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HYDROSILYLATION OF 1,4-BIS (TRIMETHYLSILYL)-1,3-BUTADIYNE

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Hydrosilylation of 1,4-bis(trimethylsily)-1,3-butadiyne with platinum and rhodium catalyst proceeded stepwise to give first 2silyl-1,4-bis(trimethylsilyl)-1-buten-3-ynes and then 1,3-disilyl-1,4-bis(trimethylsilyl)-1,2-butadienes in high yields.

Butadiyne is produced as a by-product in the transformation of natural gas to acetylene. In spite of the easily expected versatility, its application to organic synthesis has been limited mainly due to the intrinsically explosive nature. The disilyl derivative, 1,4-bis(trimethylsilyl)-1,3-butadiyne (1), on the other hand, is a stable crystalline compound and may be used as the alternative for the unsaturated C_4 synthetic unit.¹⁾ We studied introduction of functional groups into the triple bond of 1 and report herein hydrosilylation of 1 takes place in a 1,2-cis manner³⁾ initially to give 2-silyl-1,4-bis(trimethylsilyl)-1-buten-3-ynes (2) which after a prolonged reaction time are transformed under 1,4-addition⁴⁾ to 1,3-disilyl-1,4-bis(trimethylsilyl)-1,2-butadienes (3).

Typical hydrosilylation catalysts were employed for various silanes, and the results are summarized in Table 1. Hexachloroplatinic(IV) acid-catalyzed hydrosilylation with triethylsilane gave a doubly silylated product **3a** (run 1) [IR (neat): 1880 cm⁻¹; MS: m/z 426 (M⁺); ¹³C NMR (CDCl₃): δ 15.3, 69.5, 75.1, and 208.7]. Rhodium complex turned out somewhat mild and gave monosilylated product **2a** [IR (neat): 2140 cm⁻¹; MS: m/z 310 (M⁺); ¹³C NMR (CDCl₃) (off-resonance data): δ 103.0 (m, J = 2 Hz), 107.7 (d, ³J_{C-H} = 20 Hz), 142.5 (m, J = 2 Hz), and 157.1 (dm,



f: $R_3Si = Ph_2SiH$

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Run	R ₃ Sih	Catalyst	Conditions	Yield/ 2 an	* ^{b)} of d 3	:
1	Et ₃ SiH	H_2 PtCl ₆	80 °C, 0.5 h	0	100	
2	Et ₃ SiH	RhCl(PPh3)3	90 °C, 0.9 h	45	28	
3	Et ₃ SiH	RhCl(PPh ₃) ₃	90 °C, 5 h	0	83	
4	Et ₃ SiH	$Pt(PPh_3)_4$	90 °C, 2 h	83	6	
5	Et ₃ SiH	Pt(PPh ₃) ₄	90 °C, 18 h	81	18	
6	Et ₃ SiH	$\mathrm{PdCl}_{2}(\mathrm{PPh}_{3})_{2}$	90 °C, 35 h	18	0	
7	Et ₃ SiH	$Pd(PPh_3)_4$	100 °C, 14 h	8	0	
8	iPr ₃ SiH	H_2 PtCl ₆	90 °C, 8 h	92	0	
9	Me ₃ SiH	$H_2^{PtCl}_6$	100 °C, 2 h ^{C)}	40	46	
10	Me ₃ SiH	RhCl(PPh ₃) ₃	100 °C, 19 h	0	95	
11	Me ₃ SiH	RhCl(PPh ₃) ₃	100 °C, 1 h	0	90	
12	Me ₃ SiH	$Pt(PPh_3)_4$	90 °C, 1 h	69	2	
13	Me ₃ SiH	$Pt(PPh_3)_4$	90 °C, 12 h	1	94	
14	$PhMe_2SiH$	H ₂ PtCl ₆	r.t., 1.5 h; 50-60 °C, 1 h ^{C)}	70	10	
15	$PhMe_{2}SiH$	RhCl(PPh ₃) ₃	90 °C, 1 h	27	36	
16	$\mathbf{PhMe}_{2}\mathbf{SiH}$	RhCl(PPh3)3	100 °C, 2 h	0	86	
17	$PhMeSiH_2$	RhCl(PPh ₃) ₃	100 °C, 2 h	30 ^{d)}	e)	
18	${}^{\mathrm{Ph}}2{}^{\mathrm{SiH}}2$	RhCl(PPh ₃) ₃	100 °C, 4 h	49 ^{d)}	e)	

Table 1. Hydrosilylation of 1,4-Bis(trimethylsilyl)butadiyne (1)^{a)}

a) Typically a mixture of 1, hydrosilane (3-4 mol equiv.), and the catalyst (0.2 mol% of $H_2 PtCl_6$ in iPrOH or 0.5 mol% of RhCl(PPh₃)₃ and Pt(PPh₃)₄) was heated under an argon atmosphere.

b) Isolated yields after purification by preparative TLC or medium pressure LC are given. The structure was determined by IR, ¹H and ¹³C NMR, and MS spectrometries as well as elemental analysis.

- c) Disilane formation was remarkable.
- d) Many by-products are produced also.
- e) Not isolated.

J = 138 and 2 Hz)] as the major product in a short reaction period (run 2).⁵⁾ After longer reaction time the allene **3a** grew into the exclusive product (run 3). Platinum(0) complex was proved to be less reactive and gave the monosilylated product **2a** selectively (runs 4 and 5). Palladium catalyst turned out inferior for these transformations. For hydrosilylation with trimethylsilane, the catalyst reactivity order reversed: Pt(PPh₃)₄ and RhCl(PPh₃)₃ induced double silylation, whereas H₂PtCl₆ gave **2** and **3** in roughly equal amounts.



That the hydrosilylation proceeds stepwise was evidenced by the following additional experiments. When the monosilylated product 2a was heated with triethylsilane in the presence of H_2PtCl_6 catalyst, the allene 3a was produced in 99% yield. Two different silyl groups could be introduced by this stepwise procedure. For example, 2d was converted into 4 by hydrosilylation with Et₃SiH in 93% yield.

The striking change in regiochemistry⁶⁾ of the second hydrosilylation may be ascribed to steric factors: when silyl group is introduced at C(3) of 2, this will invoke severe interactions between the trialkylsilyl groups at C(2) and C(1). Thus, 1,4-addition of unprecedent regioselectivity became a favorable path to give the allene 3. The steric reason may be rationalized, when one compares the regio-chemical outcome with that of the hydrosilylation of 5,⁷⁾ which underwent normal reaction with Et₃SiH (H₂PtCl₆ catalyst) to give butadiene $6a^{5}$ [¹³C NMR (CDCl₃) (off-resonance data): δ 23.0 (=CCH₃, qd, J = 126 Hz, ³J_{H-C} = 12.5 Hz), 123.2 (dm, J = 134 Hz), 140.0 (d, J = 133 Hz), 159.3 (=CMe, dq, ³J_{H-C} = 21 Hz, J = 7 Hz), 169.3 (m)] in 71% yield. Similarly, $5b^{7}$ gave $6b^{5}$ in 93% yields.



a: X = H; **b**: X = Br

The highly silylated allenes and butadienes synthesized herein are expected to be versatile synthetic building blocks.^{2a)} Studies along these lines are in progress in our laboratory.

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