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Aluminium trichloride-promoted tandem hydroarylation–ionic hydrogenation of 3-arylpropynoic acid derivatives and 4-phenylbut-3-yn-2-one

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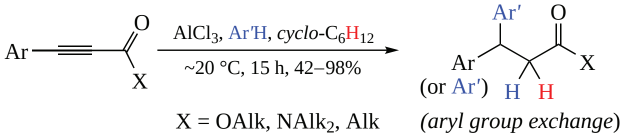
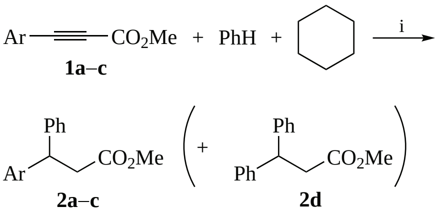
Reactions of 3-arylpropynoic acid derivatives and conjugated acetylene ketones with arenes and cyclohexane under the action of $AlCl_3$ at room temperature for 15 h afford the corresponding products of one-pot tandem hydroarylation–ionic hydrogenation of the acetylene bond of the starting compounds in 42–98% yields. This reaction is accompanied by aryl group exchange process under acidic conditions.



Keywords: arylpropynoic acids, ynones, hydroarylation, ionic hydrogenation, superelectrophilic activation, carbocations.

Ionic hydrogenation of carbon–carbon double bond in conjugated enones,[1–21] hydroxy,[20–22] ketone,[23,24] aldehyde,[25,26] aromatic,[27] and alkene[28] groups under superelectrophilic activation by Brønsted superacids and strong Lewis acids is widely used in organic synthesis. These reactions proceed through an intermediate formation of highly reactive dicationic electrophilic species, that abstract hydride ion from (cyclo)alkane molecule furnishing the hydrogenated products. However, up to the moment, acetylene derivatives have not been studied in ionic hydrogenation. We have found recently the effective method for tandem hydrophenylation–ionic hydrogenation of acetylene bond of esters and amides of 3-phenylpropynoic acid in the reaction with benzene and cyclohexane under the action of aluminum trichloride.[29] As a continuation of that study, in this work we describe hydroarylation–ionic hydrogenation of derivatives of substituted 3-arylpropynoic acids and acetylene ketone, 4-phenylbut-3-yn-2-one.

In our hands, methyl esters of acids **1a**–**c** in reaction with benzene and cyclohexane (as a hydride ion source) in the presence of 5 equiv. of $AlCl_3$ at room temperature for 15 h undergo one-pot tandem hydrophenylation–ionic hydrogenation with the formation of saturated esters **2a**–**c** (Scheme 1). However, this reaction is accompanied by an aryl group exchange. Thus, chloro- and bromo-substituted esters **1b** and **1c** afford diphenyl substituted ester **2d**, apart from the expected products **2b** and **2c**, in general yields of 43 and 79%, respectively. Contrary to compounds **1b**,**c**, ester **2a** bearing strong electron withdrawing 2-fluorophenyl group has not given the exchange product **2d**. Previously, we observed similar aryl group exchange under superacidic conditions for transformations of cinnamic acid derivatives,[30,31] trifluoromethyl-containing styrenes,[32] and conjugated dienones.[33]



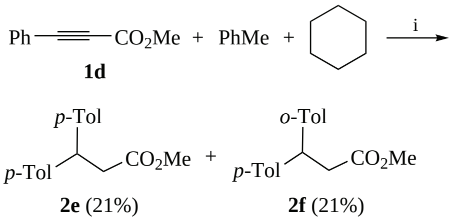
a Ar = 2-FC_6H_4 (51%)
b Ar = 4-ClC_6H_4 (20% + 23% **2d**)
c Ar = 4-BrC_6H_4 (47% + 32% **2d**)

Scheme 1 *Reagents and conditions*: i, $AlCl_3$, room temperature, 15 h.

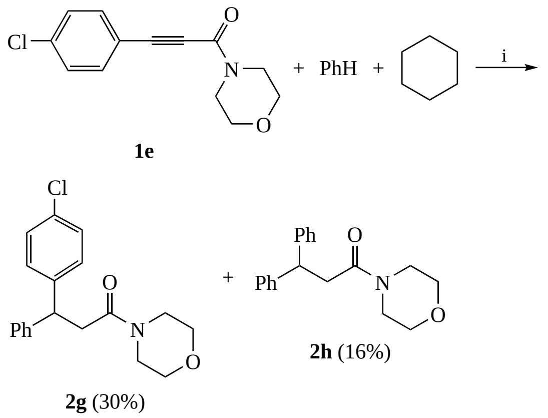
Apart from benzene, the reactions with other arenes have been investigated. However, reactions of ester **1d** with *o*-, *m*-, *p*-xylenes, anisole, and 1,2-dichlorobenzene afforded complex mixtures of oligomeric compounds. The reaction with toluene brought about two isomeric tolyl-containing products of aryl group exchange, **2e** and **2f**, having no phenyl groups from starting compound **1d**, in total yield of 42% (Scheme 2).

Similarly, the reaction of amide **1e** with benzene furnishes the expected compound **2g** of tandem hydrophenylation–ionic hydrogenation and the product **2h** of aryl group exchange (Scheme 3).

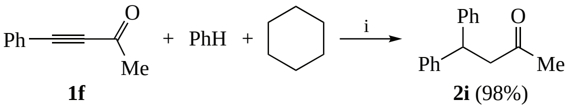
The mixtures of substances **2b** and **2d**, **2c** and **2d**, **2e** and **2f**, **2g** and **2h** (see Schemes 1–3) were thoroughly investigated by ^1H and ^{13}C NMR along with chromato-mass spectrometry to elucidate the structures and ratios of the obtained compounds.



Scheme 2 *Reagents and conditions*: i, $AlCl_3$, room temperature, 15 h.



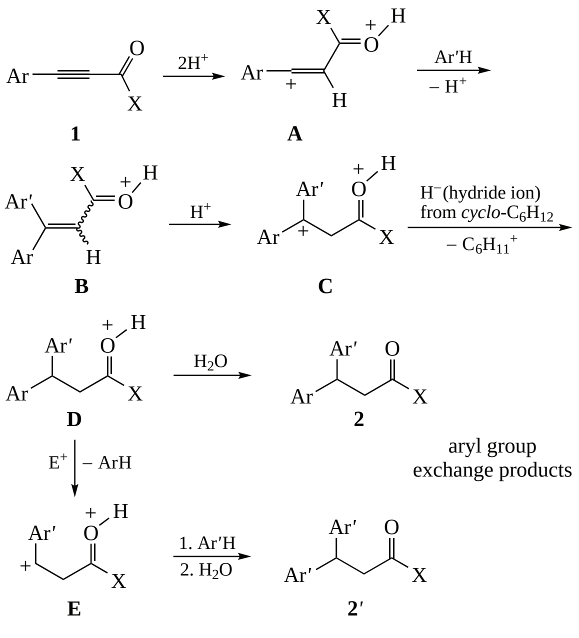
Scheme 3 *Reagents and conditions*: i, AlCl$_3$, room temperature, 15 h.



Scheme 4 *Reagents and conditions*: i, AlCl$_3$, room temperature, 15 h.

Good result has been obtained upon hydrophenylation–ionic hydrogenation of ynone **1f** giving quantitatively compound **2i** (Scheme 4).

Plausible reaction mechanism is presented in Scheme 5. It should be specially emphasized that, apart from AlCl$_3$, an electrophilic activator in this reaction may also be a proton, which arises after a deprotonation of arene Ar′H. Another source of Brønsted acidity may be traces of ubiquitous water, which reacts with AlCl$_3$ forming conjugated Brønsted Lewis superacid H$^+$[AlCl$_3$(OH)]$^-$ (see also data in our previous work[29] on hydrophenylation–ionic hydrogenation of ester **1d** in different Brønsted and Lewis superacids). Thus, for a simplicity, a plausible reaction mechanism in Scheme 5 includes a proton as an electrophilic activator. At the first stage of the reaction, protonation of the carbonyl oxygen and the carbon–carbon triple bond of compound **1** gives rise to electrophilic species **A**, which in reaction with arene affords intermediate **B**. The latter is protonated, in turn, onto the C=C bond leading to species **C**, which abstracts a hydride ion from cyclohexane forming species **D**. Hydrolysis of the latter furnishes finally compound **2**.



Scheme 5

Aryl group exchange should take place at the stage of the formation of species **D** (*cf.* refs. 30–33). Due to reversibility of electrophilic aromatic substitution, the aryl group exchange may proceed through protonation of rather donating aryl ring followed by elimination of arene molecule and formation of the corresponding benzyl type cation **E**. The latter can react further with arene giving compound of general formula **2′** as an exchange product. Thus, electron poor aromatic rings, such as 2-fluorophenyl one in ester **1a** (see Scheme 1), are hardly protonated, and that particular compound **1a** does not give a product of aryl group exchange.

In conclusion, the current study showed that the AlCl$_3$-promoted reaction of 3-arylpropynoic acid derivatives with arenes and cyclohexane, as a hydride ion source, leads to products of tandem hydroarylation–ionic hydrogenation of the acetylene bond, 3,3-diarylpropanoic acid derivatives, as mixtures of compounds with various aryl substituents.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2023.01.008.

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