** are not detected. The hydrogen source for the products is possibly 1,3-dienes **2**, because no deuterium is incorporated by the reaction in C_6D_6 and the yields based on the distannane **1b** are high. Further studies on the scope and limitation of the present dimerization–double stannation of 1,3-dienes are currently under investigation.

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[†] *Spectroscopic data* **3a**: Kugelrohr distillation 120 °C/0.5 mmHg; colourless liquid; ^1H NMR ($CDCl_3$) δ 0.07 (s, $^2J_{Sn\text{-}H}$ 53, 50 Hz, 18H), 1.67 (d, *J* 8, $^2J_{Sn\text{-}H}$ 58 Hz, 4H), 2.00 (m, 4H), 5.22 (m, 2H), 5.51 (dt, *J* 15, 8 Hz, 2H); ^{13}C NMR δ −10.26 (q, $^1J_{Sn\text{-}C}$ 323, 309 Hz), 16.26 (t, $^1J_{Sn\text{-}C}$ 314, 301 Hz), 33.54 (t), 125.94 (d, $J_{Sn\text{-}C}$ 51 Hz), 128.58 (d, $J_{Sn\text{-}C}$ 48 Hz); MS (CI : isobutane) *m/z* 421 (M^+-CH_3): Anal. Found: C 38.83, H 6.99%, Calc. for $C_{14}H_{30}Sn_2$: C 38.59, H 6.94%.

3c: Kugelrohr distillation 140 °C/0.5 mmHg; colourless liquid; ^1H NMR ($CDCl_3$) δ 0.06 (s, $^2J_{Sn\text{-}H}$ 53, 50 Hz, 18H), 0.18 (s, 18H), 1.56 (d, *J* 9, $^2J_{Sn\text{-}H}$ 57 Hz, 4H), 2.13 (s, 4H), 4.59 (t, 2H); NOE difference spectrum: when the singlet methylene proton resonance at δ 2.13 is irradiated, 15% NOE is observed at the alkene proton resonance at δ 4.59; ^{13}C NMR ($CDCl_3$) δ −9.63 (q, $^1J_{Sn\text{-}C}$ 315, 302 Hz), 0.88 (q), 9.28 (t, $^1J_{Sn=C}$ 327, 313 Hz), 35.09 (t), 105.67 (d, $^2J_{Sn\text{-}C}$ 52 Hz), 147.19 (s, $^3J_{Sn\text{-}C}$ 52 Hz); MS (CI : isobutane) *m/z* 612 (M^+).

[‡] At an earlier stage of the present study the isolation of the products **3** was rather difficult. The catalyst was still active even after complete conversion of **1a**. During the isolation procedure, the products were changed by a small amount of air in the presence of some active catalyst species. As entry 4 suggests, PPh_3 would saturate the active catalyst centre. Therefore, the isolation of **3** is carried out after adding PPh_3 (5 equiv. in toluene) to the resultant reaction mixture under argon flow and deactivating the catalyst. By this work-up procedure, the products are easily isolated without any further changes.

References

1 M. Murakami, P. G. Anderson, M. Suginome and Y. Ito, *J. Am. Chem. Soc.*, 1991, **113**, 3938; T. N. Mitchel, R. Wickenkamp, A. Amamria, R. Dicke and U. Schneider, *J. Org. Chem.*, 1987, **52**, 4868; T. Hayashi, H. Yamashita, T. Sakakura, Y. Uchimaru and M. Tanaka, *Chem. Lett.*, 1991, 245 and references cited therein.
2 Y. Tsuji and Y. Obora, *J. Am. Chem. Soc.*, 1991, **113**, 9368.
3 E. Piers and R. T. Skerlj, *J. Chem. Soc., Chem. Commun.*, 1986, 626; T. N. Mitchel, A. Amamria, H. Killing and D. Rutschow, *J. Organomet. Chem.*, 1983, **241**, C45.
4 M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworth, London, 1987, pp. 185–258.