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HUSY zeolite promoted hydrophenylation of alkynes conjugated with electron-withdrawing substituents

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Arylacetylenes, conjugated with electron-withdrawing groups, ArC=C(EWG) [EWG = SO₂Ph, PO(OEt)₂, COMe, CO₂Me] in reaction with benzene at room temperature or 130 °C (glass high pressure tube) for 1–10 h under the action of acidic zeolite HUSY (Si/Al ratio is 15) afford products of hydrophenylation of acetylene bond Ar(Ph)C=CH(EWG) in yields of 56–98%.

Acidic zeolites considered as 'green' catalysts are widely used in organic synthesis.^{1–6} Reported uses include Friedel–Crafts acylation, alkylation and alkenylation reactions,^{7–10} ionic hydrogenation,¹¹ and the synthesis of different carbo-^{8,12–14} and heterocycles.¹⁰ Zeolites can be also modified by metals, for instance Cu¹,^{15–21} that opens new opportunities in acetylene chemistry for the preparation of triazoles,^{15–17} diynes,^{18,19} or propargylamines.²⁰

We undertook this research based on our works on electrophilic activation of alkynes in Brønsted superacids²² and our recent study on zeolite-promoted cyclization of *N*-aryl amides of acetylene carboxylic acids into quinolinone derivatives,²³ and superacidic transformations of lignin.²⁴ The main goal of this work was a study of reactions of alkynes, bearing electron-withdrawing groups, with arenes under the action of acidic zeolite HUSY, which is commercially available as zeolite CBV-720.

Acetylenes RC=C(EWG) **1**, conjugated with strong electronwithdrawing groups, may be electrophilically activated only in Brønsted superacids (CF₃SO₃H, FSO₃H)²² or strong Lewis acids (AlCl₃, AlBr₃).²⁵ Thus, protonation of such acetylene substrates in Brønsted superacids gives highly reactive dications RC⁺=CH(EWG–H)⁺, which may further react with arenes to form products of hydroarylation of triple bond.

Analogously to Brønsted superacid-promoted reactions, we expected that zeolite HUSY would be capable of activating alkynes, which bear electron-withdrawing substituents, in reaction with benzene. Indeed, arylacetylenes **1a–g** reacted with benzene under the action of zeolite HUSY to produce alkenes **2a–g** (Scheme 1, Table 1). Experimental procedure is simple and involves heating of alkyne **1a–g** in excess of benzene with zeolite in glass high pressure tube at 130 °C for 1 h[†] to give hydrophenylation products



 $EWG = COMe, CO_2Me, SO_2Ph, PO(OEt)_2$

Table 1 Reactions of alkynes 1a-g with benzene under the action of acidic zeolite HUSY, leading to alkenes E,Z-2a-g.^{*a*}

Entry	Starting alkyne	Ar	EWG	T/°C	t/h	Product $(E/Z \text{ ratio})$	Yield (%)
1	1a	Ph	SO ₂ Ph	130	3	2a	98
2	1b	Ph	PO(OEt) ₂	130	1	2b	14^{b}
3	1b	Ph	PO(OEt) ₂	130	10	2b	56
4	1c	Ph	COMe	~20	10	2c	14^{b}
5	1c	Ph	COMe	130	1	2c	oligomers
6	1d	2-MeC ₆ H ₄	COMe	130	1	<i>E</i> / <i>Z</i> - 2d (0.1:1)	37
7	1d	2-MeC ₆ H ₄	COMe	~20	2	<i>E</i> / <i>Z</i> - 2d (0.1:1)	98
8	1e	Ph	CO ₂ Me	~20	10	2e	5^b
9	1e	Ph	CO ₂ Me	130	1	2e	98
10	1f	4-ClC ₆ H ₄	CO ₂ Me	130	1	<i>E</i> / <i>Z</i> - 2f (0.8:1)	94
11	1g	2-FC ₆ H ₄	CO ₂ Me	130	1	E/Z-2g (0.13:1)	82

^{*a*}A typical charge of reagents: zeolite (0.45 g), alkyne (0.2 mmol), benzene (5 ml); the ratio of alkyne: zeolite Brønsted acidic sites was $\sim 2:1$ (see estimation of zeolite acidity in Online Supplementary Materials). ^{*b*}Incomplete conversion of alkyne.

$$Ar - C \equiv C - EWG + PhH \longrightarrow Ph' E,Z-2a-g$$

Scheme 1 *Conditions*: zeolite HUSY, high pressure tube, 130 or 20 °C. For Ar and EWG, see Table 1.

2a–g in 56–98% yields. Among other investigated substrates, acetylene ketones **1c,d** afforded the target compounds **2c,d**, respectively, at room temperature (entries 4, 7). However, at higher temperature 130 °C yields of these products were much lower

For more details, see Online Supplementary Materials.

[†] Zeolite CBV-720 (obtained from Zeolyst Int.) was activated at 550 °C under air for 4 h. The activated zeolite (0.45 g), acetylene **1a–g** (0.2 mmol) and benzene (5 ml) were loaded in a 15 ml glass high pressure tube (ACE). The resulting suspension was stirred magnetically at room temperature or 130 °C for the time indicated in Table 1. After cooling, the reaction mixture was filtered to remove the zeolite catalyst. The zeolite was subsequently boiled with several portions of MeOH (3×10 ml) and filtered off each time. The combined organic phases (benzene and methanol solutions) were concen-

trated *in vacuo* to provide a residue, which was subjected to chromatographic separation on silica gel using hexane–ethyl acetate as an eluent.

Phenyl 2,2-*diphenylethenyl* sulfone **2a**. Oily compound. ¹H HMR (500 MHz, CDCl₃) δ : 7.02 (s, 1H, =CH), 7.07 (d, 2H_{arom}, *J* 7.4 Hz), 7.20 (d, 2H_{arom}, *J* 8.0 Hz), 7.27–7.35 (m, 8H_{arom}), 7.48 (t, 1H_{arom}, *J* 7.4 Hz), 7.57 (d, 2H_{arom}, *J* 8.0 Hz). MS, *m*/*z* (%): 320 M⁺ (35), 255 (5), 195 (8), 178 (100).

as oligomeric materials were formed (entries 5, 6). Concerning the stereoselectivity of the reaction, predominant formation of Z-isomers, as *syn*-addition of proton and phenyl moiety to the triple bond, was observed. Presumably, this *syn*-addition is more energetically preferable in zeolite cage.

The reaction mechanism may include electrophilic activation of alkynes 1a-g by Brønsted and Lewis acid sites of the zeolite, leading to dications (*cf.* refs. 22,25), which react with benzene.

Important that other arenes (toluene, o-, m-, p-xylenes) in the zeolite promoted reaction with alkynes 1a-g gave oligomers. These electron rich arenes may coordinate to the acidic sites of zeolites, blocking them and directing compounds 1a-g into other reaction pathways. On the other hand, these arenes, as very reactive π -nucleophiles, may participate in several reactions with cationic species derived from starting alkynes 1a-g. Apart from that, electron deficient o-dichlorobenzene did not take part in this reaction. One should search for reaction conditions (solvents, concentration of reagent, temperature, *etc.*) to involve substituted benzenes in this research.

In conclusion, for the first time, we carried out intermolecular hydrophenylation of acetylene bond of alkynes, conjugated with electron-withdrawing groups, in reaction with benzene under the action of acidic zeolite.

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Online Supplementary Materials

Supplementary data associated with this article (properties of zeolite HUSY, ¹H and ¹³C NMR spectra) can be found in the online version at doi:10.1016/j.mencom.2016.11.013.

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