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

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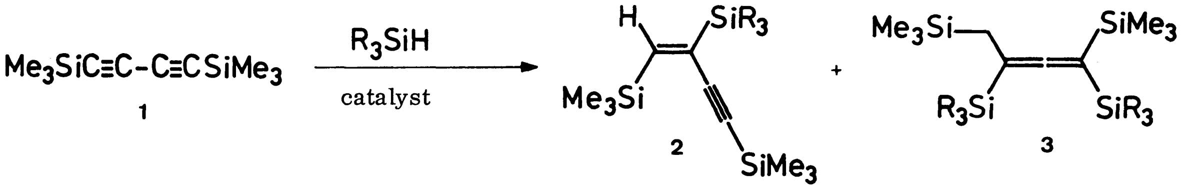
Hydrosilylation of 1,4-bis(trimethylsily)-1,3-butadiyne with platinum and rhodium catalyst proceeded stepwise to give first 2-silyl-1,4-bis(trimethylsilyl)-1-buten-3-ynes and then 1,3-disilyl-1,4-bis(trimethylsilyl)-1,2-butadienes in high yields.

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 manner$^{3)}$ 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-addition$^{4)}$ 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^+); ^{13}C NMR ($CDCl_3$): 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^+); ^{13}C NMR ($CDCl_3$) (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,



a: $R_3Si = Et_3Si$; **b**: $R_3Si = iPr_3Si$; **c**: $R_3Si = Me_3Si$; **d**: $R_3Si = PhMe_2Si$; **e**: $R_3Si = PhMeSiH$; **f**: $R_3Si = Ph_2SiH$

Table 1. Hydrosilylation of 1,4-Bis(trimethylsilyl)butadiyne (**1**)[a]

Run	R_3SiH	Catalyst	Conditions	Yield/%[b] of **2** and **3**	
1	Et_3SiH	H_2PtCl_6	80 °C, 0.5 h	0	100
2	Et_3SiH	$RhCl(PPh_3)_3$	90 °C, 0.9 h	45	28
3	Et_3SiH	$RhCl(PPh_3)_3$	90 °C, 5 h	0	83
4	Et_3SiH	$Pt(PPh_3)_4$	90 °C, 2 h	83	6
5	Et_3SiH	$Pt(PPh_3)_4$	90 °C, 18 h	81	18
6	Et_3SiH	$PdCl_2(PPh_3)_2$	90 °C, 35 h	18	0
7	Et_3SiH	$Pd(PPh_3)_4$	100 °C, 14 h	8	0
8	iPr_3SiH	H_2PtCl_6	90 °C, 8 h	92	0
9	Me_3SiH	H_2PtCl_6	100 °C, 2 h[c]	40	46
10	Me_3SiH	$RhCl(PPh_3)_3$	100 °C, 19 h	0	95
11	Me_3SiH	$RhCl(PPh_3)_3$	100 °C, 1 h	0	90
12	Me_3SiH	$Pt(PPh_3)_4$	90 °C, 1 h	69	2
13	Me_3SiH	$Pt(PPh_3)_4$	90 °C, 12 h	1	94
14	$PhMe_2SiH$	H_2PtCl_6	r.t., 1.5 h; 50-60 °C, 1 h[c]	70	10
15	$PhMe_2SiH$	$RhCl(PPh_3)_3$	90 °C, 1 h	27	36
16	$PhMe_2SiH$	$RhCl(PPh_3)_3$	100 °C, 2 h	0	86
17	$PhMeSiH_2$	$RhCl(PPh_3)_3$	100 °C, 2 h	30[d]	e)
18	Ph_2SiH_2	$RhCl(PPh_3)_3$	100 °C, 4 h	49[d]	e)

a) Typically a mixture of **1**, hydrosilane (3-4 mol equiv.), and the catalyst (0.2 mol% of H_2PtCl_6 in iPrOH or 0.5 mol% of $RhCl(PPh_3)_3$ and $Pt(PPh_3)_4$) was heated under an argon atmosphere.

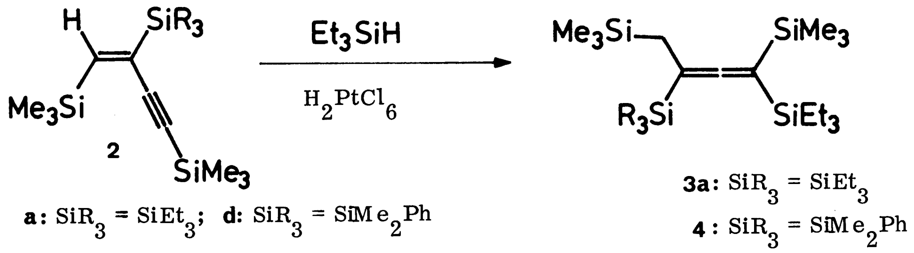
b) Isolated yields after purification by preparative TLC or medium pressure LC are given. The structure was determined by IR, ^1H and ^{13}C NMR, and MS spectrometries as well as elemental analysis.

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: $Pt(PPh_3)_4$ and $RhCl(PPh_3)_3$ induced double silylation, whereas H_2PtCl_6 gave **2** and **3** in roughly equal amounts.

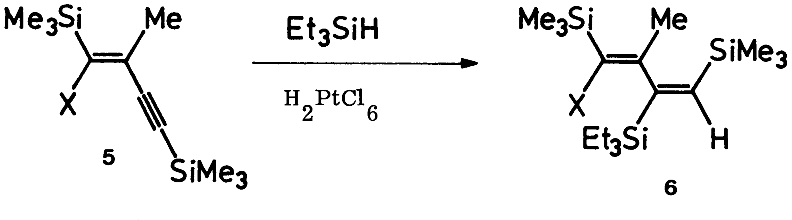


a: $SiR_3 = SiEt_3$; **d**: $SiR_3 = SiMe_2Ph$

3a: $SiR_3 = SiEt_3$
4: $SiR_3 = SiMe_2Ph$

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 Et_3SiH 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 regiochemical outcome with that of the hydrosilylation of **5**,7) which underwent normal reaction with Et_3SiH (H_2PtCl_6 catalyst) to give butadiene **6a**5) [^{13}C NMR ($CDCl_3$) (off-resonance data): δ 23.0 ($=C\underline{C}H_3$, qd, J = 126 Hz, $^3J_{H-C}$ = 12.5 Hz), 123.2 (dm, J = 134 Hz), 140.0 (d, J = 133 Hz), 159.3 ($=\underline{C}Me$, 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.

References

1) D. R. M. Walton and F. Waugh, J. Organomet. Chem., 37, 45 (1972); P. M. Jacobs, M. A. Davis, and H. Norton, J. Heterocyclic Chem., 14, 1115 (1977); W. Lohner and K. Praefcke, Chem. Ber., 111, 3745 (1978); L. Birkofer and K. Richtzenhain, Chem. Ber., 112, 2829 (1979); A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, B. Akinde, and D. R. M. Walton, J. Chem. Soc., Chem. Commun., 1979, 840; K. Wieghardt, W. Schmidt, H. Endres, and C. R. Wolfe, Chem. Ber., 112, 2837 (1979); J. Salaün and J. Ollivier, Nouv. J. Chim., 5, 587 (1980); A. B. Holmes and G. E. Jones, Tetrahedron Lett., 21, 3111 (1980); D. Liotta, M. Saindane, and W. Ott, ibid., 24, 2473 (1983).

2) a) General reviews: E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), p. 44; W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, New York (1983), p. 98; D. A. Armitage, "Comprehensive Organometallic Chemistry," Vol. 2, ed by G. Wilkinson, Pergamon Press, New York (1982), Chap. 9.1; b) Transition metal catalysis: J. L. Speier, Adv. Organomet. Chem., 17, 407 (1979); I. Ojima and T. Kogure, Rev. Silicon, Germanium, Tin, and Lead Compd., 5, 8 (1981).

3) Hydrosilylation of silylalkynes gives 1,2-disilylalkenes generally: V. B. Pukhnarevich, I. I. Tsykhanskaya, and M. G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 1984, 427 [Chem. Abstr., 100, 209970u (1984)]; H. Matsumoto, Y. Hoshino, and Y. Nagai, Chem. Lett., 1982, 1633 and the cited references; G. Fritz, H. Wilhelm, and A. Oleownik, Z. Anorg. Allg. Chem., 478, 97 (1981) [Chem. Abstr., 96, 20154p (1982)]; N. V. Komarov, L. I. Ol'khovskaya, and O. I. Baranova, Zh. Obshch. Khim., 50, 412 (1980) [Chem. Abstr., 92, 215484w (1980)]; P. F. Hudrlik, R. H. Schwartz, and J. C. Hogan, J. Org. Chem., 44, 155 (1979); O. G. Yarosh, L. V. Shchukina, E. O. Tsetlina, and M. G. Voronkov, Zh. Obshch. Khim., 48, 2059 (1978) [Chem. Abstr., 89, 215482g (1978)]; L. Birkofer and T. Kühn, Chem. Ber., 111, 3119 (1978) and references cited therein.

4) Hydrosilylation of 1,3-dienes proceeds in 1,4-manner: I. Ojima, M. Kumagai, and Y. Miyazawa, Tetrahedron Lett., 1977, 1385; Y. Kiso, K. Yamamoto, K. Tamao, and M. Kumada, J. Am. Chem. Soc., 94, 4373 (1972); I. Ojima, J. Organomet. Chem., 134, C1 (1977); I. Ojima and M. Kumagai, ibid., 134, C6 (1977); M. S. Wrighton and M. A. Schroeder, J. Am. Chem. Soc., 96, 6235 (1974).

5) $^3J_{C-H}$ (trans) = 7.0-13.9 Hz are generally larger than $^3J_{C-H}$ (cis) = 4.4-7.5 Hz: J. E. Anderson, Tetrahedron Lett., 1975, 4079. $^3J_{C-H}$ of **2a-f** were 19-20 Hz.

6) Regioselectivity in the hydrosilylation of en-ynes is elusive: A. I. Kakhniashvili, T. Sh. Gvaliya, and D. Sh. Ioramashvili, Soobshch. Akad. Nauk Gruz. SSR, 68, 609 (1972) [Chem. Abstr., 78, 97755w (1973)]; A. I. Kakhniashvili and D. Sh. Ioramashvili, Zh. Obshch. Khim., 40, 1556 (1970) [Chem. Abstr., 75, 6036m (1971)]; I. M. Gverdtsiteli and T. G. Talakvadze, Soobshch. Akad. Nauk Gruz. SSR, 79, 601 (1975) [Chem. Abstr., 84, 59690n (1976)]; A. I. Kakhniashvili and D. Sh. Ioramashvili, Tr. Tbilis. Gos. Univ., 6-7, 195 (1973) [Chem. Abstr., 81, 152319w (1974)].

7) T. Kusumoto, K. Nishide, and T. Hiyama, Chem. Lett., accompanying paper.

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