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Fluorinated acrylates via alkoxycarbonylation of 1-alkynes with fluorinated alcohols

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ABSTRACT

The system formed by combining in situ $Pd(OAc)_2$ with (2-pyridyl)diphenylphosphine (PyPPh₂) and CH₃SO₃H catalyzes efficiently the carbonylation of terminal alkynes (phenylacetylene or 1-hexyne) with alcohols having perfluorinated segments of the type $CF_3(CF_2)_m(CH_2)_n$ –OH (m=1 or 3, n=1, 2 or 3) or with pentafluorophenol. Good carbonylation rates accompanied by high regioselectivity towards acrylate ester formation are obtained under mild reaction conditions (T=60-80 °C, P(CO)=30 atm). The influence of the CO pressure, the catalyst composition, the temperature and the number (n) of protonated methylene groups on the catalysis has been studied.

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1. Introduction

Fluorinated polymers have unique chemical and physical properties (low surface tensions, low friction coefficients, high transparency, water- and oil-repellency, high chemical stability), which continue to attract a great deal of attention from both the academic and the industrial community.¹

Fluorinated acrylic esters are valuable intermediates as the corresponding polymers find a wide range of practical applications. Indeed, examples of application of fluorinated polymeric acrylates or methacrylates range from their use as sizing textile agents (they add water- and oil-repellency to natural or synthetic fabrics²) to the manufacture of optical devices (e.g., waveguides and interconnecting devices).³ Other significant application fields are in lubricants manufacture and in coatings industry.⁴

A further peculiar application of fluorinated polyacrylates is in cultural heritage preservation owing to their optical properties and resistance to aging.⁵

The approaches employed to synthesize fluorinated (meth)acrylates usually entail a variety of esterification or transesterification processes based on the reaction of fluorinated alcohols with (meth) acrylic acid or some of its derivatives (halides, esters or anhydrides) in the presence of an acid or basic catalyst;⁶ however, only the synthetic method developed by Yamaguchi^{6d} appears of general applicability.

Terminal alkynes carbonylation (see Scheme 1) is a flexible synthetic approach, which allows to obtain in one step acrylic acid derivatives starting from easily accessible building blocks.⁷ Since several years our research group has been interested in studying this reaction we successfully employed in the synthesis of some key intermediates in fine chemistry;⁸ thus, we envisioned the carbonylation of 1-alkynes in the presence of fluorinated alcohols (see Scheme 1) as a new approach for the preparation of fluorinated acrylic esters.

$$R \longrightarrow + R_{F} - OH \longrightarrow O \\ Cat. \longrightarrow O \\ R \longrightarrow OR_{F} + O \\ R \\ branched \\ linear$$

$$R_{F} = CF_{3}(CF_{2})_{m}(CH_{2})_{n}, C_{6}F_{5}$$

R = phenyl, *n*-butyl Cat.: Pd(OAc)₂ / PyPPh₂ / CH₃SO₃H

Scheme 1. Alkoxycarbonylation of 1-alkynes in the presence of fluorinated alcohols.





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The study appeared particularly intriguing since, at the best of our knowledge, in the literature there are no reports dealing with alkynes carbonylation in the presence of fluorinated alcohols.

2. Results and discussion

The carbonylation of phenylacetylene in the presence of 2,2,3,3,3-pentafluoropropanol (1) (Fig. 1) was chosen as model reaction for preliminary investigations (Scheme 1, R=phenyl, m=n=1). Phenylacetylene is an inexpensive, readily available, and easy to handle terminal alkyne, the reactivity of which is very similar to that of aliphatic alkynes in carbonylation reactions.⁹ As for the fluorinated alcohol, we thought it interesting to first study the reactivity of **1**, which having a pK_a in water of 12.40 (compare with $pK_a=12.39$ for CF₃CH₂OH¹⁰), is one of the most acidic aliphatic alcohols and suffers from steric and conformational effects¹¹ brought about by the presence of the fluoro atoms on the carbon atom α to the CH₂OH moiety.

PyPPh₂/CH₃SO₃H molar ratios], temperature and alkyne/alcohol molar ratios on the reaction.

At 60 °C the reaction proceeds with reasonably good rates; after 3 h the alkyne conversion reaches the 83% and the sought acrylate ester (the branched isomer) forms with high regioselectivity (entry 1 of Table 1). The only side product formed by the reaction is the linear ester of (*E*) configuration as inferred from its ¹H NMR spectrum in which the vinyl protons appear as two doublets centered at 7.78 (=CHPh) and 6.48 δ (=CHCO) having a coupling constant of 16.0 Hz.

Aiming to achieve complete substrate conversion, the reaction time was increased to 6 h (entry 2), but no improvement was observed. Usually in alkoxycarbonylations a large excess of the alcohol is present, thus we ascribed the incomplete alkyne conversion to the low amount of fluorinated alcohol employed. Hence, a further experiment (entry 3) was carried out doubling the alcohol to alkyne ratio, but no increase in substrate conversion was achieved.

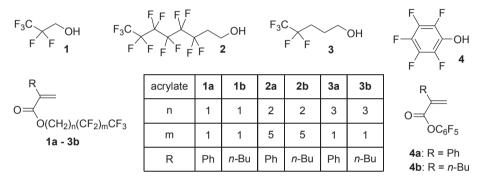


Fig. 1. Chemical structures of the starting fluorinated alcohols and the formed esters.

Owing to its high activity and selectivity, we decided to employ Drent's carbonylation catalyst, which is prepared combining in situ $Pd(OAc)_2$ with an excess of (2-pyridyl)diphenylphosphine (PyPPh₂) and methanesulfonic acid.¹²

Usually in alkyne alkoxycarbonylation the alkyne is the limiting reagent while the alcohol is present in large excess (e.g., most commonly as the reaction solvent); in our experiments only a moderate excess of the fluorinated alcohol was employed (al-kyne/alcohol molar ratio in the 1:1.5-1:3 range) owing to its cost and dichloromethane was used as the reaction solvent. In pre-liminary experiments, the *P*(CO) was set at 30 atm and the palla-dium/phenylacetylene molar ratio was 1:1300. The data gathered in Table 1 show the influence of catalyst composition [Pd(OAc)₂/

Table 1

Influence of the temperature and catalyst composition on the carbonylation of phenylacetylene with 2,2,3,3,3-pentafluoropropanol $^{\rm a}$

Entry	Pd/P/H ^{+b}	T (°C)	Alcohol/ alkyne	Conv. (%) ^c	Branched (%)	Linear (%)	TON ^d	TOF $(h^{-1})^e$
1	1/30/60	60	1.5	83	96.6	3.4	1080	360
2 ^f	1/30/60	60	1.5	83	97.0	3.0	1080	180
3	1/30/60	60	3	81	97.7	2.3	1050	350
4	1/30/60	70	3	89	97.0	3.0	1155	385
5	1/10/20	70	3	86	96.7	3.3	1125	375
6	1/30/60	80	3	91	96.8	3.2	1185	395
7	1/30/60	100	3	89	89.6	10.4	1155	385

^a Reaction conditions: alkyne: phenylacetylene (4.5 mmol); alkyne/palladium molar ratio=1300; solvent: CH₂Cl₂ (10 mL); *P*(CO): 30 atm; reaction time: 3 h.
 ^b Pd(OAc)₂/PyPPh₂/CH₃SO₃H (mol/mol/mol).

^c Alkyne (limiting reagent) conversion determined by GLC with mesitylene as the internal standard.

^d TON (turnover number): moles of substrate converted per mol of catalyst.

^e TOF (turnover frequency): moles of substrate converted per mol of catalyst per hour.

An enhancement of the catalytic activity without regioselectivity loss is observed on increasing the temperature from 60 to 80 °C, although at this temperature the reaction does not go to completion. On the other hand, a further raise of the reaction temperature from 80 to 100 °C leads to a small decrease in conversion, which is accompanied by a significant loss in regioselectivity. Detection of palladium black in the crude reaction mixture means that this latter result is likely caused by catalyst decomposition.

Finally it is worth to note that comparison of the data in entries 4 and 5 shows that the reaction course is practically unaffected by the palladium/phosphine/acid molar ratios employed in catalyst preparation.

On the basis of these experiments, we came to the conclusion that a maximum turnover number of about 1200 (entry 6) is achievable for the reaction and that likely there is some process leading to catalyst deactivation. In fact, it is worth to note that traces of palladium metal were sometimes observed in reaction crudes.

In Table 2 are reported the results obtained carrying out the reaction under different CO pressures, all other reaction conditions remaining the same employed in entry 1 of Table 1.

According to the results reported in Table 2 it appears that a minimum P(CO) of about 20 atm is necessary in order to obtain a satisfactory reaction rate accompanied by a good regioselectivity. The catalytic activity significantly increases by raising the P(CO) to 30 atm, while a further increase of P(CO) to 60 atm produces only a modest improvement.

With the optimized reaction conditions in hand, further experiments were carried out to highlight the influence of methylene groups spacing the CH₂OH from the carbon atoms bearing the fluorine substituents. Download English Version:

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