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Palladium- or Platinum-Catalyzed Novel Double Silylation of α-Diketones or a Benzoylformate with Hexamethyldisilane Affording 1,2-Bis(siloxy)ethenes or a Double Silylated Tartrate Derivative

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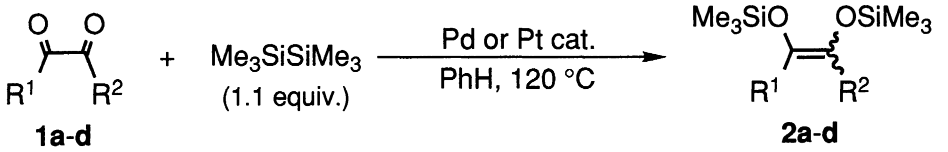
α-Diketones (benzil, methyl phenyl diketone, acenaphthenequinone, camphorquinone) reacted with hexamethyldisilane in the presence of a Pd or Pt catalyst ($PdCl_2(PMe_3)_2$, $Pt_2(dba)_3$-$P(OCH_2)_3CEt$, etc.) to give the corresponding 1,2-bis(trimethylsiloxy)ethenes in excellent to moderate yields, while methyl benzoylformate provided dimethyl 2,3-diphenyl-2,3-bis(*O*-trimethylsilyl)tartrate.

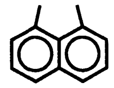
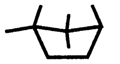
Organosilanes have attracted increasing attention owing to their versatile utilities as synthetic reagents.1) Especially, 1,2-bis(siloxy)ethenes2) are useful intermediates for the syntheses of diols, ketones, acetylenes, etc. In the course of our studies on the transformation of Si-Si bonds,3) we found that a non-activated disilane can smoothly react with α-diketones in the presence of a Pd or Pt catalyst to give 1,2-bis(siloxy)ethenes.4) In addition, we came across an unexpected double silylative reductive coupling reaction of an α-keto ester.

A mixture of benzil (**1a**, 0.40 mmol), hexamethyldisilane (0.44 mmol), $PdCl_2(PMe_3)_2$ (0.008 mmol), and benzene (0.05 cm^3) was heated in a sealed glass tube at 120 °C for 3 h. GC and GC-MS analyses of the reaction mixture revealed the formation of 1,2-diphenyl-1,2-bis(trimethylsiloxy)ethene (**2a**) in 99% GC yield, Eq. 1 (Table 1).5) Monitoring the reaction showed the presence of the induction period (≈1 min),6) indicative of the conversion of $PdCl_2(PMe_3)_2$ into active species. Although the activity was lower, $PdCl_2L_2$ (L = PEt_3, P^iBu_3) was also effective. However, a conventional catalyst ($PdCl_2(PPh_3)_2$) was almost inactive under the present conditions. By using $PdCl_2(PMe_3)_2$, methyl phenyl diketone (**1b**), acenaphthenequinone (**1c**), and camphorquinone (**1d**) underwent similar reactions to give the corresponding 1,2-bis(siloxy)ethenes (**2b-d**) in good to moderate yields.5) In the reactions of **1b** and **1d**, small amounts of tri- and/or monosilylated compounds were also formed.7,8) As to the catalyst ($PdCl_2(PMe_3)_2$) concentration, 2 mol% was usually enough. However, in the case of **1d**, a higher concentration was necessary because of the decomposition of the catalyst leading to the metal deposit. Besides Pd catalysts, a Pt catalyst system, $Pt_2(dba)_3$-$P(OCH_2)_3CEt$ (dba = dibenzylideneacetone, P/Pt = 1.65), which was found to be highly effective in the single silylation of olefins with hexamethyldisilane affording alkenylsilanes,9) was also active to give the 1,2-bis(siloxy)ethenes.



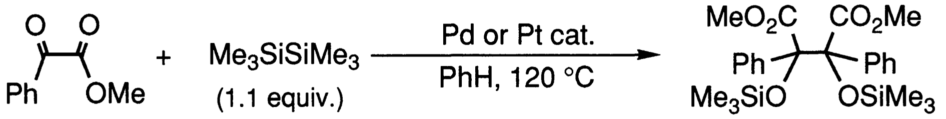
(1)

Table 1. Reactions of α-Diketones with Hexamethyldisilane[a)]

1	R^1	R^2	Catalyst	Time	**2** (Yield[b)]/%)	*cis*/*trans*[c)]
1a	Ph	Ph	$PdCl_2(PMe_3)_2$	3 h	**2a** (99 (93[d)]))	85/15
			$PdCl_2(PEt_3)_2$	1 h	**2a** (91)	87/13
			$PdCl_2(P^iBu_3)_2$	1 h	**2a** (22)	nd[e)]
			$PdCl_2(PPh_3)_2$	1 h	**2a** (1)	nd[e)]
			$Pt_2(dba)_3$-$P(OCH_2)_3CEt$[f)]	48 h	**2a** (86)	77/23
1b	Ph	Me	$PdCl_2(PMe_3)_2$	2 h	**2b** (64)	62/38
			$Pt_2(dba)_3$-$P(OCH_2)_3CEt$[f)]	24 h	**2b** (32)	nd[e)]
1c			$PdCl_2(PMe_3)_2$	1 d	**2c** (65)	-
			$Pt_2(dba)_3$-$P(OCH_2)_3CEt$[f)]	7 d	**2c** (56)	-
1d			$PdCl_2(PMe_3)_2$[g)]	20 h	**2d** (42)[h)]	-

a) α-Diketone 0.40 mmol, hexamethyldisilane 0.44 mmol, catalyst 0.008 mmol, benzene 0.05 cm^3, 120 °C. b) GC yield. c) Estimated by ^{1}H NMR. d) Catalyst 0.004 mmol, 1 h. e) Not determined. f) 0.0097 mmol Pt, P/Pt = 1.65. g) 0.024 mmol. h) Diketone **1d** (30%) was recovered.

On the other hand, when an α-keto ester, methyl benzoylformate (**3**, 0.40 mmol), was allowed to react with hexamethyldisilane (0.44 mmol) in the presence of a Pd or Pt catalyst, a double silylated dimerization product (**4**, a bis(silyl) derivative of 2,3-diphenyltartrate[10)]) was obtained as a mixture of *dl* and *meso* isomers[11)] without any expected 1 : 1 adducts, Eq. 2; **4** (*dl*/*meso* = 63/37): bp 189 °C (0.5 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$, *meso* and *dl* respectively) δ -0.03 and 0.03 (each s, 18H, H_3CSi), 3.73 and 3.81 (each s, 6H, H_3CO), 6.88-7.27 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$, *dl* and *meso* respectively) δ 1.83 (C-Si, *dl* and *meso*), 51.9 and 51.7 (H_3C-O), 85.6 and 88.2 (C-OSi), 126.0 and 126.4, 127.5 and 127.8, 128.4 and 128.5, 138.1 and 138.4 (ring C), 172.5 and 171.5 (C=O); IR (neat) 1744 (C=O), 1250 (Si-Me), 1154 (Si-O) cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 459 (M^+-15 (Me), 1.2), 310 (34), 237 (100), 207 (34), 105 (81), 73 (90); Anal. Found: C, 60.36; H, 6.99%. Calcd for $C_{24}H_{34}O_6Si_2$: C, 60.73; H, 7.22%.



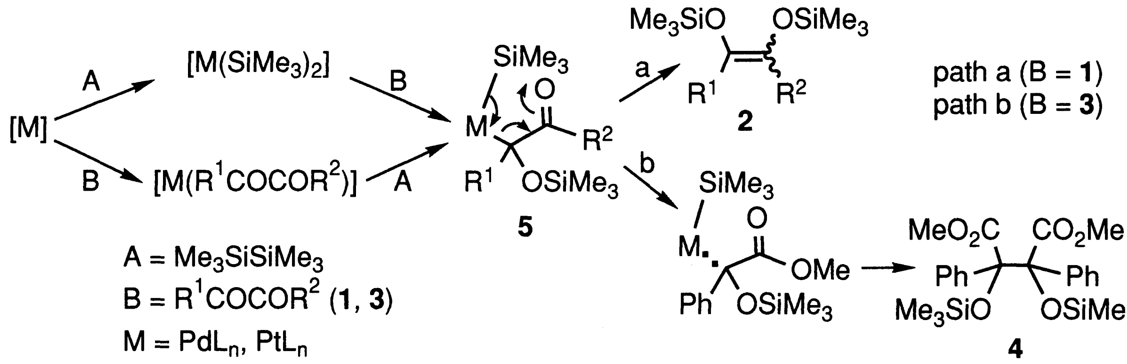
3 **4** (2)

Catalyst	Time/h	GC yield/%	*dl*/*meso*
$PdCl_2(PMe_3)_2$ (2 mol%)	4	89 (77[a)])	63/37
$Pt_2(dba)_3$-$P(OCH_2)_3CEt$ (P/Pt = 1.65, 2.4 mol%)	30	51	63/37

a) Isolated yield (6 h).

Similar reductive coupling was previously reported in the Rh-catalyzed silylation of benzoyl cyanide with triethylsilane[12a] and in the Co-catalyzed hydrogenation of ethyl benzoylformate.[12b]

The formation of the double silylated products **2** and **4** seems to be best explained by the following pathways (Scheme 1). Addition of the Si-Si bond of hexamethyldisilane to an active catalyst species[13] is followed by the insertion of a dicarbonyl compound into the silicon-metal bond[14] to give a silyl(α-siloxymethyl) intermediate (**5**). The same species may be alternatively generated by coordination of a dicarbonyl compound to the catalyst species[15] and subsequent interaction with hexamethyldisilane. In the reaction of α-diketones, the remaining carbonyl group in **5** probably reacts with the silyl ligand, possibly via five-membered transition state to give the 1,2-bis(siloxy)ethenes **2** as the final products (path a). On the contrary, the carbonyl carbon of the methoxycarbonyl group arising from **3** does not have as high electrophilicity as that from α-diketones, and would not assist the heterolytic cleavage of the metal-carbon bond of **5** so effectively. Instead, species **5** may undergo homolysis of the metal-carbon bond leading to a rather stable tertiary benzyl radical (path b). Homo-coupling between the resulting radical species will provide the double silylative dimerization product **4**.[16]



Scheme 1.

In summary, we demonstrate that 1,2-bis(siloxy)ethenes and a bis(silyl) derivative of 2,3-diphenyltartrate can be respectively obtained by Pd- or Pt-catalyzed addition of hexamethyldisilane to α-diketones and an α-keto ester. Further investigations on the mechanism and the extension to other substrates will be the coming subjects.

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworth, London (1981); W. P. Weber, "Silicon Reagents for Organic Synethesis," Springer, New York (1983).

2) For instance, J. K. Rasmussen, L. R. Krepski, S. M. Heilmann, H. K. Smith, II, and M. L. Tumey, *Synthesis*, **1983**, 457, and references cited therein.

3) For our recent studies, H. Yamashita, M. Catellani, and M. Tanaka, *Chem. Lett.*, **1991**, 241; H. Yamashita and M. Tanaka, *ibid.*, **1992**, 1547.

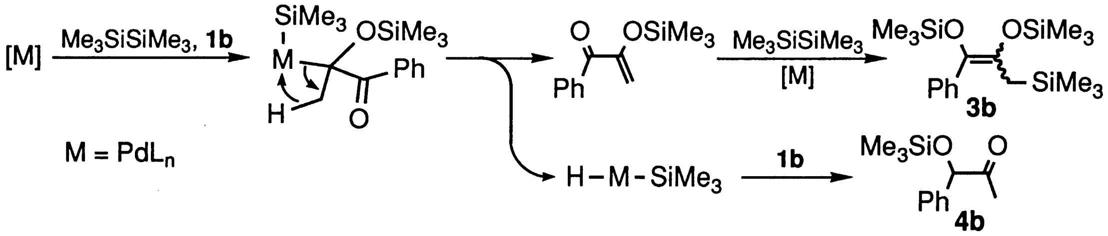
4) Although a Pd-catalyzed reaction of benzil with an activated disilane ($ClMe_2SiSiMe_2Cl$) was briefly reported, the main product was 1,3-dioxa-2-sila-4-cyclopentene. See J. D. Rich, *Organometallics*, **8**, 2609 (1989).

5) NMR data of *cis*- and *trans*-**2a**, *cis*-**2b**, and **2d** purified by Kugelrohr distillation and/or preparative GC were in good agreement with those reported.[2] The spectral data of *trans*-**2b** and **2c** were as follows. *trans*-**2b**: ^{1}H NMR ($CDCl_3$) δ 0.02, 0.06 (each s, 18H, H_3CSi), 1.99 (s, 3H, H_3CC), 7.16-7.61 (m, 5H, C_6H_5). **2c**: ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 18H, H_3CSi), 7.35-7.70 (m, ring H); MS m/z (rel intensity) 328 (M^+,

100), 240 (30), 73 (88); HRMS Found: m/z 328.1310. Calcd for $C_{18}H_{24}Si_2O_2$: M, 328.1314.

6) The yields of **2a** (time/min) were 1.3 (1), 20 (2), 35 (3), 45 (4) 65 (10), 77 (30), and 91 (60) % (catalyst 0.004 mmol). The ratios of *cis*/*trans* (time/min) were ≈95/5 (1) and around 90/10 (2-60).

7) From **1b**, 1-phenyl-3-trimethylsilyl-1,2-bis(trimethylsiloxy)-1-propene (**3b**, ≈5%) and 1-phenyl-1-trimethylsiloxypropan-2-one (**4b**, ≈8%) were obtained. **3b** (*cis*/*trans* = 77/23 (tentative assignment)): ^{1}H NMR ($CDCl_3$, *trans* and *cis* respectively) δ -0.07, 0.07, 0.14 and -0.01, 0.10, 0.22 (each s, 27H, H_3CSi), 1.82 and 1.58 (each s, 2H, CH_2), 7.13-7.52 (m, 5H, C_6H_5); MS (EI, 70 eV) m/z (rel intensity) 366 (M^+, 27), 203 (27), 189 (20), 147 (24), 130 (18), 73 (100), 45 (26). **4b**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H, H_3CSiO), 2.10 (s, 3H, H_3CCO), 5.05 (s, 1H, CH), 7.28-7.49 (m, 5H, C_6H_5); IR (neat) 1720 (C=O), 1258 (Si-Me), 1104 (Si-O) cm^{-1}; MS (EI, 70 eV) m/z (rel intensity) 207 (M^+-15 (Me), 9), 179 (82), 73 (100). The following scheme shows a possible sequence for the formation of **3b** and **4b**.



8) From **1d**, α-trimethylsiloxyketones (**4d**, a mixture of three regio- and/or stereoisomers (X, Y, and Z) of the monohydrosilylated compounds of **1d**) seemed to be formed (X : Y : Z = 1 : 4 : 5 by NMR, ≈14% combined yields), although their structures have not been confirmed yet. The proton signals of the $[(H^a{}_3C)_3SiO]CH^b$ moiety of **4d** were observed at 0.14 and 0.16 ppm for H^a (X, Y, Z) and at 3.64 (s), 3.71 (br s), and 4.10 (d, J = 4.9 Hz) ppm for H^b (X, Y, and Z respectively). IR (neat) 1754 (C=O), 1250 (Si-Me), 1125 (Si-O); MS (EI, 70 eV) m/z (rel intensity) 240 (M^+, 5), 225 (10), 143 (100), 129 (27), 73 (67).

9) The details will be reported separately.

10) S. P. Pappas, B. C. Pappas, Y. Okamoto, and H. Sakamoto, *J. Org. Chem.*, **53**, 4404 (1988).

11) The stereochemistry (*dl* and *meso*) was confirmed by the comparison of the NMR data of **4** with those of the authentic samples prepared by the silylation of *dl*- and/or *meso*-2,3-diphenyltartrate$^{10)}$ with Me_3SiCl/Et_3N.

12) a) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugaya, and Y. Nagai, *J. Organomet. Chem.*, **94**, 449 (1975); b) Y. Ohgo, M. Kimura, and S. Takeuchi, *J. Heterocycl. Chem.*, **25**, 1583 (1988).

13) For the bis(silyl) species as intermediates involved in double silylation of unsaturated compounds, T.-a. Kobayashi, T. Hayashi, H. Yamashita, and M. Tanaka, *Chem. Lett.*, **1989**, 467.

14) For insertion of carbonyl compounds into silicon-metal bonds, a) J. A. Gladysz, *Acc. Chem. Res.*, **17**, 326 (1984), and references cited therein; b) Y. Uchimaru, H.-J. Lautenschlager, A. J. Wynd, M. Tanaka, and M. Goto, *Organometallics*, **11**, 2639 (1992).

15) Coordination of α-dicarbonyl compounds to Ni(0) complexes was reported. S. D. Ittel, *J. Organomet. Chem.*, **137**, 223 (1977).

16) Examples of the formation of $[(Me_3SiO)(Ph)HC]_2$ from $(Me_3SiO)(Ph)HC$-M species (M = Mn, Fe) are known. See Ref. 14a.

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