

The intriguing methoxycarbonylation of trimethylsilylacetylene in the presence of Drent's catalytic system

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The alkoxy carbonylation of trimethylsilylacetylene has been studied in order to develop an atom economic sustainable synthesis of 2-(trimethylsilyl) acrylates, a family of valuable intermediates. Pd(OAc)₂ in combination with CH₃SO₃H and diphenyl-(pyridin-2-yl)phosphine or diphenyl-(6-methylpyridin-2-yl)phosphine is an active catalyst for the reaction affording mixtures of the sought 2-(trimethylsilyl)acrylate and the isomeric 3-(trimethylsilyl) acrylate. The phosphine ligand has a dramatic effect on the reaction. When employing diphenyl-(pyridin-2-yl)phosphine, it is necessary to carry out the reaction at 80°C in order to observe a modest catalytic activity, and the product is an almost equimolecular mixture of the two isomeric esters. On the contrary, when employing diphenyl-(6-methylpyridin-2-yl)phosphine, the reaction proceeds under much milder conditions affording with high rate (turnover frequency [TOF] up to 1200 h⁻¹) and selectivity (>95%) of the sought 2-(trimethylsilyl)acrylate. The reaction conditions have been optimized, and the effects of phosphine/palladium, acid/palladium, reaction time, temperature, and CO pressure have been investigated.

KEYWORDS

alkyne carbonylation, diphenyl-(6-methylpyridin-2-yl)phosphine, diphenyl-(pyridin-2-yl)phosphine, palladium, trimethylsilylacetylene

1 | INTRODUCTION

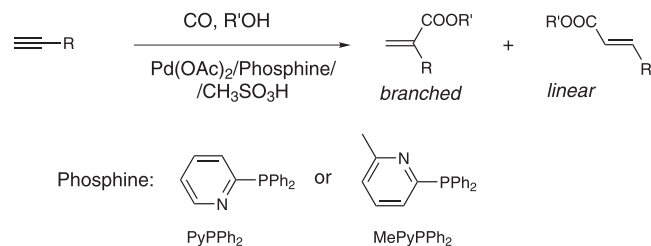
The transition metal-catalyzed mono-alkoxy carbonylation of alkynes (see, e.g., Scheme 1) is a powerful synthetic tool affording in one step α,β -unsaturated carboxylic esters from widely accessible starting compounds. There is a continuing interest in developing this reaction because it is characterized by 100% atom economy. Furthermore, many variations of the parent reaction are

known and practiced,^[1–6] such as oxidative carbonylation approaches leading to the synthesis of propiolate esters or maleic diesters.^[7,8]

In early 1990s, Drent et al. at Shell discovered that palladium acetate in combination with methanesulphonic acid (CH₃SO₃H) and diphenyl-(pyridin-2-yl)phosphine (PyPPh₂) or diphenyl-(6-methylpyridin-2-yl)phosphine (MePyPPh₂) is a very efficient catalyst for alkoxy carbonylation of alkynes.^[9,10] When applied to

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SCHEME 1 A general scheme of the alkoxy carbonylation of terminal alkynes

terminal alkynes (see Scheme 1), the process usually proceeds with high regioselectivity (e.g., >95%) towards the branched product allowing to obtain in one step 2-substituted- α,β -unsaturated carboxylic esters that are key intermediates in industrial^[11] and fine chemistry.^[12,13]

Works by Drent other researchers and us^[8–11,13–19] showed that the presence of the 2-pyridyl group in the phosphino ligand plays a crucial role, because when such type of group is not present, the efficiency of the catalytic system is by far lower.

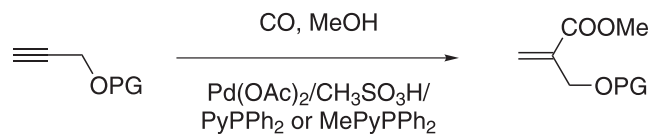
On the other hand, the presence of substituents on the pyridyl ring contributes to a minor extension to determine both rate and regioselectivity. Specifically, it appears that MePyPPh₂ is somewhat more efficient than PyPPh₂ allowing for slightly higher reaction rates and also increasing the selectivity towards the branched isomer.

It is generally assumed that the regioselectivity of the reaction is dictated by steric repulsion between the alkyne R group and the phosphine which favors the formation of the branched product^[8,9,16,17]; hence, the greater regioselectivity obtained with MePyPPh₂ has to be attributed to its higher sterical hindrance.

Our research group has long been interested in the study of innovative sustainable processes for the synthesis of fine chemicals^[20,21] using innovative catalytic systems.^[22,23] Recently, we showed that Drent's system successfully catalyzes the selective mono-carbonylation of protected propargyl alcohols affording turnover numbers (TONs) of up to 2000 with almost complete selectivity towards the branched isomer (Scheme 2).^[24]

Searching for the most suitable protecting group (PG) to employ in the reaction, we found that no reaction occurs when the PG is a trimethylsilyl (TMS). This finding aroused our attention because silicon-containing PGs such as TMS are widely employed today in organic synthesis. Hence, the development of a process for the carbonylation of "silicon-protected" alkynes would be useful in designing new synthetic schemes.

According to these considerations, we deemed it interesting to study the carbonylation of the commercially available trimethylsilylacetylene which is the simplest alkyne containing a silicon (protecting) group. It is



PG: Bn and Ac

No reaction when PG = TMS!

SCHEME 2 The alkoxy carbonylation of protected propargyl alcohol

to remark that besides being the simplest alkyne containing a silicon group, trimethylsilylacetylene is the substrate in which the presence of a silicon atom is expected to have the largest effects being in α position with respect the C \equiv C triple bond.

To the best of our knowledge, the alkoxy carbonylation of trimethylsilylacetylene has been scantily investigated in the past. Takeuchi and Sugiura demonstrated that ethoxy carbonylation of trimethylsilylacetylene is efficiently catalyzed by [PdCl₂(dppf)] but only in combination with SnCl₂·2H₂O yielded linear (*E*)-3-trimethylsilylprop-2-enoate with >80% yield.^[25] In contrast, only 25% yield of branched methyl 2-(trimethylsilyl)acrylate was reached by Reetz et al. via Pd(OAc)₂/2-pyrimidyl-diphenylphosphine-catalyzed methoxy carbonylation reaction.^[14] In 2010, a photochemical approach was developed by Mathur et al. in the presence of iron pentacarbonyl Fe(CO)₅, which however allowed to recover methyl 2-(trimethylsilyl)acrylate in low yields.^[26]

All this in mind, we were interested in developing a sustainable synthesis of 2-(silyl)acrylates that are useful intermediates allowing a broad spectrum of organic transformations.^[27,28]

2 | EXPERIMENTAL

2.1 | Materials

All the operations were carried out under argon in Schlenk-type glassware. Methanol (Sigma-Aldrich) was distilled from magnesium, whereas amylene-stabilized dichloromethane (Sigma-Aldrich) was distilled from CaH₂ before use. Diphenyl-(pyrid-2-yl)phosphine (PyPPh₂) and diphenyl-(6-methyl-pyrid-2-yl)phosphine (MePyPPh₂)^[29] were synthesized in accordance to literature methods. Trimethylsilylacetylene and methanesulfonic acid were commercial products (Sigma-Aldrich) and used as received. Pd(OAc)₂ was purchased from Engelhard Industries. High purity CO was obtained by SIAD. The ¹H and ¹³C NMR spectra were registered in CDCl₃ solutions on

a Bruker AVANCE 300 spectrometer operating at 300.1 and 75.44 MHz, respectively. Gas-liquid chromatography (GLC) analyses were performed on an Agilent 6850 gas chromatograph; gas chromatography-mass spectrometry (GC-MS) analyses were performed on a HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector.

2.2 | Carbonylation experiments

The carbonylation experiments were carried out in a magnetically stirred stainless steel autoclave (total volume 150 ml) connected to a thermostatic bath in order to maintain the reaction temperature constant within $\pm 1^\circ\text{C}$. As an example, the experimental details for Entry 5 of Table 2 are reported.

Under inert atmosphere, in a Schlenk flask containing a small magnetic bar were introduced 10 ml of anhydrous MeOH, 42.70 mg (1.5×10^{-1} mmol) of diphenyl-(6-methyl-pyridin-2-yl)phosphine, and 1.1 mg of Pd(OAc)₂ (5.0×10^{-3} mmol). Then, under nitrogen were added 0.72 ml (5.0 mmol) of trimethylsilylacetylene and, finally, 10.0 μl (1.5×10^{-1} mmol) of methanesulfonic acid. The resulting yellow-orange solution was transferred via cannula into the autoclave. Then, the reactor was pressurized with 30 atm of CO and heated at 60°C and kept under constant magnetic stirring. After 3 h, the autoclave was cooled to room temperature, and the residual gas was carefully vented off. The raw reaction mixture was analyzed by GLC to determine substrate conversion and product composition. The reaction crudes were purified by flash chromatography (silica gel, 60 Å, 70–230 mesh, and a 1:1 mixture of ethylacetate and *n*-hexane) to give 2-(trimethylsilyl)acrylate as clear colorless oil (65% yield).

2.3 | Acrylates characterization

2.3.1 | Methyl 2-(trimethylsilyl)acrylate

¹H NMR (300 MHz, CDCl₃): δ 6.75 (d, 1H, $J = 3.0$ Hz), 5.99 (d, 1H, $J = 3.0$ Hz), 3.71 (s, 3H), 0.14 (s, 9H).

¹³C NMR (75.44 MHz, CDCl₃): δ 168.7 (1C), 149.0 (1C), 138.6 (1C), 50.8 (1C), -2.0 (1C).

GC-MS (m/z): 157 (M-H)⁺, 143 (M-CH₃)⁺, 127 (M-OCH₃)⁺, 113 (M-CH₃)₃⁺, 73 Si(CH₃)₃⁺.

2.3.2 | Methyl 3-(trimethylsilyl)acrylate

¹H NMR (300 MHz, CDCl₃): δ 7.22 (d, 1H, $J = 17.9$ Hz), 6.21 (d, 1H, $J = 17.9$ Hz), 3.71 (s, 3H), 0.11 (s, 9H).

¹³C NMR (75.44 MHz, CDCl₃): δ 165.6 (1C), 143.6 (1C), 133.2 (1C), 50.9 (1C), -2.5 (1C).

GC-MS (m/z): 157 (M-H)⁺, 143 (M-CH₃)⁺, 127 (M-OCH₃)⁺, 113 (M-CH₃)₃⁺, 73 Si(CH₃)₃⁺.

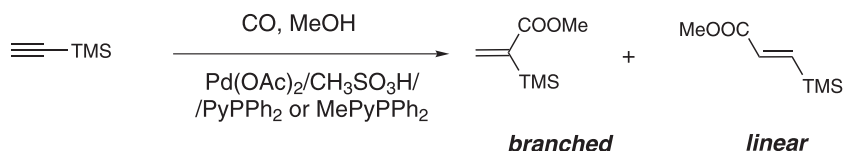
3 | RESULTS AND DISCUSSION

In initial experiments (Scheme 3 and Table 1), the methoxycarbonylation of trimethylsilylacetylene was carried out in the presence of the catalytic system Pd(OAc)₂/CH₃SO₃H/PyPPh₂. The adopted reaction conditions were those usually employed with Drent's catalyst^[9,10,12,24] that imply the use of an excess of the phosphine, reaction temperature in the 50°C to 80°C range, P(CO) in the 10- to 50-atm range.

The reaction turned out to be a challenging task, and after a certain number of preliminary experiments, we found that the best substrate conversions were obtained when the reaction was carried out in a mixture of dichloromethane/methanol (see Table 1).

With the catalyst composition set at Pd/CH₃SO₃H/PyPPh₂ = 1/20/20, it was necessary to carry out the reaction at 80°C in order to observe a reasonable catalytic activity. Working with a substrate/palladium molar ratio of 1000:1 and a P(CO) pressure of 20 atm, 62% of alkyne conversion was attained after 24 h (Entry 1 of Table 1).

GLC and GC-MS analyses showed that the product was a 61/39 mixture of methyl 2-(trimethylsilyl)acrylate (*branched isomer*) and methyl 3-(trimethylsilyl)acrylate (*linear isomer*), respectively. Given the high activity of Drent's catalyst with aliphatic alkynes, such as propyne, allowing to obtain turnover frequency (TOF) numbers of about 40,000 h⁻¹ with selectivities towards the branched isomer greater than 98%, the obtained result appears quite poor indicating that the presence of the TMS group has a dramatic negative effect on both the reaction rate



SCHEME 3 The methoxycarbonylation of trimethylsilylacetylene

TABLE 1 Methoxycarbonylation of trimethylsilylacetylene in the presence of the catalytic system Pd(OAc)₂/CH₃SO₃H/PyPPh₂

Entry	Sub./Pd	PyPPh ₂ /Pd	Acid/Pd	P(CO) (atm)	Conv. (%) ^a	Σ _{TON}	TOF (h ⁻¹)	Selectivity ^{a,b}	
								B(%)	L(%)
1	1000	20	20	20	62	620	26	61	39
2 ^c	500	20	20	40	70	350	15	57	43
3 ^c	500	10	10	40	68	340	14	50	50

Note: Reaction conditions: trimethylsilylacetylene = 10.0 mmol; Pd(OAc)₂ = 0.010 mmol; PyPPh₂ = 0.10 mmol; CH₃SO₃H = 0.10 mmol; solvent/reactant: CH₂Cl₂ (10.0 ml)/CH₃OH (2.0 ml); reaction time = 24 h; T = 80°C.

Abbreviations: GLC, gas-liquid chromatography; TOF, turnover frequency.

^aBy GLC.

^bB: branched isomer; L: linear isomer.

^cPd(OAc)₂ = 0.020 mmol; PyPPh₂ = 0.20 mmol; CH₃SO₃H = 0.20 mmol.

and the regioselectivity. In particular, we were astonished by the low branched to linear isomer ratio because we expected that the high hindrance of the TMS group would contribute to strongly favor the formation of the branched product.

A few other experiments (Entries 2–3 of Table 1) were carried out to increase the efficiency of the process and assess the effects of catalyst composition, temperature, and P(CO).

When the substrate to palladium ratio was decreased at 500:1 and the pressure was increased to 40 atm, alkyne conversion slightly increased (70%) whereas the branched/linear isomer ratio decreased to 57/43. In a third experiment, both the CH₃SO₃H/Pd and PPh₂Py/Pd ratios were decreased to 10:1. The reaction allowed to obtain 68% conversion affording a 50/50 mixture of branched and linear product (substrate/palladium = 500, Entry 3, Table 1).

Deceived by these modest results, we decided to test MePyPPh₂ as the ligand. As a matter of fact, according to the seminal works of Gadge and Bhanage^[8] and Drent et al.^[9,10] on propyne carbonylation, the catalytic activity of the methylated ligand is expected to be slightly higher (about 20%) than that of PyPPh₂. Furthermore, a higher efficiency of MePyPPh₂ is also predicted by the density functional theory (DFT) studies carried out by Crawford et al.^[18,19] We were interested to test MePyPPh₂ also because we reasoned that if steric factors were at the basis of the deceiving results achieved with PyPPh₂, their effects would be even more marked when employing the bulkier MePyPPh₂, allowing to determine the reasons for the scarce catalytic activity.

Surprisingly, we observed that the use of the methylated ligand changes dramatically the course of the reaction. In fact, in a first experiment carried out under the same experimental conditions of Table 1 in the presence of MePyPPh₂ with an alkyne/palladium ratio of 1000:1, almost complete substrate conversion was achieved in

24 h (Entry 1 of Table 2). Also, more strikingly, the reaction proceeded with a very high selectivity (96%) in favor of the branched isomer.

Nowadays, the development of new chemical processes has to take into consideration also the sustainability, so that tests were planned in order to explore if it were possible to avoid the use of the “non-green” dichloromethane in the reaction medium. Accordingly, the following experiments were carried out in pure methanol, fulfilling the role of solvent and reactant at the same time, and the reaction temperature was decreased to 60°C. We were delighted to find that the reaction proceeds efficiently also in the absence of dichloromethane giving 87% substrate conversion in only 3 h accompanied by high selectivity (96%) in the branched isomer (Entry 2 of Table 2).

Looking for complete substrate conversion, the reaction time was increased to 6 h (Entry 3 of Table 2) and then to 24 h (Entry 4 of Table 2). Even at long reaction times, we failed to obtain complete substrate conversion, but it is worth noting that, for synthetic purposes, the final conversion achievable in 6 h appears satisfactory.

Aiming at understanding the factors affecting catalyst activity, some experiments were carried out using different catalyst compositions, that is, using different phosphine to palladium ratios. Two reactions were carried out at 3 h under the same conditions used for Entry 1 of Table 2 except for the phosphine/acid/palladium ratio that in one case was 10:10:1 and in the other 30:30:1; the relevant data are reported in Entries 5 and 6 of Table 2, respectively.

On decreasing the phosphine to palladium ratio to 10:1, both the substrate conversion and the regioselectivity slightly decreased. On the contrary, when the phosphine to palladium ratio was set at 30:1, almost complete (96%) substrate conversion was obtained, and the regioselectivity remained very good. Prompted by these outstanding results, we carried out a further set of

TABLE 2 Methoxycarbonylation of trimethylsilylacetylene in the presence of the catalytic system Pd(OAc)₂/CH₃SO₃H/MePyPPh₂: influence of the phosphine/palladium molar ratio

Entry	Sub./Pd	Solvent	Phosp./Pd	Acid/Pd	T (°C)	t (h)	Conv. (%) ^a	TOF (h ⁻¹)	Selectivity B(%) ^{a,b}
1 ^c	1000	CH ₃ OH/CH ₂ Cl ₂	20	20	80	24	96	41	96
2	1000	CH ₃ OH	20	20	60	3	87	290	96
3	1000	CH ₃ OH	20	20	60	6	93	155	96
4	1000	CH ₃ OH	20	20	60	24	95	40	96
5	1000	CH ₃ OH	10	10	60	3	85	280	92
6	1000	CH ₃ OH	30	30	60	3	96	320	96
7 ^d	4000	CH ₃ OH	10	10	60	3	53	686	92
8 ^d	4000	CH ₃ OH	20	20	60	3	66	880	94
9 ^d	4000	CH ₃ OH	30	30	60	3	73	970	95

Note: Reaction conditions: trimethylsilylacetylene = 10.0 mmol; Pd(OAc)₂ = 0.010 mmol; solvent: CH₃OH (10.0 ml); P(CO) = 30 atm; T = 60°C.

Abbreviations: GLC, gas-liquid chromatography; TOF, turnover frequency.

^aBy GLC.

^bB: branched isomer.

^cCH₃OH (2 ml); CH₂Cl₂ (10 ml).

^dPd(OAc)₂ = 0.0025 mmol.

TABLE 3 Methoxycarbonylation of trimethylsilylacetylene in the presence of the catalytic system Pd(OAc)₂/CH₃SO₃H/MePyPPh₂: influence of temperature and P(CO)

Entry	T (°C)	P(CO) (atm)	Conversion ^a (%)	Σ _{TON}	TOF (h ⁻¹)	Selectivity B(%) ^{a,b}
1	50	30	50	2000	660	95
2	60	30	73	2920	970	95
3	70	30	82	3280	1090	94
4	80	30	90	3600	1200	93
5	60	15	55	2200	730	95
6	60	20	80	3200	1060	95
7	60	40	60	2400	800	94

Note: Reaction conditions: trimethylsilylacetylene = 10.0 mmol; solvent: CH₃OH (10.0 ml); Pd(OAc)₂ = 0.0025 mmol; substrate/palladium/acid/phosphine = 4000:1:30:30; t = 3 h.

Abbreviations: GLC, gas-liquid chromatography; TOF, turnover frequency.

^aBy GLC.

^bB: branched isomer.

experiments in which the substrate to palladium molar ratio was increased to 4000:1 (Entries 7–9 of Table 2). Also, these experiments confirmed the important role played by the ligand to palladium ratio and the benefits achievable using a large excess of phosphine.

In fact, using a phosphine/palladium ratio of 30:1 (Entry 9), it was possible to obtain a very interesting TON of about 3000 in 3 h. It must be pointed out that on increasing the substrate to palladium ratio, the dependence of the regioselectivity on the P:Pd ratio remained unchanged and that at 30:1, an excellent branched/linear isomer ratio of 95:5 was obtained.

Further experiments were carried out to assess the effects of temperature and CO pressure, all other reaction conditions being kept constant (substrate/palladium = 4000, phosphine/palladium = 30, acid/phosphine = 1, reaction time = 3 h). From the relevant results (Table 3), it appeared that on increasing the temperature from 50°C to 80°C, the reaction rate increased progressively, but that was accompanied by a decrease in selectivity. Accordingly, it seems that the best compromise was reached when the reaction was carried out at 60°C.

Inspection of the data obtained at 60°C (Entries 2 and 5–7 of Table 3) shows that the conversion of the reaction

Entry	Acid/phosphine	Conversion ^a (%)	Selectivity <i>B</i> (%) ^{a,b}
1	0.5	17	94
2	1	73	95
3	2	52	92

TABLE 4 Methoxycarbonylation of trimethylsilylacetylene in the presence of the catalytic system Pd(OAc)₂/CH₃SO₃H/MePyPPh₂: influence of acid/phosphine molar ratio

Note: Reaction conditions: trimethylsilylacetylene = 10.0 mmol; solvent: CH₃OH (10.0 ml); Pd(OAc)₂ = 0.0025 mmol; substrate/palladium = 4000; phosphine/palladium = 30; P(CO) = 30 atm; *T* = 60°C; *t* = 3 h.

^aConversion and selectivity were determined by gas chromatography.

^b*B*: branched isomer.

increases on increasing the P(CO) until a maximum conversion was attained working at 20 atm. At higher pressure, the reaction slowed down, probably because of competition between CO and the substrate for coordination to the metal center.

Final investigations were devoted to verify the influence of the acid/phosphine ratio. Accordingly, we carried out some reactions in which the acid/phosphine ratio was changed in the 0.5:1–2:1 range (Table 4); all the other conditions were kept constant (substrate/Pd(OAc)₂ = 4000, phosphine/palladium = 30, P(CO) = 30 atm, temperature = 60°C, reaction time = 3 h).

The highest conversion was achieved at 1:1 acid/phosphine molar ratio. A decrease (Entry 1) or increase (Entry 3) of acid/phosphine ratio brought to a decrease of conversion. It is also worth to note that when the reaction was carried out using an acid/phosphine ratio greater of 1:1, we observed the formation of palladium black in the reaction crudes. Therefore, the lower substrate conversion obtained when an excess of acid is present is due, at least partially, to a lower catalyst longevity. Also, this aspect contrasts with what is observed in carbonylation of simple aliphatic alkynes that is preferably carried out in the presence of two equivalents of acid per mole of ligand.^[9–11]

4 | CONCLUSIONS

In conclusion, we have developed an efficient protocol for the carbonylation of trimethylsilylacetylene. According to the good TON and TOF obtained, the process appears as a practically feasible one. Owing to the complete atom economy, it represents a sustainable synthetic route to 2-trimethylsilylacrylates, a family of intriguing intermediates until now accessible only through multistep synthetic schemes.^[30]

Beyond the synthetic success, this study reveals that, in spite of the close structural similarity, the difference in catalytic activity between MePyPPh₂ and PyPPh₂ is actually greater than it appeared from all previous

studies. The most intriguing results are connected with the large differences in regioselectivity observed with the two ligands. The higher selectivity towards acrylates observed when employing MePyPPh₂ has been attributed to its greater steric hindrance; however, our results indicate that also electronic effects are at work. This aspect is worthy of further investigations.

Moreover, our results suggest that electronic and steric factors play a crucial role in determining the regioselectivity of the reaction.

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AUTHOR CONTRIBUTIONS


Roberto Sole: Conceptualization; data curation; investigation; methodology; project administration; supervision. **Alberto Scrivanti:** Conceptualization; data curation; funding acquisition; investigation; project administration; supervision. **Md. Mahbubul Alam:** Investigation; methodology; visualization. **Valentina Beghetto:** Conceptualization; funding acquisition; project administration; resources; validation; visualization.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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