Palladium-Catalyzed Carboxylation of Vinyl Triflates. Electrosynthesis of α, β-Unsaturated Carboxylic Acids

Anny Jutand *, Serge Négri

Ecole Normale Supérieure, Département de Chimie, URA CNRS 1679, 24 Rue Lhomond, 75231 Paris Cedex 5. France

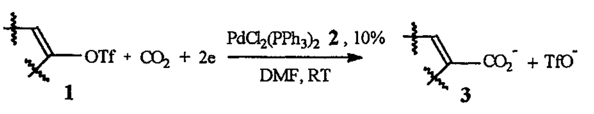
Fax: 33 1 44 32 33 25; E-mail: jutand@chimene.ens.fr

Received 25 February 1997

Abstract: The electrocarboxylation of vinyl triflates performed with carbon dioxide and a catalytic amount of $PdCl_2(PPh_3)_2$ affords α,β-unsaturated carboxylic acids. The reactivity of vinyl triflates has been reversed in the presence of an electron source, since they now react with electrophiles. The reaction proceeds by an activation of the C-O bond of the vinyl triflate by a palladium(0) complex followed by an activation by electron transfer, of the vinylpalladium(II) complex formed in the oxidative addition.

Vinyl triflates usually undergo cross-coupling reactions with nucleophiles [1] such as hydrides [2], organostannanes [3,4] and alkynes [5] in the presence of a catalytic amount of palladium complexes, affording substituted alkenes. They also react with alkenes (Heck reaction) [6] and allenes.[7] The reactions are supposed to proceed *via* a nucleophilic attack on a σ-vinylpalladium(II) complex resulting from the oxidative addition of a palladium(0) complex with the vinyl triflate.[3]

We wish to report that it is possible to invert the reactivity of vinyl triflates **1** and to bring them to react with electrophiles, in the presence of an electron source and a palladium catalyst. In the presence of carbon dioxide as the electrophile, α,β-unsaturated carboxylic acids are synthesized in good yields with $PdCl_2(PPh_3)_2$ **2** as catalyst (Scheme 1, Table 1).

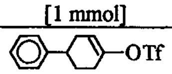
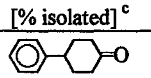
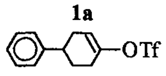
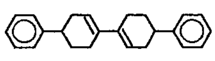
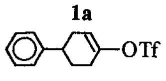
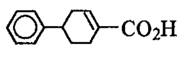
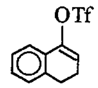
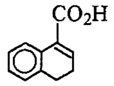
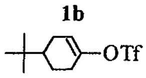
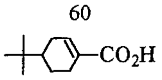
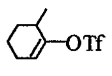
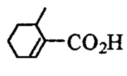
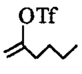
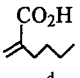
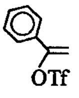
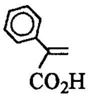


Scheme 1

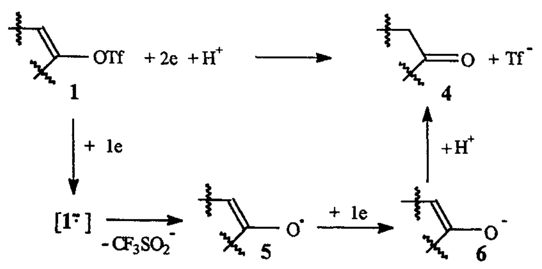
Vinyl triflates **1** are electroactive compounds. Their reduction peak potentials are gathered in Table 2. The direct electrochemical reduction of vinyl triflates, performed in the absence of any catalyst, provided after hydrolysis, the corresponding ketone **4** in quantitative yield (Table 1, entry 1, Scheme 2).

This shows that the direct reduction of vinyl triflates **1** results in an activation and cleavage of the O-S bond in the triflate group. The first electron transfer most probably affords the radical anion $\mathbf{1}^{\bullet-}$ (Scheme 2). After cleavage of the O-S bond, a vinyloxy radical **5** is formed whose further reduction provides the enolate **6** and after protonation, the ketone **4**.

Table 1. Electrocarboxylation of Vinyl Triflates Catalyzed by $PdCl_2(PPh_3)_2$ in DMF at 20 °C (Scheme 1)

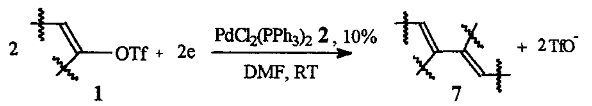
entry	vinyl-OTf [1 mmol]	catalyst [mmol]	CO_2 [atm]	E [a]	F/ mol [b]	ketone 4 [% isolated] [c]	diene 7 [% isolated] [c]	vinyl-CO_2H 3 [% isolated] [c]
1	 **1a**	0	0	-2.6	2.1	 98	-	-
2	 **1a**	0.1	0	-2.0	1.1	0	 96	-
3	 **1a**	0.1	1	-2.0	2.4	0	0	 85
4	 **1b**	0.1	1	-1.6	2.0	0	0	 60
5	 **1c**	0.1	1	-2.0	2.2	0	0	 80
6	 **1d**	0.1	1	-2.0	2.1	0	0	 86
7	 **1f**	0.1	1	-2.2	2.3	0	0	 70 [d]
8	 **1g**	0.1	1	-1.7	2.1	0	0	 32

[a] Electrolysis potentials in Volt *vs* SCE. [b] Faraday per mol of vinyl triflate. [c] Yields are related to the vinyl triflate completely converted. [d] Formation of 8 % of 1-hexene.



Scheme 2

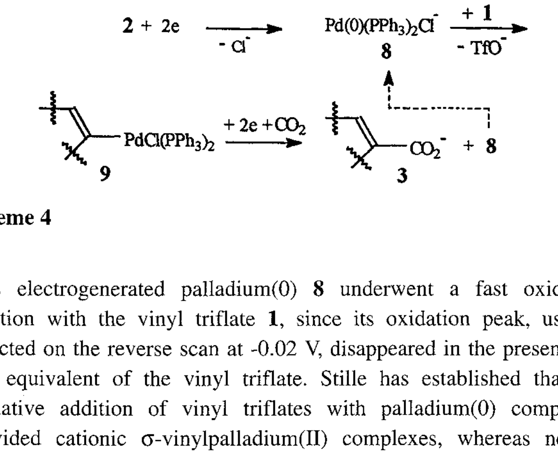
In the presence of a catalytic amount of $PdCl_2(PPh_3)_2$, the formation of the ketone **4** was completely inhibited and a conjugated diene **7** was obtained in quantitative yield (Table 1, entry 2, Scheme 3), showing that, under these conditions, the activation of the C-O bond of the vinyl triflate *via* a palladium complex, was highly favored. This is the first reported homocoupling of vinyl triflates catalyzed by palladium.



Scheme 3

The electrochemical reduction performed in the presence of $PdCl_2(PPh_3)_2$ and carbon dioxide, resulted in the formation of α,β-unsaturated carboxylic acids **3** (Scheme 1, Table 1). The carboxylation was performed from cyclic and linear vinyl triflates and is regiospecific. Vinyl triflates are more reactive than aryl triflates since their electrocarboxylation was performed at room temperature, instead of 90 °C for aryl triflates.[8]

Preliminary investigations on the mechanism of the carboxylation by means of cyclic voltammetry, showed that $PdCl_2(PPh_3)_2$ **2** was first reduced to a palladium(0) complex at -0.90 V (*vs.* standard calomel electrode, SCE). It is well established that the electrochemical reduction of $PdCl_2(PPh_3)_2$ generates a palladium(0) complex ligated by a chloride anion **8** (Scheme 4).[9]

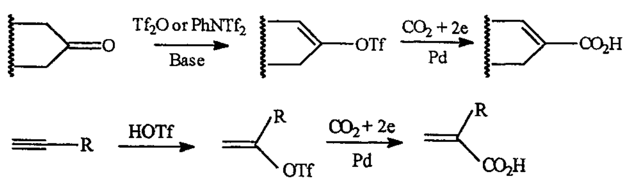


Scheme 4

This electrogenerated palladium(0) **8** underwent a fast oxidative addition with the vinyl triflate **1**, since its oxidation peak, usually detected on the reverse scan at -0.02 V, disappeared in the presence of one equivalent of the vinyl triflate. Stille has established that the oxidative addition of vinyl triflates with palladium(0) complexes provided cationic σ-vinylpalladium(II) complexes, whereas neutral σ-vinylpalladium(II) chloride complexes **9**, were formed when the oxidative addition was performed in the presence of chloride anions.[3] Thus, in the present case, i.e. in the presence of the electrogenerated chloride-ligated complex **8**, the oxidative addition led to the neutral σ-vinylpalladium(II) chloride complex **9**.

When the electrochemical reduction was performed beyond the reduction of $PdCl_2(PPh_3)_2$, a new reduction peak was observed at a less negative potential than the reduction potential of the vinyl triflate **1** (Table 2), whereas the reduction peak of the vinyl triflate was no longer detected on the voltammogram. This new reduction peak was assigned to the reduction of the neutral σ-vinylpalladium(II) chloride complex **9** resulting from the oxidative addition (Scheme 4). In all cases investigated here, the σ-vinylpalladium(II) complex **9** was more easily reduced than the precursor vinyl triflate **1** (Table 2). The magnitude of its reduction peak grew as the concentration of the vinyl triflate was increased, evidencing a catalytic reaction. The reduction of the vinylpalladium(II) complex **9** in the presence of carbon dioxide, afforded the corresponding α,β-unsaturated carboxylic acid **3**, in a catalytic process.[10] The electrosynthesis of the α,β-unsaturated carboxylic acid **3** was then performed at the reduction potential of the vinylpalladium(II) complex **9**, i.e. at a potential less negative than the reduction potential of the vinyl triflate, thus avoiding its direct reduction to ketone.[11]

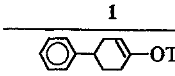
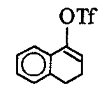
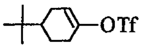
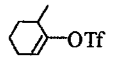
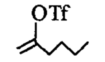
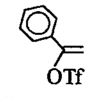
Thus, the electrocarboxylation of vinyl triflates proceeds *via* a double activation of the vinyl triflate: firstly, activation of the C-O bond of the vinyl triflate by a palladium(0) complex and secondly, activation by electron transfer, of the vinylpalladium(II) complex **9** resulting from the oxidative addition. It is interesting to note that vinyl triflates are synthesized by two different routes (Scheme 5): cyclic vinyl triflates (compounds **1a-d**) are synthesized by reaction of ketone enolates with a triflating reagent[12] whereas linear vinyl triflates (compounds **1f-g**) are obtained by addition of HOTf on alkynes.[13]



Scheme 5

Our work shows that cyclic ketones and alkynes are transformed to α,β-unsaturated carboxylic acids in the presence of CO_2, a palladium catalyst and an electron source, *via* the vinyl triflates (Scheme 5). This new reaction is an alternative route to the palladium-catalyzed synthesis of α,β-unsaturated carboxylic acids from vinyl triflates and carbon monoxide[14] under basic conditions.[15]

Table 2. Reduction Peak Potentials of Vinyl Triflates and of the Vinylpalladium(II) Complexes Resulting from the Oxidative Addition: $Pd(0)(PPh_3)_2Cl^- + vinyl\text{-}OTf \rightarrow vinyl\text{-}Pd\text{-}Cl(PPh_3)_2 + TfO^-$

Vinyl-OTf **1**	Vinyl-OTf **1** E^p_{red} [a]	Vinyl-Pd-Cl$(PPh_3)_2$ **9** E^p_{red} [a]
	-2.95	-2.15
	-2.16	-2.08
	-2.91	-2.10
	-2.95	-1.75
	-2.94	-2.20
	-1.94	-1.92

[a] Volt *vs* SCE. Reduction peak potentials were determined at a steady gold disk electrode at the scan rate of 0.2 V s^{-1}, in DMF containing $n\text{-}Bu_4NBF_4$ (0.3 mol dm^{-3}). 20 °C.

Typical experimental procedure: electrocarboxylation of compound **1d** (Table 1, entry 6). The electrocarboxylation was performed in a divided cell. The cathode was a piece of carbon cloth (10 cm^2) and the anode a magnesium rod. The cathodic compartment containing 50 mL of anhydrous DMF and n-Bu_4NBF_4 (0.1 mol dm^{-3}) was charged with 244 mg (1 mmol) of **1d**, followed by 70 mg (0.01 mmol of $PdCl_2(PPh_3)_2$). The anodic compartment contained 5 mL of anhydrous DMF and n-Bu_4NBF_4 (0.1 mol dm^{-3}). A cyclic voltammetry performed prior the electrolysis allowed the determination of the electrolysis potential (Tables 1 and 2). Carbon dioxide was then bubbled into the cathodic compartment and the electrolysis was conducted at a controlled potential until the current dropped to 5% of its initial value. The mixture was hydrolyzed overnight with aqueous HCl (1 mol dm^{-3}). After extraction with diethyl ether and evaporation of the solvent, the crude mixture was analyzed by ^{1}H NMR spectroscopy. The signals of the α,β-unsaturated carboxylic acid were detected contaminated with some triphenylphosphine oxide. The carboxylic acid was purified by solubilization in aqueous NaOH (1 mol dm^{-3}). After extraction with diethyl ether, the basic aqueous phase was treated with aqueous HCl. The acidic aqueous phase was then extracted with diethyl ether. Evaporation of the solvent afforded 120 mg (86 %) of pure 6-methylcyclohex-1-ene-1-carboxylic acid as white crystals. mp 102 °C; ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.04 (d, 3H, J = 7 Hz, $C\underline{H}_3$), 1.45-1.60 (m, 4H, $C\underline{H}_2$-$C\underline{H}_2$), 2.06-2.17 (m, 2H, $C\underline{H}_2$-CH=), 2.54-2.67 (m, 1H, $C\underline{H}$-CH_3), 7.03 (t, 1H, J = 4 Hz, =$C\underline{H}$), 11.60 (br. s, 1H, $O\underline{H}$) ppm; ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.99, 20.10, 26.12, 27.40, 29.43, 134.69, 142.17, 173.14 ppm; IR (KBr pellet): 3200-2700 (O-H), 2965, 2945, 2918, 2870, 1677 (C=O), 1635 (C=C), 1422, 1274, 1251, 1068, 939 cm^{-1}; MS: m/z (%) = 140 (M^+), 125, 95(100).

Acknowledgements. This work has been supported by the Centre National de la Recherche Scientifique (CNRS, URA 1679, "Processus d'Activation Moléculaire") and the Ministère de l'Enseignement Supérieur et de la Recherche (Ecole Normale Supérieure) .

References and Notes

(1) Reviews: Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25,* 508. Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21,* 47. Ritter, K. *Synthesis* **1993**, 735.

(2) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25,* 4821. Cacchi, S.; Morera, E.; Ortar, G. *Org. Synth.* **1990,** *68,* 138.

(3) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106,* 4630. Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108,* 3033.

(4) Krolski, M. E.; Renaldo, A. F.; Rudisill, D. E.; Stille, J. K. *J. Org. Chem.* **1988**, *53,* 1170. Arcadi, A.; Cacchi, S.; Marinelli, F. *Tetrahedron Lett.* **1989**, *30,* 2581. Baker, S. T.; Roth, G. P.; Sapino, C. *Synth. Commun.* **1990**, *20,* 2185. Piers, E.; Friesen, R.; Keay, B. *Tetrahedron* **1991**, *47,* 4555. Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1994,** *35,* 2405.

(5) Arcadi, A.; Cacchi, S.; Delmastro, M.; Marinelli, F. *Synlett* **1991**, 409. Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34,* 6403.

(6) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984,** *25,* 2271. Cacchi, S.; Morera, E.; Ortar, G. *Synthesis* **1986**, 320. Arcadi, A.; Bernocchi, E.; Cacchi, S.; Cagliot, L.; Marinelli, F. *Tetrahedron Lett.* **1990**, *31,* 2463.

(7) Friess, B.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1988**, *29,* 4089.

(8) Jutand, A.; Négri, S.; Mosleh, A. *J. Chem. Soc. Chem. Commun.* **1992**, 1729.

(9) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991,** *113,* 8375.

(10) Starting from compound **1a**, a reduction peak was observed at around -2.70 V, in the absence of carbon dioxide. This reduction peak was assigned to the reduction of the conjugated diene **7**, by comparison with an authentic sample. It disappeared in the presence of carbon dioxide, demonstrating that the carboxylation was actually more efficient than the dimerization (Table 1, entries 2 and 3).

(11) The reduction peak potential of CO_2 in DMF containing n-Bu_4NBF_4 (0.1 mol dm^{-3}) is -2.32 V *vs* SCE at 20 °C. All the vinylpalladium chloride complexes **9** investigated here are more easily reduced that CO_2 (Table 2). Since the electrolyses were conducted at the reduction potential of complexes **9** (Table 1), the reduction of CO_2 did not occur and the electrosyntheses afforded the desired carboxylic acids **3**. On the other hand, CO_2 is more easily reduced than most of the vinyl triflates **1** investigated here (except for compounds **1b** and **1g**, Table 2). Thus, for compounds **1a, c, d, f**, in the absence of any palladium catalyst, reduction of CO_2 will occur before their own reduction. As an example, the electrochemical reduction of **1a** was performed at -2.6 V, in the presence of CO_2, without the palladium catalyst **2**. After consumption of 4 Faraday per mole, ketone **4** was isolated in 46 % yield together with 49 % of recovered **1a**. The consumption of more than 2 F/mol of **1a** shows that reduction of CO_2 occurred together with that of **1a** and that the direct reduction of **1a** to ketone **4** was not affected by the reduction of CO_2.

(12) Stang, P. J.; Hanack, M.; Subramanian, L. *Synthesis* **1982**, 85. Mc Murry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24,* 979.

(13) Summerville, R. H.; Senkler, C. A; Schleyer, P. R.; Dueber, T. E.; Stang, P. J. *J. Am. Chem. Soc.* **1974**, *96,* 1100.

(14) Cacchi, S.; Lupi, A. *Tetrahedron Lett.* **1992**, *33,* 3939.

(15) This work is also an alternative route to the uncatalyzed[16] and palladium-catalyzed[17] electrocarboxylation of vinyl halides which has been reported in only one case, for β-bromostyrene.

(16) Sock, O.; Troupel, M.; Périchon, J. *Tetrahedron Lett.* **1985**, *26,* 1509.

(17) Torii, S.; Tanaka, H.; Hamatani, T.; Morisaki, K.; Jutand, A.; Pflüger, F.; Fauvarque, J. F. *Chem. Lett.* **1986**, 169.