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Palladium(0)-Catalyzed Carbonylation of 1-Alkyl-2-trialkylsilyl-2-propenyl Carbonates

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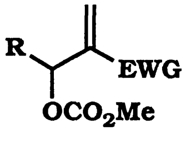
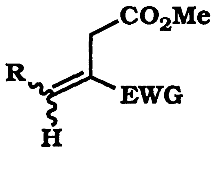
Pd(0)-catalyzed carbonylation of methyl 1-alkyl-2-trialkylsilyl-2-propenyl carbonates required forcing conditions [CO (60 atm), 70 °C] to give respective methyl (*E*)-3-trialkylsilyl-3-alkenoate as a major product along with the (*Z*)-isomer as well as an unusual regioisomeric product, methyl 2-alkyl-3-trialkylsilyl-3-butenoate to various extent.

It has been reported by Tsuji et al.[1)] that allylic carbonates are very susceptible to an oxidative addition to Pd(0) species, undergoing facile decarboxylative carbonylation to give 3-butenoate derivatives in good yields under mild conditions. Their procedure appears to occupy a prominent place among a variety of Pd(0)-catalyzed carbonylations of allylic compounds due to its facility.

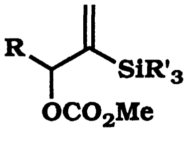
We have been concerned with the regio- and stereoselective carbonylation of 2-[1-(methoxycarbonyloxy)alkyl]acrylates (**1a**) and -acrylonitrile (**1b**) to give predominantly (*E*)-alkylidenesuccinates (**2a**) and (*Z*)-3-cyano-3-alkenoate (**2b**), respectively.[2)] The reaction involves an interesting issue of remarkable steric effects of the two electron-withdrawing groups (EWG) which occupy the 2-position of 1,2-disubstituted π-allylpalladium intermediates. To our best knowledge, few studies on the Pd-mediated reactions regarding these systems have been reported.[3)] We wish to report here a Pd(0)-catalyzed carbonylation of methyl 1-alkyl-2-trialkylsilyl-2-propenyl carbonates (**3**) having electron-donating silyl groups



1a : EWG = CO_2Me
b : EWG = CN



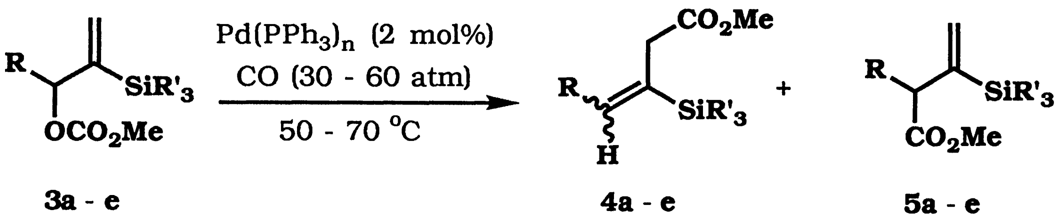
2a : (*E*) major
b : (*Z*) major



3a : R = *n*-Bu, R' = Me
b : R = Me, R'_3 = Me_2Ph
c : R = *i*-Bu, R'_3 = Me_2Ph
d : R =*n*-Bu, R' = Et
e : R = *i*-Bu, R' = Et

instead of EWG. Thus, the reaction may complement our previous work as to both steric and electronic effects of the silyl group on the reactivity of π-allylpalladium intermediates and, in turn, on the stereoselectivity in the carbonylation products.

The required silyl group-substituted allylic alcohols were readily prepared by a known procedure,[4] and derived into the corresponding carbonates **3** in good yields using methyl chloroformate and excess pyridine in CH_2Cl_2. As a typical example, the Pd(0)-catalyzed carbonylation of **3a** (1 mmol) was carried out under CO (30 atm) in the presence of $Pd(OAc)_2$ (2 mol%) and PPh_3 (4 mol%) without solvent at 50 °C for 15 h in a 50-mL micro autoclave. From the reaction mixture was removed the Pd complex through a short column of Florisil with a CH_2Cl_2 eluent and the filtrate was concentrated. The crude products consisting of three components were isolated by HPLC to give methyl (*E*)- and (*Z*)-3-trimethylsilyl-3-octenoate (**4a**)[5] and methyl 2-butyl-3-trimethylsilyl-3-butenoate (**5a**)[6] in the ratio 74 : 10 : 16 in 83% combined yield taking a 39% recovery of **3a** into account. Carbonylation of **3a** was complete under forcing conditions [CO (55 atm), 70 °C] compared to the previous ones.[2] Similarly, carbonylation of **3b** - **3e** proceeded cleanly to give methyl (*E*)-3-silyl-3-alkenoates (**4b** - **4e**) as major products (Eq. 1). The results are given in Table 1.[7] The carbonylation of **3** was accompanied by the formation of methyl 2-alkyl-3-silyl-3-butenoates (**5b** - **5e**) to various extent. We did not observe at all such a type of product as **5** in the cases of carbonylation of **1**.



(1)

Three significant features in the present carbonylation of **3** may be drawn from Table 1: (1) The overall reactivity of **3** toward Pd(0)-catalyzed carbonylation diminished as compared with that of **1** in terms of the reaction time required for completion even at 70 °C under a higher CO pressure. It is evident, however, that carbonylations of **3b** and **3c** both containing a Me_2PhSi group were complete in 40 h (Entries 3 and 7), whereas **3a** with a Me_3Si group required much reaction time (Entry 2). (2) The ratio of (*E*)-**4** to (*Z*)-**4** appears to depend on the bulkiness of both alkyl groups (Me < *n*-Bu ≅ *i*-Bu) and trialkylsilyl groups (Me_3Si ≅ Me_2PhSi < Et_3Si). The high (*E*) over (*Z*) stereoselectivity (93 : 7) was attained with **3d** and **3e**, respectively, having the bulky Et_3Si group (Entries 8 and 10). (3) Unusual, competitive carbonylation took place at the substituted terminus of 1,2-disubstituted π-allylpalladium moiety, giving **5** in a significant amount. The extent of forming **5** in the carbonylation catalyzed by $Pd(PPh_3)_n$ depends evidently upon the inverse of bulkiness of alkyl groups (Me > *n*-Bu > *i*-Bu) (Entries 3, 2, 8, 7, and 10), irrespective of that of trialkylsilyl groups (e.g., **3a** *vs.* **3d**). In addition, a high CO pressure did not change the composition of products (Entry 5).

Table 1. Pd(0)-Catalyzed Carbonylation of **3a** - **e**

Entry	Substrate			Conditions			Yield[a]/%	Composition[b]/%	
		R	R'$_3$	CO/atm	Temp/°C	Time/h		(E)-**4** + (Z)-**4** :	**5**
1	**3a**	^{n}Bu	Me$_3$	30	50	15	83 [c]	84 (88/12) :	16
2	**3a**	^{n}Bu	Me$_3$	55	70	82	88	84 (89/11) :	16
3	**3b**	Me	Me$_2$Ph	60	70	40	81	78 (85/15) :	22
4	**3b**	Me	Me$_2$Ph	60	70	60	97	77 (88/12) :	23
5	**3b**	Me	Me$_2$Ph	100	70	61	72	80 (84/16) :	20
6	**3b**[d]	Me	Me$_2$Ph	90	70	64	89	53 (78/22) :	47
7	**3c**	^{i}Bu	Me$_2$Ph	60	70	40	83	93 (90/10) :	7
8	**3d**	^{n}Bu	Et$_3$	60	70	65	88 [e]	84 (93/7) :	16
9	**3d**[d]	^{n}Bu	Et$_3$	60	70	60	88 [f]	82 (89/11) :	18
10	**3e**	^{i}Bu	Et$_3$	60	70	62	81	89 (93/7) :	11
11	**3e**[d]	^{i}Bu	Et$_3$	60	70	60	81	93 (88/12) :	7

a) Combined yield (**4**+ **5**). b) Determined by capillary GLC (HR-1, 0.25 mm × 25 m). Ratio (E)-**4**/(Z)-**4** given in parentheses. c) **3a** 39% recovered. d) Pd(OAc)$_2$ and dppe used as a catalyst (2 mol%); dppe = bis(diphenylphosphino)ethane.
e) **3d** 2% recovered. f) **3d** 5% recovered.

That the presence of an electron-donating silyl group attached to the olefin is, in principle, less advantageous for the olefin coordination of **3** to Pd(PPh$_3$)$_n$ prior to the oxidative addition may explain the diminished reactivity of **3** toward the Pd(0)-catalyzed carbonylation. In this context, a Me$_2$PhSi group may accelerate the reaction owing to its more electronegative character compared to a Me$_3$Si group, and this is the case. High (E) over (Z) selectivity in **4** can be understood in terms of a highly biased *anti*- over *syn*-1-alkyl-2-trialkylsilyl-π-allylpalladium intermediates which undergo carbonylation.[8] It is noted that the observed regioisomeric carbonylation giving **4** and **5** appears unprecedented.[9] It is difficult to explain why **5** is formed to a significant extent. In order to elucidate the regiochemistry, we have carried out the carbonylation using Pd(OAc)$_2$ and dppe (2 mol%) as a catalyst and found, in the case of **3b**, a remarkable increase in forming **5b** (Entry 6), though the other two cases did not apply (Entries 9 and 11) due presumably to the bulkier butyl groups present. Much investigation requires to gain an insight into the regiocontrol of the novel carbonylation. Since Pd(dppe) holds smaller steric bulk than that of Pd(PPh$_3$)$_2$ moiety, it is presumed that, when the σ-allylpalladium intermediate formed from **3b** enters the crucial carbonylation step, relatively easy accommodation of the Pd(II) moiety on the substituted terminus takes place, resulting in the formation of **5b**.

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3) For reactions of 1,2-disubstituted π-allylpalladium intermediates with soft nucleophiles such as dimethyl sodiomalonate, see B. M. Trost, L. Weber, P. E. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Am. Chem. Soc.*, **100**, 3416 (1978); I. Shimizu and J. Tsuji, *Chem. Lett.*, **1984**, 233; M. Ahmar, J.-J. Barieux, B. Cazes, and J. Goré, *Tetrahedron*, **43**, 513 (1987).
4) R. K. Boeckman, Jr., D. M. Blum, B. Ganem, and N. Halvey, *Org. Synth.*, Coll. Vol. 6, 1033 (1988).
5) Data on (*E*)-**4a**: ^{1}H NMR (90 MHz $CDCl_3$, TMS) 0.07(s, 9H), 0.90(br t, 3H), 1.37(m, 4H), 2.10(m, 2H), 3.14(br s, 2H), and 5.93(tt, J = 6.8, 1.1 Hz, 1H); ^{13}C NMR(22.5 MHz) -1.5, 14.0, 22.5, 28.7, 31.4, 34.6, 51.5, 133.0, 144.5, and 172.6; IR(neat) 1741 cm^{-1}; GC-MS(CI) m/z 229(M+1). (*Z*)-**4a**: ^{1}H NMR 0.08(s, 9H), 0.83(br t, 3H), 1.25(m, 4H), 2.07(m, 2H), 3.00(br s, 2H), 3.59(s, 3H), and 5.97(t, J = 7.5 Hz, 1H); IR(neat) 1743 cm^{-1}; GC-MS(CI) m/z 229(M+1). For the chemical shifts of diagnostic vinylic protons in (*E*)- and (*Z*)-vinylsilanes (underlined), see, T. H. Chan, W. Mychajlowskij, and R. Amouroux, *Tetrahedron Lett.*, **1977**, 1605.
6) Data on **5a** : ^{1}H NMR 0.11(s, 9H), 0.89(br t, 3H), 1.17(m, 6H), 3.13(m, 1H), 3.65(s, 3H), 5.50(d, J = 2.0 Hz, 1H), and 5.78(d, J = 2.0 Hz, 1H); IR(neat) 1738 cm^{-1}; GC-MS(CI) m/z 229(M+1).
7) All new compounds **4** and **5** given in Table 1 were characterized by NMR and GC-MS.
8) It is controversial that the crucial carbonyl insertion step into the presumed π-allylpalladium methoxide proceeds via either 3-butenoyl- or rather methoxycarbonyl-palladium intermediate. For a detailed discussion, see Y.-J. Kim, K. Osakada, K. Sugita, T. Yamamoto, and A. Yamamoto, *Organometallics*, **7**, 2182 (1988).
9) For a Pd(0)-catalyzed carbonylation of 2-cyclohexen-1-ol derivatives, see S. Murahashi, Y. Imada, Y. Taniguchi, and S. Higashiura, *Tetrahedron Lett.*, **29**, 4945 (1988).

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