Accepted Manuscript

A novel application of terminal alkynes as the homogeneous catalysts for acetalization and esterification

Lada Sekerová, Eliška Vyskočilová, Libor Červený, Jan Sedláček

PII: S0040-4020(19)30403-X

DOI: https://doi.org/10.1016/j.tet.2019.04.013

Reference: TET 30258

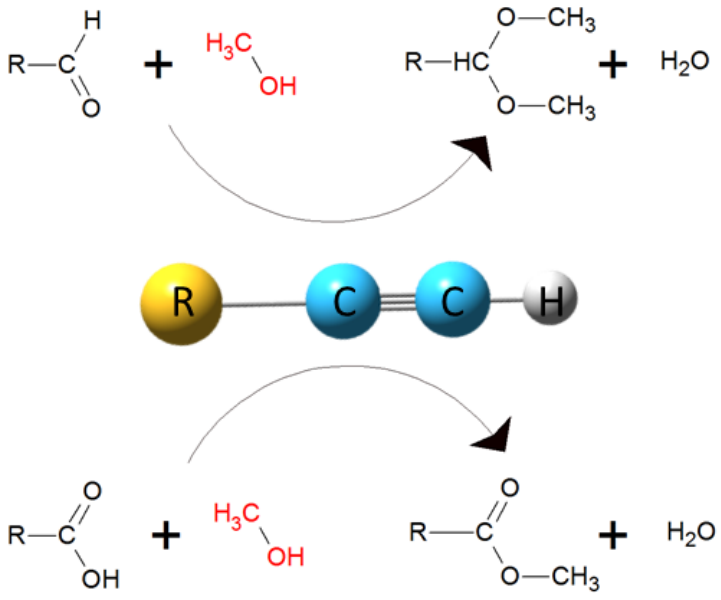
To appear in: *Tetrahedron*

Received Date: 14 January 2019

Revised Date: 2 April 2019

Accepted Date: 3 April 2019

Please cite this article as: Sekerová L, Vyskočilová Eliš, Červený L, Sedláček J, A novel application of terminal alkynes as the homogeneous catalysts for acetalization and esterification, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.04.013.



A novel application of terminal alkynes as the homogeneous catalysts for acetalization and esterification

Lada Sekerová[1]*, Eliška Vyskočilová[1], Libor Červený[1], Jan Sedláček[2]

[1]*Department of Organic Technology, University of Chemistry and Technology Prague, 166 28, Prague 6, Czech Republic*

[1]*Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, 128 40, Prague 2, Czech Republic*

*corresponding author: *Lada.sekerova@vscht.cz*

Abstract

The theoretical study focused on the possible use of low-molecular-weight mono- as well as multifunctional terminal alkynes as catalysts for two reactions, which are known to be typically acid catalyzed - acetalization and esterification, is presented in this study. Multifunctional terminal alkynes [(diethynylbenzenes, triethynylbenzene, and tetrakis(4-ethynylphenyl)methane] were significantly more active than the monofunctional ones (cyclopropylacetylene, phenylacetylene, 3-cyclohexylprop-1-yne, 1-ethynyl-2-fluorobenzene, 1-ethynyl-4-fluorobenzene, 4-ethynyltoluene, 4-*tert*-butylphenylacetylene, and 2-ethynyl-α,α,α-trifluorotoluene), this fact can be partly explained by the higher amount of ethynyl groups per alkyne molecule. We confirmed that terminal ethynyl groups in low-molecular-weight alkynes can successfully act as acid catalytic centers for acetalization as well as for esterification.

Keywords: acid catalysis; terminal alkynes; homogeneous catalysis; acetalization; esterification

1 Introduction

Terminal alkynes may find use in many syntheses. The catalyzed addition of water to the triple bond yields methyl ketones or aldehydes (using the specific type of catalyst to direct the reaction by anti-Markovnikov rule) [1,2]. Cyclotrimerization and cocyclotrimerization of alkynes provide trisubstituted benzenes or more complex cyclic products. [3,4] Acetylides (prepared by deprotonation of terminal alkynes using a variety of organometallic bases) are used as agents for the introduction of reactive alkyne fragments into organic molecules in various multistep syntheses of fine chemical [5]. Terminal alkynes also serve as unique building blocks for the synthesis of mostly conjugated polymers (polyacetylenes, polyaryleneethynylenes, polyarylenebutadiynylenes, polyarylenes) of linear or cross-linked architecture [6-9].

The references about the use of terminal alkynes as catalysts or co-catalysts are scarce. As an example, we found the use of terminal alkynes as co-catalysts in a binary catalytic system $RuCl_2$(*N*-heterocyclic carbene)(*p*-cymene)/alkyne in ring-opening metathesis polymerization (ROMP) of norbornene derivatives [10]. The addition of alkyne tuned the activity of Ru catalysts in organic as well as aqueous media and improved the molecular weight control of polymers in aqueous media. The catalytic activity was tuned by variations in alkyne substituent structure. Another binary catalytic system $AuCl_3$/phenylacetylene [11] was developed for the boost of Ferrier rearrangement of glycals and 2-acetoxymethylglycals with different nucleophiles in good yields with anomeric selectivity at room temperature. This system can be also used for *O*-glycosylation of 1-*O*-acetylsugars forming various glycosides. The carbonylation of alcohols to alkyl formates was boosted by alkyne/phosphine catalytic system [12]. Both components of this catalytic system were essential for providing the activity in mentioned reactions. Using phenylacetylene and tri-*n*-butylphosphine the highest yields and reaction rates were obtained (selectivity 100%, 93% conversion of alcohol). Nevertheless, in

these three cases, terminal alkynes participated as the ligands of more complex catalyst molecules and the acidity of the acetylenic hydrogen was not probably the main reason for the catalytic activity.

As already mentioned above, the terminal alkynes contain acidic (acetylenic) hydrogen, which can be especially in the case of arylacetylenes very easily split off and replaced with e.g. a metal cation under formation of an acetylide [13]. In our recent research, we revealed that the acidity of acetylenic hydrogen was sufficient to catalyze efficiently acetalization and esterification reactions, i.e. reactions which are known to be typically acid catalyzed. We particularly confirmed and reported as a conference contribution [14] the possible use of phenylacetylene as a homogeneous catalyst in acetalization of aliphatic aldehydes (C3 – C7) by methanol and also in esterification of syringaldehyde or ethylvanillin by acetic anhydride. Moreover, we found microporous polymer networks decorated with pendant ethynyl groups as efficient heterogeneous catalysts for acetalization of aliphatic aldehydes with methanol, esterification of carboxylic acids with methanol and izomerization of *β*-pinene oxide, as well [15,16].

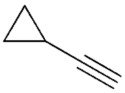
The aim of this study is to compare catalytic properties of a series of low-molecular-weight terminal alkynes possessing various number of ethynyl groups [cyclopropylacetylene, 3-cyclohexylprop-1-yne, 1,3- and 1,4-diethynylbenzenes, 1-ethynyl-2-fluorobenzene, 1-ethynyl-4-fluorobenzene, 4-ethynyltoluene, phenylacetylene, 4-*tert*-butylphenylacetylene, 2-ethynyl-*α,α,α*-trifluorotoluene, tetrakis(4-ethynylphenyl)methane and 1,3,5-triethynylbenzene] in model acetalization and esterification reactions. The reaction rate and yields of products are the evaluative factors for making conclusions.

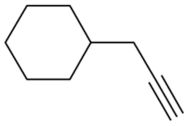
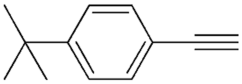
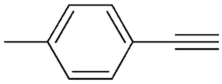
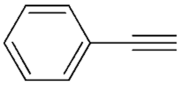
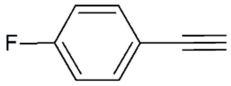
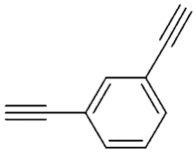
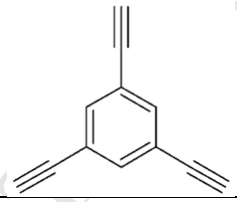
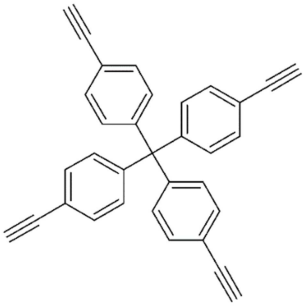
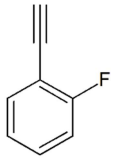
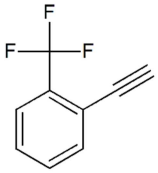
2 Results and discussion

2.1 Acidity characterization

The comparison of the catalytic activities of 12 terminal alkynes was performed based on kinetic studies of acetalization and esterification. Both monofunctional alkynes, (cyclopropylacetylene, 3-cyclohexylprop-1-yne, 1-ethynyl-2-fluorobenzene, 1-ethynyl-4-fluorobenzene, 4-ethynyltoluene, 4-*tert*-butylphenylacetylene, 2-ethynyl-*α,α,α*-trifluorotoluene, phenylacetylene [14]) and multifunctional alkynes [1,3-diethynylbenzene, 1,4-diethynylbenzene, 1,3,5-triethynylbenzene, and tetrakis(4-ethynylphenyl)methane], were involved in the study. Our previous study performed with polymer networks decorated with pendant ethynyl groups [15] showed that the hydrogen atoms of ethynyl groups of these materials acted as acid catalytic centers. We expected similar behavior in the case of hydrogen atoms of ethynyl groups of low molecular weight alkynes used in this study. In order to qualitatively assess the acidity of the alkynes used, the chemical shifts (*δ*) of the signal of their acetylenic hydrogen(s) in ^{1}H NMR spectra were determined. The ^{1}H NMR spectra were measured in CD_3OD and DMSO-d_6, the *δ* values of ≡C-*H* are given in Table 1 (for full spectra see Supplementary material).

Table 1. The chemical shift (*δ*) of ^{1}H NMR signal of hydrogen in ethynyl functional groups of terminal alkynes (in DMSO-d_6 and CD_3OD)

Terminal alkyne	Formula	(*δ*) of ≡C-*H* (in ppm)	
		in CD_3OD	in DMSO-d_6
Cyclopropylacetylene (Cy3ac)		2.00	2.5

3-Cyclohexylprop-1-yne (3CyHex1yn)		2.17	2.7
4-*tert*-Butylphenylacetylene (tBuPhac)		3.38	4.1
4-Ethynyltoluene (4ETOL)		3.39	4.1
Phenylacetylene (Phac)		3.47	4.2
1-Ethynyl-4-fluorobenzene (1E4FB)		3.47	4.2
1,3-Diethynylbenzene (1,3-DEB)		3.54	4.2
1,4-Diethynylbenzene (1,4-DEB)		3.63	4.4
1,3,5-Triethynylbenzene (1,3,5-TEB)		3.65	4.4
tetrakis(4-Ethynylphenyl)methane (TEPM)		[a]	4.2
1-Ethynyl-2-fluorobenzene (1E2FB)		3.73	4.5
2-Ethynyl-α,α,α-trifluorotoluene (2E3FTOL)		3.87	4.6

[a] Not soluble in methanol at 25 °C

The position of the signal of acetylenic hydrogen in ^{1}H NMR spectrum qualitatively correlates with the acidity of this hydrogen: with increasing acidity of acetylenic hydrogen, its ^{1}H NMR signal is downfield shifted (i.e. it is shifted to higher values of *δ*) and *vice versa*. [17,18] Both applied aliphatic alkynes (Cy3ac and 3CyHex1yn) showed low values of *δ* (*δ* < 3, Table 1), i.e. the acetylenic hydrogens of these alkynes were of lower acidity probably as a result of an electron-donating effect of aliphatic substituents. The values of *δ* obtained for aromatic alkynes were higher (*δ* ranging from 3.38 to 3.87 in CD_3OD and from 4.06 to 4.6 in DMSO-d_6 Table 1) that indicated higher acidity of acetylenic hydrogens due to the conjugation of ethynyl groups with aromatic segments in the molecules of these alkynes. Particularly high *δ* values were ascertained for 1E2FB and 2E3FTOL, i.e. the aromatic alkynes containing substituents with inductive electron-withdrawing effect (-F, -CF_3). Based on ^{1}H NMR measurement, these alkynes should be considered as the most acidic among of the alkyne series applied in our study. It should be noted, that the lower *δ* value and corresponding lower acidity of 1-ethynyl-4-fluorobenzene (1E4FB) (an aromatic alkyne that also contains -F substituent, however, in the position 4 on the ring) can be ascribed to the formation of bimolecular hydrogen-fluorine bonds between two oppositely oriented planar and symmetrical molecules of 1E4FB [19].

2.2 Acetalization

Acetalization is an acid catalyzed reaction, which is often used for the protection of functional groups in aldehydes, ketones, alcohols, and diols during reactions. This reaction is very often used in the preparation of biologically active compounds or fragrant compounds [20]. The acetalizations of pentanal, isopentanal, and heptanal with methanol selected as model reactions provided only traces of respective acetals if performed without any catalyst. Conversely, if a terminal alkyne from Table 1 was added as a catalyst to the reaction mixture, the acetalization provided moderate to high yields of respective dimethyl acetals as the only products. Probably due to the instability of hemiacetals in the reaction mixture (e.g. [20]), no traces of these compounds were detected. The yield of acetals ranged from 13% (acetalization of isopentanal catalyzed with Cy3Hex1yn) to 88% (acetalization of heptanal catalyzed with TEPM). Obtained results of acetalization reactions expressed as reaction rate, r_{240}, and turn over number, TON were summarized in Table 2 (monofunctional terminal alkynes applied as catalysts) and Table 3 (multifunctional terminal alkynes applied as catalysts).

Table 2 Acetalization of pentanal, isopentanal and heptanal by methanol using monofunctional terminal alkynes as catalysts (100 mg aldehyde, 10 mg catalyst, 3 mL methanol, 60 °C, reaction time 240 min for r_{240} and 24 h for TON)

Catalyst	Aldehyde					
	Pentanal		Isopentanal		Heptanal	
	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON
Cy3ac	5.4	5.0	2.5	3.3	1.2	3.6
3CyHex1yn	1.5	4.0	0.9	2.1	1.8	4.0
tBuPhac	2.2	6.4	---	---	---	---
4ETOL	1.7	4.3	---	---	---	---
Phac [9]	1.5	4.2	0.8	2.5	1.2	3.2
1E4FB	3.8	7.4	---	---	---	---
1E2FB	9.0	7.9	4.3	6.1	2.4	5.2
2E3FTol	12.5	11.4	6.7	8.4	3.5	7.5

Table 2 clearly shows that all applied monofunctional terminal alkynes act as homogeneous catalysts for acetalization of aldehydes (pentanal, isopentanal, and heptanal) with methanol. We assume, that

the partly acid acetylenic hydrogen atoms of these alkynes act as catalytically active species in the acetalization reactions.

In the reaction of the branched aldehyde, isopentanal, the reaction rates were notably lower in comparison to the reaction rate of acetalization of the linear izomer, i.e. pentanal. This indicates the steric hindrance of the hydrocarbon chain of the aldehyde molecule may be an important factor in decreasing the efficiency of alkyne-catalyzed acetalization. Likewise, the reaction rates and TONs are significantly lower in the case of the acetalization of heptanal in comparison to the acetalization of pentanal showing also the negative influence of the length of the chain on the reaction course.

Assuming the TON values as the measure of the catalytic activity, the most active catalyst among tested monofunctional terminal alkynes was 2-ethynyl-α,α,α-trifluorotoluene followed by comparably active 1-ethynyl-2-fluorobenzene. These catalysts are phenylacetylenes bearing in the ortho position to the ethynyl group electron withdrawing groups (CF_3, F) reducing the electron density of ≡C-H bond that leads to an increase in acidity of acetylenic hydrogen. This seems to be supported by relatively high values of the chemical shift of acetylenic hydrogen of 2-ethynyl-α,α,α-trifluorotoluene and 1-ethynyl-2-fluorobenzene in ^{1}H NMR spectra (Table 1). High TON value was obtained also for acetalization catalyzed by 1E4FB, i.e. phenylacetylene with electron-withdrawing F substituent in position 4 on the ring. Other monofunctionalized terminal alkynes were less active and the differences between their activities were slight and mostly in the range of experimental error (Table 2). Surprisingly, the catalytic activities of the two alkylacetylenes tested (Cy3ac and 3CyHex1yn) were comparable to the activity of phenylacetylene and its alkyl-substituted derivatives. In the case of arylacetylenes, the ethynyl group is partially conjugated with the aromatic ring, which reduces the electron density of the ethynyl group and increases the acidity of acetylenic hydrogen. Conversely, in the case of alkylacetylenes, the alkyl substituent increases the electron density of the ethynyl group, which reduces the acetylenic hydrogen acidity. The expected difference between the acidity of alkyl- and arylacetylenes is well supported by ^{1}H NMR spectroscopy (Table 1). However, the results in Table 2 show that the acetylenic hydrogen acidity may not be the only factor affecting the catalytic activity of the alkynes used. For example, the catalytic activity of arylacetylenes may be reduced due to π-π stacking interactions between planar aromatic segments of the molecules [21]. In this context, it is worth mentioning that the catalytic activity of tBuPhac with a strong electron donating *tert*-butyl substituent was higher than the catalytic activity of unsubstituted Phac (Table 2). This finding is consistent with the idea that a bulky *tert*-butyl substituent prevents π-π stacking interactions between benzene rings of tBuPhac, while these interactions are favored between planar molecules of Phac. The high catalytic activity of alkylacetylenes may also reflect good compatibility of alkyl substituents of aldehyde substrates with alkyl substituents of the alkylacetylene catalysts.

Table 3 Acetalization of pentanal, isopentanal and heptanal by methanol using multifunctional terminal alkynes as catalysts (100 mg aldehyde, 10 mg catalyst, 3 mL methanol, 60 °C, 240 min for r_{240} and 24 h for TON)

Catalyst	Aldehyde					
	Pentanal		Isopentanal		Heptanal	
	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON	r_{240} ($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)	TON
1,3-DEB	10.3	12.0	8.1	11.9	5.5	9.2
1,4-DEB	6.7	11.5	5.7	11.1	6.2	8.4

1,3,5-TEB	7.3	14.1	4.7	10.7	7.3	12.9
TEPM	13.6	40.6	15.6	37.6	23.6	37.3

The multifunctional terminal alkynes possessing two, three or four terminal ethynyl groups per molecule were demonstrated as active homogeneous catalysts of acetalization of model aldehydes (Table 3), as well. The highest catalytic activity was attained in the acetalization of pentanal. The acetalization of isopentanal and heptanal proceeded with slightly lower reaction rates and slightly lower TON values were achieved.

1,3-DEB, 1,4-DEB, and 1,3,5-TEB are di- and trifunctional terminal alkynes with planar aromatic molecules, which are structurally similar to phenylacetylene and differ mainly in the number of ethynyl groups. The TON values obtained with these catalysts in the acetalizations were significantly higher than the TON values achieved using phenylacetylene as the catalyst of the same reactions (Table 2 and 3). Such results could reflect the higher content of ethynyl groups in the molecules of these di- and trifunctional terminal alkynes. Nevertheless, the increase in catalytic activity of 1,3-DEB, 1,4-DEB, and 1,3,5-TEB compared to the activity of phenylacetylene was mostly more pronounced than would correspond to an increase in the number of ethynyl groups in their molecules. This was especially apparent in the case of the acetalization of isopentanal and heptanal. For example, the TON values of 2.5 and 11.1 were achieved in acetalization of isopentanal catalyzed with Phac (one ethynyl group per molecule) and 1,4-DEB (two ethynyl groups per molecule), respectively. We think this is because of the presence of more ethynyl groups in the molecules of 1,3-DEB, 1,4-DEB and 1,3,5-TEB that increased the overall conjugation of these molecules and led to an increase in the acidity and catalytic efficiency of the acetylenic hydrogens of these terminal alkynes. The highest TON values were, however, achieved in acetalizations catalyzed with TEPM (TON values from 37.3 to 40.6 in dependence on the substrate, see Table 3). The TON value achieved with this tetrafunctional alkyne in acetalization of pentanal was 9.7 times higher than the TON value achieved in the same reaction catalyzed with Phac. In the case of acetalization of isopentanal, the TON value increased even 15 times if TEPM was applied as the catalyst instead of Phac. It should be noted that the conjugation between the benzene rings in the TEPM molecule is significantly limited both because of the tetragonal geometry of the molecule and the presence of the central sp^3 carbon in the molecule. On the other hand, the tetragonal geometry of the TEPM molecule, which differentiates TEPM from other applied multifunctional alkynes, may be responsible for the observed high catalytic activity of TEPM. The non-planar tetragonal geometry of the TEPM most probably prevents intermolecular π-π stacking interactions thus allowing the ethylene groups of TEPM to be fully involved in the catalytic process.

2.3 Esterification

Esterification is another typical acid catalyzed reaction, which does not proceed without catalyst addition (except for oxalic acid). That was why we have evaluated and compared the catalytic activity of the mono- and multifunctional terminal alkynes under study in esterification of acetic, lauric and benzoic acid with *n*-butanol. The achieved results were summarized in Table 4.

Table 4 Esterification of acetic, lauric, benzoic and *p*-nitrobenzoic acid with *n*-butanol catalyzed with mono- and multifunctional terminal alkynes (100 mg acid, 10 mg catalyst, 5 mL *n*-butanol, under reflux, 420 min for r_{240} and 24 h for TON)

Catalyst	Acid							
	Acetic		Lauric		Benzoic		*p*-Nitrobenzoic	
	r_{420}	TON	r_{420}	TON	r_{420}	TON	r_{420}	TON

	(*)		(*)		(*)		(*)	
Cy3ac	1.6	7.0	0.2	0.9	0.02	0.2	0.04	0.1
Phac	3.9	11.8	0.2	1.4	0.07	0.8	0.05	0.2
3CyHex1yn	4.6	17.2	0.1	1.1	0.02	0.3	0.02	0.3
1E2FB	3.2	13.3	0.1	0.9	0.03	0.3	0.03	0.2
2E3FTOL	5.4	22.7	0.1	2.8	0.03	1.4	0.05	0.4
1,3-DEB	7.3	20.2	0.4	1.5	0.14	0.4	0.05	0.3
1,4-DEB	7.5	21.3	0.5	2.7	0.12	1.1	0.03	0.3
TEPM	26.6	55.0	2.1	11.5	0.52	3.0	0.10	0.8

*($mol \cdot l^{-1} \cdot min^{-1} \cdot mol^{-1}$)

All three carboxylic acids provided respective *n*-butyl esters in the presence of all the alkynes tested as catalysts. The esterification efficiency, however, significantly depended on the type of carboxylic acid and the type of catalyst as well. Using acetic acid as a substrate significantly higher reaction rates and TON values were achieved in comparison to lauric, benzoic and *p*-nitrobenzoic acids. 2E3FTOL with strongly electron-withdrawing CF_3 substituent and both diethynyl benzene izomers exhibited particularly high activity in acetic acid esterification (TON ~ 20, the yield of ester ~ 92 %). Nevertheless, this esterification was the most efficient if tetrafunctional TEPM was used as the catalyst (TON = 55, yield = 92 %). Simultaneously TEPM was the only alkyne that was promising also for esterification of lauric and benzoic acids. The decreased efficiency in esterification of lauric, benzoic and *p*-nitrobenzoic acids (compared to acetic acid) is not surprising because the esterification of carboxylic acids with longer aliphatic chains and aromatic carboxylic acids is usually more complicated [22,23]. The achieved conversions of *p*-nitrobenzoic acid were lower in comparison to benzoic acid, despite of the higher acidity (pKa 3.41 resp. 4.19 [24]). This confirms that fact, that the acidity of used acid is not the only parameter, which influences the overall rate of esterification. Nevertheless, the differences between reaction rates using these two acids as substrates were really slight (the differences between achieved conversions were about 5 % after 24 h using the same catalyst). That is the reason why making the general conclusions is not possible. As expected, the acidity of mentioned terminal alkynes is definitely not comparable to the acidity of catalysts commonly used in esterification (e.g. mineral acids or exchange resins).

3 Conclusions

In this paper, we confirmed that the wide spectrum of aromatic and aliphatic alkynes with a variable amount of terminal ethynyl groups can be applied as acid catalysts for particular organic reactions. The possible use of mono- as well as multifunctional alkynes, was described and their catalytic activities were compared.

The activity of terminal alkynes applied as catalysts in acetalization of aliphatic aldehydes decreased with increasing length and the branching of aldehydic chain. In general, all the alkynes were most efficient in acetalization of pentanal. The most active monofunctional terminal alkynes were 2-ethynyl-α,α,α-trifluorotoluene and 1-ethynyl-2-fluorobenzene, which can be explained by their relatively high acidity (confirmed also by ^{1}H NMR spectroscopy). The multifunctional terminal alkynes exhibited significantly higher catalytic activity in acetalization than monofunctional ones. This increase in catalytic activity was partly due to the higher number of ethynyl groups per alkyne molecule and partly due to the higher extent of conjugation (di- and triethynylbenzenes) and suppression of π-π stacking interactions [tetrakis(4-ethynylphenyl)methane].

Esterification of acetic acid by *n*-butanol proceeded with good yields using all aforementioned terminal alkynes as catalysts (over 70% in 24 h). The reactions of the three other substrates, lauric, benzoic and *p*-nitrobenzoic acid, featured with the significantly lower reaction rate, what was expected because of their structure. Only tetrafunctional alkyne, tetrakis(4-ethynylphenyl)methane, was promising as the catalyst for these esterifications.

It can be stated that the acidity of hydrogen of terminal ethynyl groups of alkynes is sufficient for performing typically acid catalyzed reactions – acetalization and esterification, resulting in dimethyl acetals and esters of acetic acid in good yields.

4 Experimental part

4.1 Materials

All chemicals were used as obtained, namely acetic acid (Lach-Ner, 99%), benzoic acid (Lachema, p.a.), butan-1-ol (Penta, p.a.), cyclopropylacetylene (Cy3ac, UCT Prague, 99.4%), 3-cyclohexylprop-1-yne (3CyHex1yn, Sigma-Aldrich, 98%), 1,3-diethynylbenzene (1,3-DEB, TCI Chemicals, >96%), 1,4-diethynylbenzene (1,4-DEB, TCI Chemicals, >98%), dimethyl sulfoxide (DMSO, Penta, p.a.), heptanal (Sigma-Aldrich, >92%), isopentanal (Sigma-Aldrich, 98%), lauric acid (Sigma-Aldrich, 97%), methanol (Penta, p.a.), *p*-nitrobenzoic acid (Lachema, p.a.), pentanal (Sigma-Aldrich, 97%), tetrahydrofuran (THF, Penta, p.a.), 1-ethynyl-2-fluorobenzene (1E2FB, Sigma-Aldrich, 97%), 1-ethynyl-4-fluorobenzene (1E4FB, Sigma-Aldrich, 99%), 4-ethynyltoluene (4ETOL, Sigma-Aldrich, 97%) 2-ethynyl-*α,α,α*-trifluorotoluene (2E3FTOL, Sigma-Aldrich, 97%), 4-*tert*-butylphenylacetylene (tBuPhac, Sigma-Aldrich, 96%), tetrakis(4-ethynylphenyl)methane (TEPM, TCI Chemicals, >98%) and 1,3,5-triethynylbenzene (1,3,5-TEB, TCI Chemicals, >98%)).

4.2 Catalytic tests

4.2.1 Acetalization

100 mg of aldehyde, 10 mg of catalyst and 3 mL of methanol were introduced into the flask (25 mL) and kept under stirring (400 rpm) at 60 °C for 24 h.

4.2.2 Esterification

100 mg of carboxylic acid, 10 mg of catalyst and 5 mL of *n*-butanol were introduced into the flask (25 mL) and kept under stirring (400 rpm) under reflux for 24 h.

4.3 Analytical

The taken samples from reaction mixtures were analyzed using gas chromatography (GC) to determine the composition of the reaction mixture and gas chromatography with a mass spectrometer (GC/MS) for confirmation of the product´s structure.

Reaction rates and turn over numbers (TONs) were calculated according to the following equations (Eq. 1, 2).

$$r_t = \frac{\Delta c}{\Delta t \cdot n_{cat}} \quad \left(\frac{mol}{l \cdot min \cdot mol}\right) \qquad \text{Equation 1}$$

$$TON = \frac{\Delta n_{products}}{n_{cat}} \quad (-) \qquad \text{Equation 2}$$

Where Δc is the change in analytical concentration of reactant during Δt time interval, $\Delta n_{products}$ is the change in the molar amount of the products during total reaction time, n_{cat} is the amount of the catalyst in the reaction mixture.

4.4 ^{1}H NMR

^{1}H NMR analyses of alkynes were performed in DMSO-*d6* or CD_3OD using an NMR spectrometer (Bruker 600 Avance^{III}). The spectra were referenced to solvent signals.

Acknowledgment

This work was realized within the Operational Programme Prague – Competitiveness (CZ.2.16/3.1.00/24501) and "National Program of Sustainability" ((NPU I LO1613) MSMT-43760/2015). We acknowledge grant project GACR 17-03474S and Specific University Research project (MSMT No 21-SVV/2018).

References

1. L. Hintermann, A: Labonne, Synthesis 8 (2007) 1121.

2. Y. Fukuda, K. Utimoto, J. Org. Chem. 56(11) (1991) 3729.

3. S. Saito, Y. Yamamoto, Chem. Rev. 100 (2000) 2901.

4. P. Štěpnička, I. Císařová, J. Sedláček, J. Vohlídal, M. Polášek, Collect. Czechoslov. Chem. Commun. 62 (1997) 1577.

5. A.B. Smith, S.S.-Y. Chen, F. Nelson, J.M. Reichert, B.A. Salvatore, J. Am. Chem. Soc. 119 (1997) 10935.

6. J. Sedláček, H. Balcar, Polym. Rev. 57(1) (2017) 31.

7. J. Liu, J.W.-Y. Lam, B. Z. Tang, Chem. Rev. 109 (2009) 5799.

8. R. Dawson, A. Laybourn, R. Clowes, Y.Z. Khimyak, D.J. Adams, A.I. Cooper, Macromolecules 42 (2009) 8809.

9. E. Slováková, M. Ješelnik, E. Žagar, J. Zedník, J. Sedláček, S. Kovačič, Macromolecules 47 (2014) 4864.

10. B.O. Öztürk, S.K. Sehitoglu, Appl. Organometal. Chem. 30 (2016) 367.

11. R. Roy, P. Rajasekaran, A. Mallick, Y.D. Vankar, Eur. J. Org. Chem. 25 (2014) 5564.

12. F. Piacenti, M. Bianchi, P. Frediani, G.J. Menchi, Mol. Catal. 83 (1993) 83.

13. P. Patnaik In A Comprehensive Guide to the Hazardous Properties of Chemical Substances, John Wiley & Sons: Hoboken, NJ, USA, 2007, Vol. 3, pp 592-597.

14. L. Sekerová, M. Frýbová, E. Vyskočilová, L. Červený, *Proceeding Paper*, 5th International Conference on Chemical Technology, Mikulov, CZ, 10.-12.4.2017.

15. L. Sekerová, M. Lhotka, E. Vyskočilová, T. Faukner, E. Slováková, J. Brus, L. Červený, J. Sedláček, Chem. Eur. J., 24 (2018) 14742.

16. L. Sekerová, M. Frýbová, E. Vyskočilová, L. Červený, J. Sedláček, T. Faukner, *Proceeding Paper*, 6th International Conference on Chemical Technology, Mikulov, CZ, 16.-18.4.2018.

17. Y. Okamoto, K.L. Chellappa, S.K. Kundu, J. Org. Chem. 37 (1972) 3185.

18. R. Sivkova, O. Trhlíková, J. Zedník, J. Sedláček, Macromol.Chem. Phys. 2016 (2015) 2115.

19. A.K. Howard, V.J.Hoy, D. O´Hagan, G.T. Smith, Tetrahedron 52(38) (1996) 12613.

20. T.L. Lemke, V.F. Roche, W.S. Zito In Review of Organic Functional Groups: Introduction to medicinal Organic Chemistry, Lippincott Williams & Wilkins: Baltimore, USA, 2003), Vol. 3, pp 35-37.

21. S. Maity, G.N. Patwari, R. Sedlak, P. Hobza, Phys. Chem. Phys. 13 (2011) 16706.

22. M. Aslam, G.P. Torrence, E.G. Zey In Kirk-Othmeer Encyclopedia of Chemical Technology, A. Seidel, Ed., John Wiley and Sons: New York, 2000, Vol. 5, pp 770.

23. M. Mirza-Aghayan, R. Boukherroub, M. Rahimifard, Turk. J. Chem. 38 (2014) 859.

24. K. Gupta, S. Giri, P. K. Chattaraj, New J. Chem. 32 (2008) 1945.