



One-pot tandem hydrophenylation and ionic hydrogenation of 3-phenylpropynoic acid derivatives under superelectrophilic activation



Denis I. Nilov^a, Aleksander V. Vasilyev^{a,b,*}

^aInstitute of Chemistry, Saint Petersburg State University, Universitetskaya nab., 7/9, Saint Petersburg 199034, Russia

^bDepartment of Chemistry, Saint Petersburg State Forest Technical University, Institutsky per., 5, Saint Petersburg 194021, Russia

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ABSTRACT

The reactions of esters and amides of 3-phenylpropynoic acid with strong Lewis acids AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) or conjugate Brønsted–Lewis superacids $\text{HX}\text{-AlX}_3$ ($\text{X} = \text{Cl}, \text{Br}$) in benzene and cyclohexane at room temperature afforded 3,3-diphenylpropanoic acid derivatives in up to 94% yield. This tandem reaction of the acetylene bond proceeded by hydrophenylation followed by ionic hydrogenation.

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Introduction

The acetylene bond is a highly reactive functional group that is capable of undergoing various transformations via their reactions with electrophiles, nucleophiles, and radicals.^{1,2} Activation of the triple carbon–carbon bond in superelectrophilic (superacidic) systems is widely used in organic synthesis,^{3,4} and is an effective means to achieve various transformations of alkynes where the triple bond is conjugated with an electron withdrawing group (carbonyl, alkoxy carbonyl, cyano).⁴ However, there are no examples of the involvement of such conjugated alkynes in ionic hydrogenation reactions.

Ionic hydrogenation is used for the reduction of alkene and carbonyl bonds. This process includes the formation of a carbocationic species followed by abstraction of a hydride ion from a suitable donor. Different combinations of electrophile/hydride ion sources: trifluoroacetic acid/silicon hydride,^{5–7} metal halide/silicon hydride,⁸ and trialkylboron/aryl tin hydride have been reported.⁹ However, the ionic hydrogenation of alkenes under mild conditions is not a versatile reaction and suitable starting materials are limited. Thus, reduction of alkene bonds in deactivated conjugated enones requires the use of superacids $\text{HF}\text{-SbF}_5$ or AlX_3 ($\text{X} = \text{Cl}, \text{Br}$) to generate the *O,C*-diprotonated enone form (dication),³

which are reactive enough to abstract a hydride ion from cycloalkane donors.^{10–24}

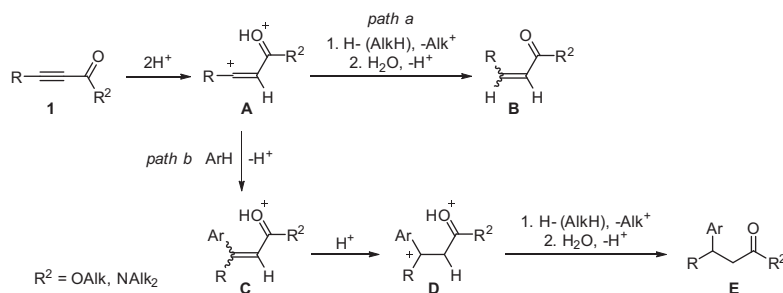
Based on our research on the chemistry of alkynes in superacids,⁴ in this work, we describe the reactions of 3-phenylpropynoic acid derivatives (esters and amides) with various Brønsted and Lewis superacids in cycloalkanes (as the hydride ion source) and arenes.

Protonation of the carbonyl oxygen and acetylene carbon of conjugated ynone **1** in Brønsted superacids (or coordination of these basic centers with Lewis acid) leads to formation of the reactive dication **A** (or its complex with a Lewis acid) (Scheme 1).⁴ This species may abstract a hydride ion from an alkane, leading to enone **B** (*path a*). On the other hand, dication **A** in the presence of an arene, results in alkenylation of the aromatic molecule affording aryl enone **C**. Protonation of the latter gives dication **D**, which in turn may abstract a hydride ion to form structure **E** (*path b*). It should be noted that α -aryl substituted vinyl cations are linear according to DFT calculation.²⁵ Moreover, experimental X-ray data on the structure of the α -*tert*-butyl substituted vinyl cation clearly demonstrate its linear structure.²⁶

In order to examine the different potential reactions of ynone **1** (*paths a and b*, Scheme 1) we undertook the study reported herein. Initially, we examined the reaction of methyl 3-phenylpropynoate **1a** with various Lewis and Brønsted superacids in cyclohexane or methylcyclohexane, as hydride ion sources (Table 1). In the reactions with AlCl_3 or AlBr_3 in low coordinating solvents such as

* Corresponding author.

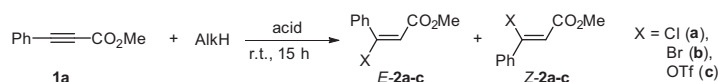
E-mail addresses: alekxvasil@mail.ru, a.vasilyev@spbu.ru (A.V. Vasilyev).



Scheme 1. Possible transformations of conjugated ynone **1** under superelectrophilic activation, in the presence of arenes and alkanes (as the hydride ion source).

Table 1

Reaction of methyl 3-phenylpropynoate **1a** with various Lewis and Brønsted superacids in cycloalkanes

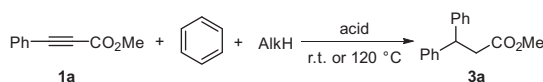


Entry	Acid ^a	Solvent	AlkH	Reaction product		
				No.	Ratio E:-Z-	Yield (%)
1	AlCl ₃ (5 equiv)	CH ₂ Cl ₂	c-C ₆ H ₁₂	2a	1.7:1	90
2	AlBr ₃ (5 equiv)	CH ₂ Br ₂	c-C ₆ H ₁₂	2b	2.3:1	80
3	AlCl ₃ (5 equiv)	CS ₂	c-C ₆ H ₁₂	Oligomers	—	—
4	AlBr ₃ (5 equiv)	CS ₂	c-C ₆ H ₁₂	2b	1:1	88
5	TfOH (H ₀ -14) ^a (30 equiv)		c-C ₆ H ₁₂	2c	19:1	82
6	TfOH-SbF ₅ (H ₀ -18) ^a (30 equiv)		c-C ₆ H ₁₂	Oligomers	—	—
7	TfOH-SbF ₅ (H ₀ -18) ^a (30 equiv)		Me-c-C ₆ H ₁₁	Oligomers	—	—
8	HCl-AlCl ₃ (H ₀ < -13) ^a (5 equiv)	CS ₂	c-C ₆ H ₁₂	Oligomers	—	—
9	HBr-AlBr ₃ (H ₀ < -13) ^a (5 equiv)	CS ₂	c-C ₆ H ₁₂	Oligomers	—	—

^a Note: Values of the Hammett acidity function H₀ are taken from Ref. 3a.

Table 2

Transformation of methyl 3-phenylpropynoate **1a** into methyl 3,3-diphenylpropanoate **3a** using various Lewis and Brønsted superacids in various mixtures of benzene and cycloalkanes



Entry	Acid ^a	AlkH	Reaction time, (h) ^b	Yield (%)
1	AlCl ₃ (5 equiv)	c-C ₆ H ₁₂	15	85
2	AlCl ₃ (5 equiv)	Me-c-C ₆ H ₁₁	15	83
3	AlCl ₃ (5 equiv)	Me-c-C ₅ H ₉	15	88
4	AlCl ₃ (5 equiv)	Adamantane	15	86
5	AlBr ₃ (5 equiv)	c-C ₆ H ₁₂	15	90
6	HCl-AlCl ₃ (H ₀ < -13) ^a (5 equiv)	c-C ₆ H ₁₂	3	92
7	HBr-AlBr ₃ (H ₀ < -13) ^a (5 equiv)	c-C ₆ H ₁₂	3	70
8	TfOH-SbF ₅ (H ₀ -18) ^a (30 equiv)	c-C ₆ H ₁₂	1	20 ^c
9	Zeolite CBV-720 (30 equiv)	c-C ₆ H ₁₂	30	29

^a Note: Values of Hammett acidity function H₀ are from ref. 3a.

^b Note: Entries 1–8 were performed at rt, Entry 9 was performed at 120 °C.

^c Note: Large amounts of benzene cycloalkylation product formed.

CH₂Cl₂, CH₂Br₂, or CS₂ (Entries 1, 2, 4) the corresponding vinyl halogenides *E*-**Z-2a** or *E*-**Z-2b** were obtained resulting from the addition of HCl or HBr to the triple bond. In the same manner, vinyl triflates *E*-**Z-2c** were formed in TfOH (Entry 5). The use of AlCl₃ in CS₂ afforded oligomeric material, presumably due to the partial solubility of the Lewis acid in this solvent (Entry 3). These data showed that the corresponding vinyl dication **A** does not abstract a hydride ion from cycloalkanes (*path a*, Scheme 1), but prefers to react with other nucleophiles, such as counter ions from the reaction medium ([Al_nX_{3n+1}]⁺ or TfO⁻). Increasing the acidity of the reaction medium using conjugate Brønsted–Lewis systems

TfOH-SbF₅ or HX-AlX₃ (X = Cl, Br) gave unsatisfactory results, and only complex mixtures of oligomeric materials were obtained (Entries 6–9).

The same reactions of compound **1a** were then carried out in mixtures of benzene and various cycloalkanes (Table 2). The reactions with Lewis acids AlX₃ (X = Cl, Br) at room temperature for 15 h led smoothly to ester **3a** in high yields 83–90% (Entries 1–5). Compound **3a** was formed by tandem hydrophenylation of the acetylene bond of substrate **1a** followed by ionic hydrogenation (*path b*, Scheme 1). The same result was achieved using HX-AlX₃ (X = Cl, Br) (Entries 6, 7), but took less time (3 h). In the

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