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Acid anhydrides as alternatives to acid chlorides in the palladium-catalyzed reaction with silacyclobutanes

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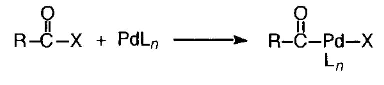
The palladium-catalyzed reaction of acid anhydrides with silacyclobutane gives a mixture of cyclic silyl enol ether, carboxy(propyl)silane, and 3-(carboxysilyl)ketone. In the presence of *N,N*-dicyclohexylcarbodiimido (DCC), the reaction preferentially provides a cyclic silyl enol ether in a good yield. In addition, the palladium-catalyzed reaction of benzoic acid with silacyclobutane in the presence of two equivalents of DCC also affords a cyclic silyl enol ether in a moderate yield. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: acid anhydrides; caboxylic acids; palladium complex; silacyclobutanes; cyclic silyl enol ethers

Most acid anhydrides (**1**) do not contain halogen atoms (Table 1). However, anhydrides **1** can react with transition-metal complexes at their carbon–oxygen bond as well as at the carbon–halogen bond in acid halides to form acyl(carboxylate)metal complexes [Eqn. (1)].[1,2] They have a great potential for organic synthesis, but the catalytic potential has not been well studied.[3,4] For instance, aldehyde and carboxylic acid synthesis by hydrogenation of acid anhydrides,[1,2] decarbonylative arylation of alkenes,[5] and hydroacylation of alkenes[6] have been reported. On the other hand, we reported a palladium-catalyzed reaction of 1,1-dimethyl-1-silacyclobutane (**2**) with an acid chloride giving a cyclic silyl enol ether (**3**) in a excellent yield.[7,8] We confirmed that the reaction proceeds *via* an acyl(chloro)palladium complex as an intermediate. In this paper, we report a reaction of acid anhydrides **1** as an alternative to acid chlorides with silacyclobutane **2** providing a cyclic silyl enol ether (**3**) in a good yield without using organic halide compounds, which have a negative influence on the natural environment.

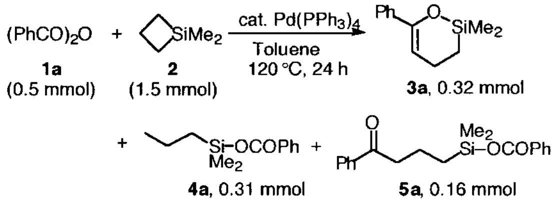


$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}X} + \mathrm{PdL}_n \longrightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\underset{L_n}{Pd}{-}X} \qquad (1)$$

X = Cl, OCOR'

RESULTS AND DISCUSSION

Reaction of benzoic anhydride (**1a**, 0.5 mmol) with 1,1-dimethyl-1-silacyclobutane (**2**, 1.5 mmol) in the presence of $Pd(PPh_3)_4$ (0.02 mmol) gave three products: 1,1-dimethyl-1-sila-2-oxa-3-phenyl-3-cyclohexene (**3a**, 0.32 mmol), benzoyloxy(propyl)dimethylsilane (**4a**, 0.31 mmol), and 1-phenyl-3-(benzoyloxy(dimethyl)silyl)-1-butanone (**5a**, 0.16 mmol) [Eqn. (2)]. Compound **4a** was believed to be obtained from a reaction of **2** with benzoic acid.[9]



(2)

The present catalysis is best explained by the reaction sequence outlined in Scheme 1. At first, oxidative addition of acid anhydride **1** to the palladium species forms an acyl(carboxylate)–palladium complex followed by reaction with silacyclobutane **2**, providing compound **5**. Ring closure of compound **5** gives cyclic silyl enol ether **3** accompanied by the formation of carboxylic acid (**6**). Acid **6** reacts with **2** to produce a ring-opened adduct **4**.[9]

Thus, co-product **4** must be suppressed for the purpose of selective formation of **3**. Actually, a reaction of **1a** with **2** in the presence of a catalytic amount of $Pd(PPh_3)_4$ and a stoichiometric amount of *N,N*-dicyclohexylcarbodiimido (DCC), which is a well-known dehydration–condensation reagent, gave silyl enol ether **3a** in good yield [70% yield by

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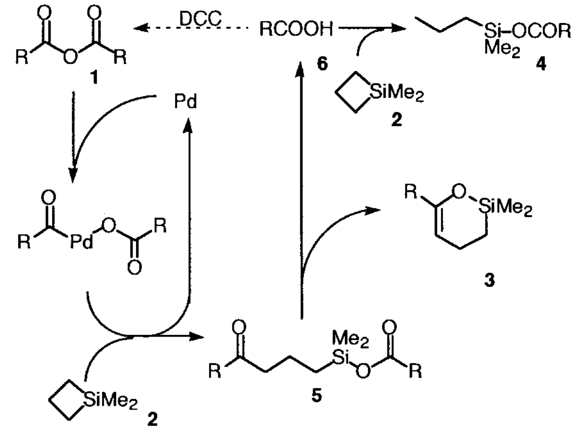
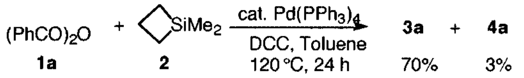


Scheme 1.

gas chromatography (GC)] along with a small amount of **4a** (3% GC yield) [Eqn. (3)]:

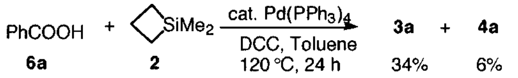


(3)

$PdCl_2(PPh_3)_2$ also catalyzed the reaction in Eqn. (3) to give **3a**, although the reaction was less selective (**3a**, 66% GC yield; **4a**, 15%). $NiCl_2(PPh_3)_2$ could catalyze the reaction to produce **3a** only in a low yield (11% GC yield) because of its low activity in the present reaction.

Selected results are summarized in Table 1. In the presence of DCC and $Pd(PPh_3)_4$, aromatic acid anhydrides **1a–d** reacted with **2** to afford **3a–d** in good yields along with **4a–d** in low yields. At a lower temperature (80 °C), reaction of **1a** with **2** proceeded, although the reaction was slower and provided a lower yield. Cinnamic anhydride (**1e**) reacted smoothly with **2** to give the silyl enol ether **3e** in a 54% yield.

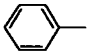
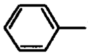
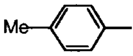
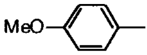
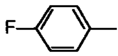
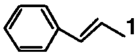
During the reaction, carboxylic acid **6** was generated as a co-product followed by reaction with DCC to regenerate acid anhydride **1** (see broken line of Scheme 1). Therefore, the use of acid **6** instead of anhydride **1** as the starting material is believed to promote the above reaction. In practice, the $Pd(PPh_3)_4$-catalyzed reaction of benzoic acid **6a** with **2** in the presence of two equivalents of DCC gave **3a** in a 34% yield along with **4a** (6% GC yield) [Eqn. (4)]:



(4)

In conclusion, palladium-catalyzed reactions of acid anhydrides **1** with silacyclobutane **2** in the presence of DCC gave silyl enol ethers **3** in good yields. The reaction of benzoic acid **6a** with silacyclobutane **2** in the presence of two equivalents of DCC also afforded **3** in a moderate yield. Further extension of the present reaction using various acids, acid anhydrides, and acid derivatives is in progress.

Table 1. Palladium-catalyzed reactions of acid anhydrides (**1**) with silacyclobutane (**2**) and DCC[a]

		Yield (%)[b]	
$(RCO)_2O$ (**1**) R	Temp. (°C)/Time (h)	**3**	**4**
 **1a.**	120/24	70	3
 **1a.**	80/24	53	1
 **1b.**	120/24	48	4
 **1c.**	120/24	67	12
 **1d.**	120/24	57	3
 **1e.**	120/24	54	2

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.5 mmol), DCC (0.6 mmol), $Pd(PPh_3)_4$ (0.02 mmol), toluene (0.5 ml), 120 °C, 24 h in a sealed tube.

[b] Determined by GC.

EXPERIMENTAL

General

^1H NMR spectra in solution were measured on a JEOL AlPHA-400 instrument (400 MHz). $CDCl_3$ was used as solvent unless otherwise noted. Chemical shifts in solution are referenced to Me_4Si (0 ppm) and $CHCl_3$ (7.26 ppm). GC–mass spectrometry (MS) (EI, 70 eV) were measured on Shimazu QP-2000 spectrometer. GC analyses were carried out with a CBP1-W12 (10 m) capillary column using internal standards.

All liquid starting materials or solvents were dried with an appropriate drying agent, such as sodium, CaH_2, or molecular sieve 4A, and distilled under nitrogen or *in vacuo*. 1,1-Dimethyl-1-silacyclobutane was purchased and distilled before use. Each reaction was carried out under nitrogen in a sealed tube.

Reaction of 1a with 2 in the presence of a catalytic amount of $Pd(PPh_3)_4$

A mixture of benzoic anhydride (**1a**, 0.5 mmol), 1,1-dimethyl-1-silacyclobutane (**2**, 1.5 mmol), $Pd(PPh_3)_4$ (0.02 mmol), and toluene (0.5 ml) in a sealed tube was heated at 120 °C for 24 h. GC and GC–MS analysis of the reaction mixture showed formation of 1,1-dimethyl-1-sila-2-oxa-3-

phenyl-3-cyclohexene (**3a**, 0.39 mmol), benzoyloxy(propyl)-dimethylsilane (**4a**, 0.37 mmol), and 1-phenyl-3-(benzoyloxy-(dimethyl)silyl)-1-butanone (**5a**, 0.24 mmol) [Eqn. (2)].

Compounds **3a, 4a**, and **5a** showed satisfactory ^{1}H NMR and MS data. ^{1}H NMR spectral data in $\mathrm{CDCl_3}$ and MS data of **3a**, **4a**, and **5a** are as follows.

3a: ^{1}H NMR δ 0.29 (s, 6H, $\mathrm{SiCH_3}$), 0.82 (t, *J* = 7.2 Hz, 2H, $\mathrm{SiC}\mathit{H}_2$), 2.40 (dt, *J* = 4.9 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 5.42 (t, *J* = 4.9 Hz, 1H, $=\mathrm{CH}$), 7.20–7.58 (m, 5H, $\mathrm{C_6H_5}$); GC–MS *m/z* (relative intensity) 204 (100, $\mathrm{M^+}$), 203 (93), 190 (13), 189 (71), 161 (19), 130 (72), 129 (55), 128 (23), 115 (29), 102 (15), 94 (14), 87 (30), 77 (24), 61 (22), 59 (25), 51 (19).

4a: ^{1}H NMR δ 0.38 (s, 6H, $\mathrm{SiCH_3}$), 0.85–0.90 (m, 2H, $\mathrm{CH_2Si}$), 1.00 (t, *J* = 7.3 Hz, 3H, $\mathrm{CH_3}$), 1.43–1.53 (m, 2H, $\mathrm{CH_2}$), 7.41–8.07 (m, 5H, $\mathrm{C_6H_5}$); GC–MS *m/z* (relative intensity) 207 (13, $\mathrm{M^+ - Me}$), 179 (100), 135 (27), 121 (11), 105 (76), 77 (65).

5a: ^{1}H NMR δ 0.42 (s, 6H, $\mathrm{SiCH_3}$), 0.95–1.05 (m, 2H, $\mathrm{CH_2Si}$), 1.86–1.97 (m, 2H, $\mathrm{CH_2}$), 3.05 (t, *J* = 7.2 Hz, 2H, $\mathrm{CH_2CO}$), 7.38–8.22 (m, 10H, $\mathrm{C_6H_5}$); GC–MS *m/z* (relative intensity) 205 (11, $\mathrm{M^+ - PhCOO}$), 204 (40), 189 (24), 179 (100), 135 (18), 105 (89), 77 (58).

Reaction of 1a with 2 in the presence of DCC and a catalytic amount of $\mathrm{Pd(PPh_3)_4}$

A mixture of **1a** (0.5 mmol), **2** (1.5 mmol), DCC (0.6 mmol), $\mathrm{Pd(PPh_3)_4}$ (0.02 mmol), and toluene (0.5 ml) in a sealed glass tube was heated at 120 °C for 24 h. GC and GC–MS analysis of the reaction mixture showed the formation of **3a** (0.70 mmol) and **4a** (0.03 mmol). After filtration of the reaction mixture, the filtrate was concentrated *in vacuo* (room temperature/7 mmHg) and residual oil was purified by Kugelrohr distillation under 7 Torr at 122 °C to give analytically pure **2a** (129 mg, 63% isolated yield) as a colorless oil.

Reactions of **2** with other acid anhydrides, *p*-toluic anhydride (**1b**), *p*-anisic anhydride (**1c**), *p*-fluorobenzoic anhydride (**1d**), and cinnamic anhydride (**1e**) under the same conditions provided similar products **3b–e** along with small amounts of **4b–e** respectively. Compounds **3b–e** and **4b–e** showed satisfactory ^{1}H NMR, MS, and/or analytical data. ^{1}H NMR spectral data in $\mathrm{C_6D_6}$ and MS data of **3b–e** and **4b–e** are as follows.

3b: ^{1}H NMR δ 0.33 (s, 6H, $\mathrm{SiCH_3}$), 0.86 (t, *J* = 7.2 Hz, 2H, $\mathrm{CH_2Si}$), 2.37 (s, 3H, $\mathrm{C_6H_4C}\mathit{H}_3$), 2.45 (dt, *J* = 4.9 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 5.42 (t, *J* = 4.9 Hz, 1H, $=\mathrm{CH}$), 7.14–7.52 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 218 (50, $\mathrm{M^+}$), 217 (29), 204 (18), 203 (100), 144 (11), 129 (31), 128 (12), 115 (11), 94 (11), 75 (20).

3c: ^{1}H NMR δ 0.31 (s, 6H, $\mathrm{SiCH_3}$), 0.84 (t, *J* = 7.2 Hz, 2H, $\mathrm{CH_2Si}$), 2.42 (dt, *J* = 4.9 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 3.80 (s, 3H, $\mathrm{OCH_3}$), 5.32 (t, *J* = 4.9 Hz, 1H, $=\mathrm{CH}$), 6.84–7.54 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 234 (100, $\mathrm{M^+}$), 233 (83), 220 (13), 219 (66), 203 (34), 160 (24), 159 (32), 145 (13), 135 (19), 129 (17), 115 (15), 103 (13), 102 (28), 77 (12), 75 (27), 59 (17).

3d: ^{1}H NMR δ 0.32 (s, 6H, $\mathrm{SiCH_3}$), 0.85 (t, *J* = 7.2 Hz, 2H, $\mathrm{CH_2Si}$), 2.43 (dt, *J* = 4.9 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 5.37 (t, *J* = 4.9 Hz, 1H, $=\mathrm{CH}$), 6.98–7.58 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 222 (100, $\mathrm{M^+}$), 221 (68), 208 (16), 207 (84), 179 (13), 148 (75), 147 (45), 146 (17), 133 (18), 127 (14), 97 (12), 96 (29), 75 (36), 59 (22), 47 (16).

3e: ^{1}H NMR δ 0.25 (s, 6H, $\mathrm{SiCH_3}$), 0.66 (t, *J* = 5.5 Hz, 2H, $\mathrm{CH_2Si}$), 1.72–1.80 (m, 2H, $\mathrm{CH_2}$), 4.48 (t, *J* = 5.8 Hz, 1H, $\mathrm{SiCH_2CH_2C}\mathit{H}$), 6.24–6.29 (m, 1H, $\mathrm{PhCH{=}C}\mathit{H}$), 6.58–6.63 (m, 1H, $\mathrm{PhC}\mathit{H}$), 7.21–7.41 (m, 4H, $\mathrm{C_6H_5}$); GC–MS *m/z* (relative intensity) 230 (100, $\mathrm{M^+}$), 229 (29), 215 (25), 203 (17), 202 (81), 201 (50), 189 (26), 155 (22), 153 (20), 141 (35), 128 (56), 115 (28), 100 (19), 91 (15), 77 (25), 75 (72), 61 (19), 59 (37), 51 (17).

4b: ^{1}H NMR δ 0.37 (s, 6H, $\mathrm{SiCH_3}$), 0.84–0.89 (m, 2H, $\mathrm{CH_2Si}$), 1.00 (t, *J* = 7.2 Hz, 3H, $\mathrm{CH_3}$), 1.42–1.53 (m, 2H, $\mathrm{CH_2}$), 2.41 (s, 3H, $\mathrm{C_6H_4CH_3}$), 7.20–8.04 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 221 (15, $\mathrm{M^+ - Me}$), 193 (100), 149 (30), 135 (13), 119 (60), 91 (39).

4c: ^{1}H NMR δ 0.36 (s, 6H, $\mathrm{SiCH_3}$), 0.83–0.88 (m, 2H, $\mathrm{CH_2Si}$), 1.00 (t, *J* = 7.3 Hz, 3H, $\mathrm{CH_3}$), 1.43–1.51 (m, 2H, $\mathrm{CH_2}$), 3.86 (s, 3H, $\mathrm{OCH_3}$), 6.84–8.02 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 237 (11, $\mathrm{M^+ - Me}$), 209 (87), 165 (62), 151 (23), 135 (100), 107 (14), 92 (28), 77 (36).

4d: ^{1}H NMR δ 0.38 (s, 6H, $\mathrm{SiCH_3}$), 0.84–90 (m, 2H, $\mathrm{CH_2Si}$), 1.00 (t, *J* = 7.3 Hz, 3H, $\mathrm{CH_3}$), 1.42–1.53 (m, 2H, $\mathrm{CH_2}$), 7.38–7.98 (m, 4H, $\mathrm{C_6H_4}$); GC–MS *m/z* (relative intensity) 225 (12, $\mathrm{M^+ - Me}$), 197 (100), 153 (21), 123 (41), 95 (40).

4e: ^{1}H NMR δ 0.34 (s, 6H, $\mathrm{SiCH_3}$), 0.82–0.88 (m, 2H, $\mathrm{CH_2Si}$), 1.00 (t, *J* = 7.2 Hz, 3H, $\mathrm{CH_3}$), 1.40–1.52 (m, 2H, $\mathrm{CH_2}$), 6.38–7.85 (m, 7H, $\mathrm{C_6H_5CH{=}CH}$); GC–MS *m/z* (relative intensity) 205 (3, $\mathrm{M^+} - 43$), 177 (5), 163 (12), 124 (15), 83 (48), 81 (44), 67 (20), 55 (100), 43 (93).

Reaction of 6a with 2 in the presence of DCC and a catalytic amount of $\mathrm{Pd(PPh_3)_4}$

A mixture of benzoic acid (**6a**, 1.0 mmol), **2** (1.5 mmol), DCC (1.1 mmol), $\mathrm{Pd(PPh_3)_4}$ (0.02 mmol), and toluene (0.5 ml) in a sealed tube was heated at 120 °C for 24 h. GC and GC–MS analysis of the reaction mixture showed the formation of **3a** (0.34 mmol) and **4a** (0.06 mmol).

Acknowledgements

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REFERENCES

1. Nagayama K, Kawataka F, Sakamoto M, Shimizu I and Yamamoto A. *Bull. Chem. Soc. Jpn.* 1999; **72**: 573.
2. Nagayama K, Shimizu I and Yamamoto A. *Yuki Gosei Kagaku Kyokaishi*, 1999; **57**: 775 and references cited therein.
3. Yamamoto A. *Adv. Organomet. Chem.* 1994; **34**: 111.
4. Lin Y-S and Yamamoto A. In *Topics in Organometallic Chemistry*, Murai S (ed). Springer: 1999.
5. Stephane MS, Teunissen AJJM, Verzijl GKM and de Vries JG. *Angew. Chem. Int. Ed. Engl.* 1998; **37**: 662.

6. Kokubo K, Miura M and Nomura M. *Organometallics* 1995; **14**: 4521.
7. Tanaka Y, Yamashita H and Tanaka M. *Organometallics* 1996; **15**: 1524.
8. Chauhan BPS, Tanaka Y, Yamashita H and Tanaka M. *Chem. Commun.* 1996; 1207.
9. Nametkin NS, Vdovin VM and Grinberg PL. *Dokl. Akad. Nauk SSSR* 1964; 849.