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Highly Regioselective Anti-Markovnikov Palladium-Borate-Catalyzed Methoxycarbonylation Reactions: Unprecedented Results for Aryl Olefins

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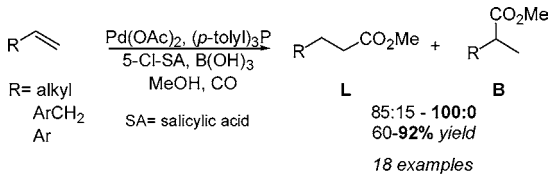
ABSTRACT



A general, highly efficient and regioselective methoxycarbonylation, by means of a palladium-salicylicborate-catalyzed protocol, of terminal alkyl and aryl olefins is described. The substrates include aliphatic alkenes, allylbenzenes, and styrene derivatives. The yields are very good (60–92%) and the regioselectivity, in favor of the linear ester, is up to quantitative—unprecedented in the case of styrenes.

Carbon−carbon bond formation is a long-standing challenge to organic chemists and several catalytic approaches have been developed during the past decades.[1] The palladium-catalyzed hydroesterification (Reppe carbonylation) is well-known as a powerful strategy—due to its atom economy—for the preparation of esters from easily available unsaturated moieties.[2] There are numerous methods for the synthesis of branched esters in racemic or asymmetric fashion.[3] However, only a few protocols lead to linear esters in reasonable regioselectivity.[4] As a matter of fact, all instances rely on substrate specificity, and the ligand is tailored to the substrate.[2b]

Given that long-chain esters play a crucial role in the manufacture of lubricants and surfactants,[5] together with the fact that petroleum derivatives are eligible candidates as raw materials, we believe that the establishment of a general and highly regioselective hydroesterification protocol still constitutes a significant challenge for homogeneous and heterogeneous catalysis. Herein, we wish to report our results concerning the first palladium-borosalicylic acid-catalyzed methoxycarbonylation of alkenes—including long-chain olefins, allylbenzenes, and styrenes—in high regioselectivity for the linear product.

During studies on the Pd-catalyzed methoxycarbonylation of ethylene, salicylborates were found to be quite effective acid promoters.[6] We found that, by using in situ generated borosalicylic acid (BSA) (Scheme 1), 1-decene gave the

Scheme 1. Formation of the Salicylborates

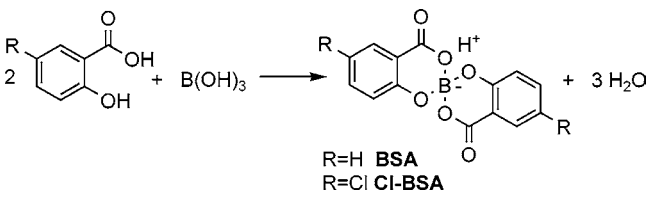


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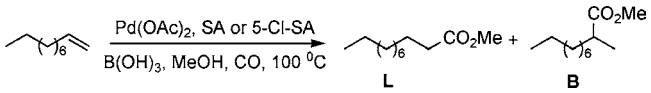
Table 1. Selected Screening for Methoxycarbonylation of 1-Decene with $Pd(OAc)_2$, Using BSA and 5-Cl-BSA[a]



entry	borate (mol %)[b]	$Pd(OAc)_2$ (mol %)	phosphine (mol %)	CO (psi)	time (h)	conversion (%)[c]	L/B ratio	yield (%)[d]	Pd black
1	BSA (10)	1	PPh_3 (10)	300	15	100	97:3	55	yes
2	BSA (20)	1	PPh_3 (10)	300	12	100	92:8	74	yes
3	BSA (20)	1.5	PPh_3 (15)	300	20	100	87:13	71	yes
4	BSA (20)	1	(*m*-tolyl)$_3$P (10)	300	15	85	95:5	64	no
5	5-Cl-BSA (10)	1	PPh_3 (15)	300	15	100	95:5	69	no
6	5-Cl-BSA (10)	1.5	PPh_3 (15)	300	15	100	87:13	78	no
7	5-Cl-BSA (10)[e]	1.5	PPh_3 (15)	400	18	100	96:4	64	yes
8	5-Cl-BSA (10)	1	(*o*-tolyl)$_3$P (10)	300	20	5			no
9	5-Cl-BSA (10)	1.5	(*p*-tolyl)$_3$P (10)	400	18	100	97:3	92	no

[a] The reactions were performed with 1 mmol of 1-decene in 3 mL of MeOH at 100 °C. [b] Prepared in situ in a 2:1 ratio between the salicylic acid and $B(OH)_3$. [c] Determined by GC. [d] Isolated yields. [e] MeOH/Et_2O (1:1) as solvent.

linear ester in up to 97% selectivity under 300 psi of CO. Unfortunately, palladium black plating was observed, which makes this approach of no utility.

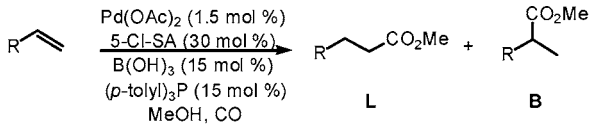
Preliminary experiments to determine the optimum phosphine ligands (see Table 1 for a selected screening) revealed that the more electron-rich tris-*p*-tolylphosphine was a suitable ligand, and 5-chloroborosalicylic acid (Table 1, entry 9) was a better promoter than BSA itself, leading to the undecanoic methyl ester in comparable and excellent selectivity, but in higher yield and without the undesirable formation of Pd black. With preformed Cl-BSA,[7] only 60% conversion and 90% selectivity was achieved. In all attempts to use bidentate phosphines, such as dppe, dppb, dppp, and *rac*-BINAP, as well as more hindered aryl phosphines, only low or no conversion was observed.

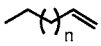
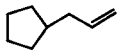
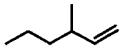
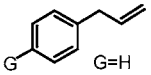
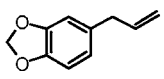
Having found the best catalytic system for the hydroesterification reaction, we applied the same conditions to other aliphatic alkenes (Table 2, entries 2−4) and quite similar selectivities were obtained. It is worthy of note that such high regioselectivities are highly unusual for Pd systems involving monodentate phosphine ligands, and until now only achievable by using specific bulky bidentate phosphine ligands.[4a]

When allylbenzenes (Table 2, entries 5−7) were used instead, after a small increase in CO pressure, the selectivity for our system proved to be higher than previously reported,[8] and only ca. 5% of double bond isomerization was observed by GC analysis.

We were gratified to observe that, when the protocol was investigated for styrene derivatives (Table 3), an unprecedented regioselectivity was achieved (85 to 100%), in favor of the linear ester. It is worth mentioning that the best reported selectivity for such hydroesterifications of styrene is 85%.[9] Even the more hindered geminal disubstituted styrenes (Table 3, entries 9−11) were susceptible to hy-

Table 2. Methoxycarbonylation of 1-Alkenes and Allylbenzenes with $Pd(OAc)_2$ in the Cl-BSA System[a]



entry	substrate	time (h)	L/B ratio	yield (%)[b]
1	 n=6	18	97:3	92
2	n=10	18	98:2	60
3		24	90:10	70
4		22	98:2	75
5	 G=H	18	97:3	92
6	OMe	18	98:2	60
7		24	90:10	74

[a] The reactions were performed in a 2 mmol scale in 3 mL of MeOH, under 400 psi of CO, at 100 (entries 1−4) and 110 °C (entries 5−7). The L/B ratio was determined by ^1H NMR. No Pd black plating was observed. [b] Isolated yields.

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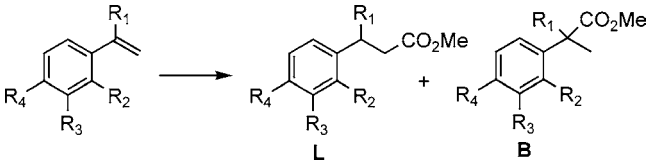
(7) Cl-BSA was prepared by refluxing 5-Cl-SA and $B(OH)_3$, in a 2:1 ratio, in toluene until 3 equiv of H_2O was collected.

Table 3. Methoxycarbonylation of Styrenes with $Pd(OAc)_2$ in the Cl-BSA System[a]



entry	R_1	R_2	R_3	R_4	time (h)	L/B ratio	yield (%)[b]
1	H	H	H	H	24	90:10	66
2	H	H	H	^{t}Bu	24	88:12	91
3	H	H	H	Cl	40	85:15	72
4	H	H	H	F	48	90:10	72
5	H	Me	H	H	24	97:3	60
6	H	Br	H	H	24	98:2	65
7	H	H	OMe	H	24	85:15	84
8	H	H	Cl	H	36	89:11	66
9	Me	H	H	H	48	97:3	74
10	Me	H	H	Cl	48	95:5	71
11	Ph	H	H	H	48	100:0	73

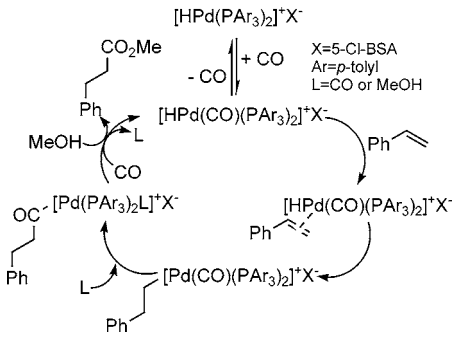
[a] The reactions were performed with the same conditions reported in Table 2, under 500 (600 for entries 9−11) psi of CO, at 110 °C. The L/B ratio was determined by ^{1}H NMR. No Pd black plating was observed. [b] Isolated yields.

droesterification in up to quantitative regioselectivity. However, the protocol failed for substrates containing a nitrogen atom, such as 1-allylimidazole and 4-vinylpyridine, and palladium black deposition was observed.

In mechanistic terms, a viable species that could be the starting point for the catalytic cycle is a palladium(II) hydride, as previously proposed in the literature.[10] Assuming that the borosalycilic counterion is weakly coordinated to the palladium(II) species, it would favor the cationic reaction pathway, which would support the observed selectivity. Although the exact role of the salicylborate remains unclear, it is known that the counteranion is critical in the determination of the regioselectivity in hydroesterification reactions.[11]

Another important feature of the borosalicylic counterion is its bulkiness, which, by hindrance, would favor the formation of the linear esters. Possible evidence for such an effect is the failure, using this protocol, in the methoxycarbonylation of internal olefins, such as 2-octene and 1,2-dihydronaphthalene. A postulated mechanism is depicted in Scheme 2, based on a pathway proposed previously for the hydroesterification of styrene with *p*-TSA as the acid promoter.[10a,b]

Scheme 2. Suggested Mechanism for the Methoxycarbonylation of Styrene by Means of Palladium Salicylborate Catalysis



In summary, this Letter describes the high catalytic activity of Pd-borates that allows the preparation of one-carbon elongated esters from olefins in very good isolated yields and good to outstanding regioselectivity. This is a general and highly effective entry for the synthesis of linear esters—unprecedented for aryl olefins—and is of significant industrial interest.

Acknowledgment. We are indebted to SASOL Technology for financial support of this work.

Supporting Information Available: A general procedure for the methoxycarbonylation reaction is described and full characterization of new compounds is reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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