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Title: NaOH or H2O as a Switch for the Direct Synthesis of Aryl Acetylenes or 1-Bromoethynylarenes from Aldehydes

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DBU-Mediated Synthesis of Aryl Acetylenes or 1-Bromoethynylarenes from Aldehydes

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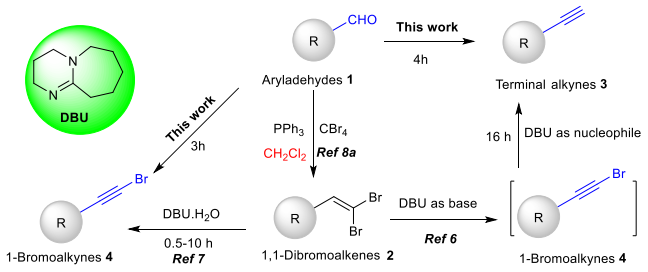
Abstract. Two well known synthetic organic reactions Ramirez olefination and Corey-fuchs reactions are integrated in one-pot sequential manner for the synthesis of arylacetylenes and 1,3-enynes starting directly from commercially available aldehydes. The bicyclic amidine 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) along with additive NaOH not only exclusively afforded the terminal alkynes directly from the aldehydes, but also enhanced the reaction rate. The dynamic nature of DBU also facilitated the isolation of 1-bromoalkynes intermediate products. Selection of additive from NaOH and H_2O served as a switch for the synthesis of terminal alkyne and 1-bromoalkynes, respectively.

Keywords: Aldehyde; Terminal alkyne; 1-Bromoarylacetylenes; Ramirez olefination; Corey-Fuchs reaction; DBU

Introduction

It is well known that alkynes,[1,2] enynes,[3] and 1-bromoalkynes[4] are important synthons in the synthesis of pharmaceuticals and agricultural chemicals, as well as being used in material industry.[5] Recently, we have identified 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as an efficient reagent for the synthesis of terminal alkynes[6] **3**, and 1-bromoalkynes[7] **4** starting from 1,1-dibromoalkenes **2** which are obtained from aldehydes **1** (Scheme 1).[8] In the present work, we describe a challenging one-pot synthetic process to access enynes, terminal alkynes **3** and 1-bromoalkynes **4** starting directly from commercially available aldehydes **1** (Scheme 1).



Scheme 1. Schematic for the one-pot Synthesis of terminal alkynes and 1-bromoalkynes using DBU

Few methods report[9] the direct synthesis of terminal alkynes **3** from aldehydes **1.** Only Ohira-Bestman reagent[10] (dimethyl 1-diazo-2-oxopropylphosphonate) is currently widely used; this useful transformation is popularly known as Seyferth-Gilbert homologation. However, diazo reagents used in this method are relatively expensive, unsafe and also have limitations in the synthesis of 1,3-enynes starting from cinnamaldehydes.[11] Therefore, the two-step synthesis of terminal alkynes **3** from aldehydes **1** is still more widely used than the Seyferth-Gilbert homologation method. This synthesis generally involves two consecutive reactions: i) Ramirez olefination of aldehydes **1** to give 1,1-dibromoalkenes **2** using triphenyl phosphine (PPh_3) and Carbon tetrabromide (CBr_4) in dichloromethane solvent.[8] ii) Corey-Fuchs reaction of dibromoalkenes **2** to give terminal alkynes **3** using n-BuLi at -78 °C in tetrahydrofuran.[12] The one-pot procedure for the above two steps would be difficult due to the incompatibility of pyrophoric reagent n-BuLi with CBr_4 used in the first step.

Results and Discussion

Due to the need for the direct synthesis of alkyne derivatives from aldehydes, this experiment looked to

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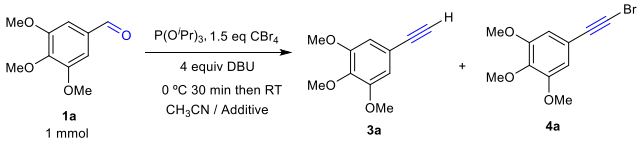
evaluate the feasibility of one-pot synthesis of terminal alkynes **3** from aldehydes **1** (Table 1) using modified Ramirez olefination (CBr_4 / $P(O^iPr)_3$ / CH_2Cl_2) reported by Lautens *et al.*[13] followed by modified Corey-Fuchs reaction (DBU / CH_3CN) reported by us.[6] Triisopropyl phosphite $P(O^iPr)_3$ was chosen instead of generally employed triphenylphosphine (PPh_3) in the first stage of the two-step procedure is to avoid tedious and solvent-consuming removal of generated waste crystalline triphenylphosphine oxide in the final purification.

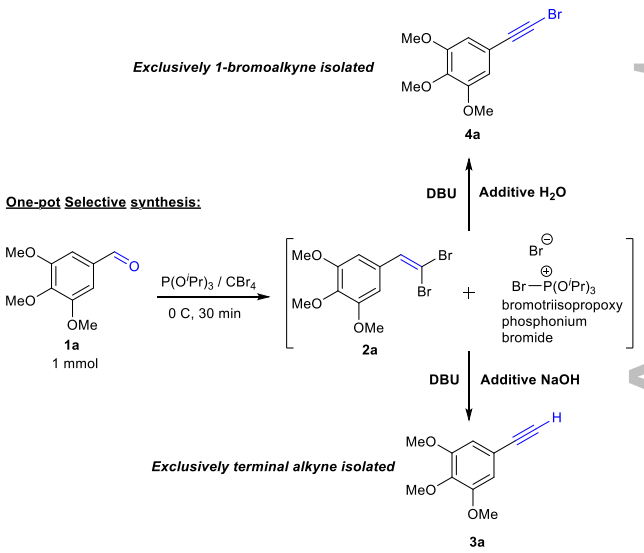
Table 1. Optimization study[a]



Entry	CH_3CN in mL	Additive 5 mmol	Time	Yield[b] **3a** %	Yield[b] **4a** %
1	3	-	16 h	10	81
2	3	-	48 h	7	78
3	3	DBU	24 h	27	-
4	3	$NaHCO_3$	16 h	62	-
5	3	NaOMe	9 h	75	-
6	3	NaOH	6 h	83	-
7	3	KOH	6 h	79	-
8	**2**	**NaOH**	**4 h**	**95**	-
9	1	NaOH	9 h	65	-
10	**2**	**H_2O**	**3 h**	-	**94**

[a]Reaction conditions: Aldehyde (1 mmol), CBr_4 (1.5 mmol), $P(O^iPr)_3$ (2 mmol), DBU (4 mmol) in CH_3CN added at 0 °C and then and additive (5 mmol) at RT [b]Isolated yields.

Firstly, we started a reaction of aryl aldehyde **1a** (1 mmol) with triisopropyl phosphite $P(O^iPr)_3$ (2 mmol) and tetrabromomethane CBr_4 (1.5 mmol) in acetonitrile (3 mL)[14] at 0 °C. After 10 min, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 4 mmol) was added to the reaction mixture at 0 °C and the mixture was allowed to stir at room temperature (Table 1, entry 1). After 16 hours there was complete consumption of aldehyde **1a** starting material and formation of alkyne **3a** *albeit* in a low yield of 10%, along with 1-bromoalkyne **4a** in 81% yield (Table 1, entry 1). This result clearly reveals that the 4 equiv of DBU added at a later stage could not completely convert in situ formed 1,1-dibromoalkene **2a** to terminal alkyne **3a** even after running reaction for 48 h (Table 1, entry 2). These results are in accordance with the known dual role of DBU on 1,1-dibromoalkenes **2;** as a base it produces 1-bromoalkyne **4**, and subsequently it acts as a nucleophile which produces terminal alkyne **3** (Scheme 1).[6] The low yields of terminal alkyne **3a** (Table 1, entries 1-2) can be rationalized by the reduced nucleophilic activity of DBU (Scheme 1). This reduced activity could be caused by the electrophilic by-product bromotriisopropoxyphosphonium bromide[13] $P(O^iPr)_3Br_2$ formed in the Ramirez olefination (Scheme 2). To increase the yield of terminal alkyne, excess DBU was added to the reaction mixture (Table 1, entry 3). Terminal alkyne **3a** was isolated as a single product in 27% yield, with no trace of 1-bromoalkyne **4a**. From this result, we hypothesize that excess DBU caused decomposition of the reaction mixture (Table 1, entry 3). Next, the electrophilic by-products formed *in situ* were iteratively quenched by the addition of powdered alkaline bases sodium bicarbonate (Table 1, entry 4), sodium methoxide (Table 1, entry 5), sodium hydroxide (Table 1, entry 6) and potassium hydroxide (Table 1, entry 7). Sodium hydroxide was found to be best in terms of yielding terminal alkyne **3a**; this could be the result of quenching the by-product in the first stage Ramirez olefination, but also due to an increase in the overall rate of the reaction (Table, entry 6) since the base-catalyzed reaction was completed in 9 hours. Concentration of reagents (Table 1, entries 6,8-9) was found to play an important role in obtaining the best yield (Table 1, entry 8, 97 %) of terminal alkyne **3a.** Increased rate of reaction was observed, when 2 mL of solvent per a mmol of starting material was used (Table 1, entry 8). Interestingly, when water was used as an additive (Table 1, entry 10) instead of NaOH, (Table 1, entry 8) 1-bromoalkyne **4a** was produced exclusively with no trace of terminal alkyne **3a**. This result clearly demonstrates that water controls the nucleophilic character of DBU during the synthesis of 1 bromoalkyne **4a**.[7]



Scheme 2. Switched role of additive NaOH/H_2O after the addition of DBU in the selective one-pot synthesis of terminal alkynes and 1-bromoalkynes

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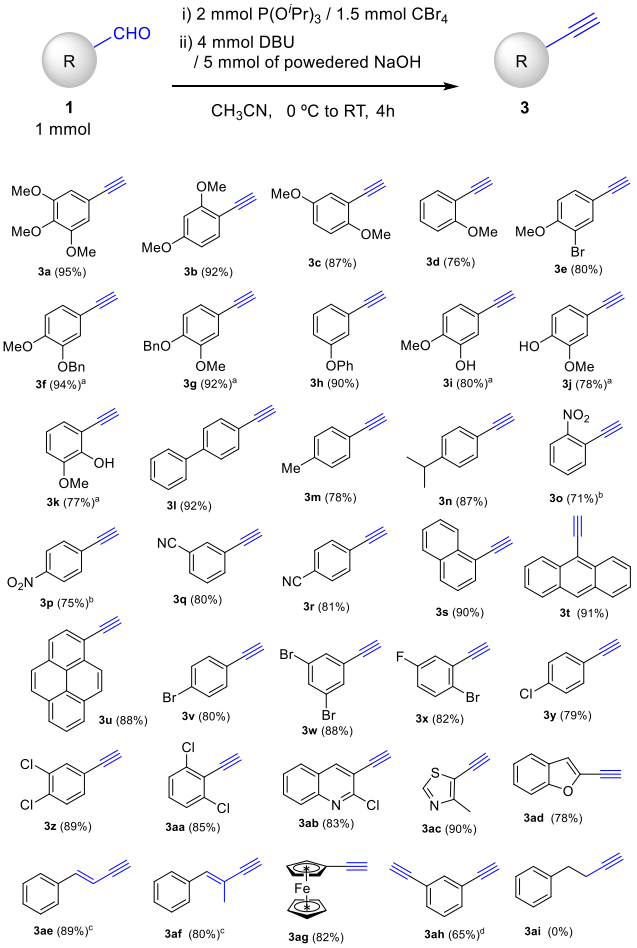
With this newly-established synthetic protocol for the synthesis of terminal alkynes and 1-bromoalkynes from aldehydes in hand (Table 1, entries 8, 10), the scope for the synthesis of terminal alkynes **3** from aldehydes **1** (Scheme 3) was probed using optimized conditions (Table 1, entry 8).

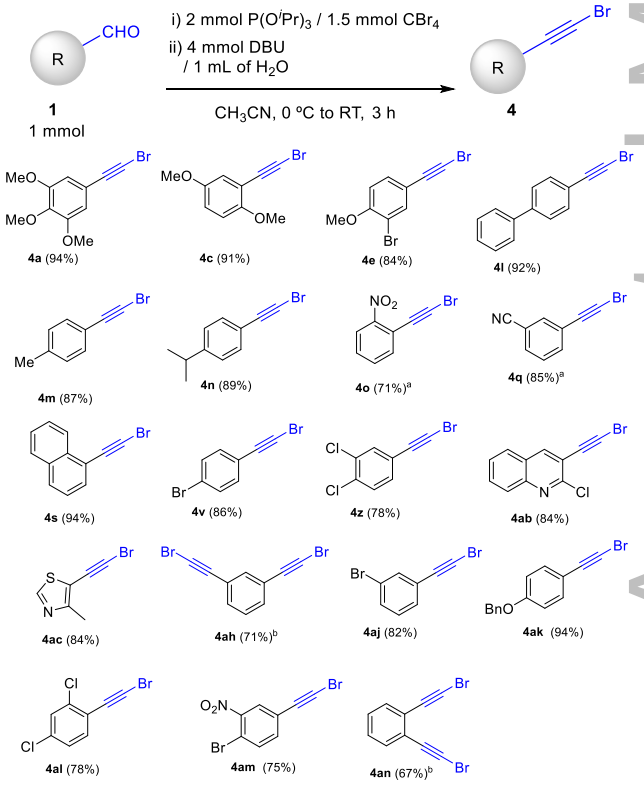


[a] Reaction time 5 h. [b] Reaction time 2 h and only 2 mmol of DBU used. [c] Reaction time 8 h.
[d] 4 mmol P(OiPr)3, 3 mmol CBr4, 8 mmol of DBU and 10 mmol NaOH.

Scheme 3. Substrate scope of aryl acetylenes

Substrates bearing electron-donating (**1a-n**) as well as electron deficient (**1o-r**) groups containing aldehydes were well tolerated, affording good to excellent yields of terminal alkynes **3a-r**. To our delight, hydroxyl group containing arylaldehydes **1i-k** also furnished corresponding terminal alkynes **3i-k** in very good yields (Scheme 3). In addition, polyaromatic substrates **1s-u** were successfully converted to terminal alkynes **3s-u** in excellent yields. Significantly, halogen containing substrates **1v-1ab**, including the sensitive compound **1ab**, underwent the one-pot transformation cleanly to give the desired alkynes in good yields. Furthermore, heteroaromatic compounds **1ab-1ad** such as thioazo compound **1ac** and benzofuran **1ad** were well tolerated and resulted in the production of the alkynes in very good yields. Notably, styryl aldehydes **1ae** and **1af** could produce 1,3-enynes **3ae** and **3af** in very good yields, which cannot be produced using Gilbert-Stayferth homologation.[10] Importantly, the described method is also useful for the synthesis of alkyne **3ag** bearing an organometallic ferrocene. The synthetic utility of this method was further evaluated with a substrate containing two aldehydes groups **1ah**, resulting in the isolation of bis-acetylene **3ah** in moderate yield (55%). In contrast, the alkylated aldehyde **3ai** did not react to give the corresponding alkyne, further highlighting the selectivity of aryl substrates over alkyl substrates in this transformation.

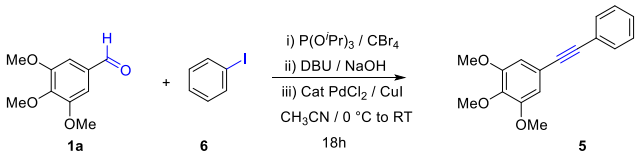
Having extensively evaluated the scope of aldehyde substrates **1** for the synthesis of terminal alkynes **3**, the substrate scope for the one-pot economic synthesis of 1-bromoalkynes **4** was explored (Scheme 4) by using optimized reaction conditions (Table 1, entry 10)**.** Other than previously explored aldehydes **1a, 1c, 1e, 1l-o, 1q, 1s, 1z, 1ab, 1ac, 1ah,** new aldehyde substrates **1aj, 1ak, 1al, 1am, 1an** (Scheme 4) were tested to give their corresponding 1-bromoalkynes **4**. To our delight, 1-bromoalkynes bearing electron-donating (**4a, 4c, 4e, 4m, 4n, 4ak**) electron-withdrawing (**4o, 4q**, **4am**), halogenated **(4v, 4z, 4ab, 4al, 4am**), polyaromatic (**4s**), and heteroaromatic (**4ab, 4ac**) functional groups gave good to excellent yields (Scheme 4). The reactions of isophthalaldehyde **1ah** and phthalaldehyde **1am** proceeded cleanly to give their corresponding bis(bromoethynyl)benzenes **4ah** and **4an** respectively in moderate yields (Scheme 4).



[a] Reaction time 2 h [b]4 mmol P(OiPr)3, 3 mmol CBr4, 6 mmol of DBU

Scheme 4. Substrate scope of 1-bromoethynylarenes

Although this method is currently limited to the selective synthesis of terminal alkynes or 1-bromoalkynes, we envision that sequential Sonogashira coupling would provide the first example for the synthesis of an internal alkyne **5** directly from aldehyde **1a** and coupling partner aryl iodide **6** (Scheme 5). To this end, 1.1 mmol of aryl iodide ArI **6**, catalytic amounts of $PdCl_2$ (0.05 mmol) and CuI (0.1 mmol) was added to the same vessel after completion of the Corey-Fuchs reaction, giving desired internal alkyne in 90 % yield **5** at ambient temperature (Scheme 5). This result shows our protocol is amenable to integration of three popular reactions: Ramirez olefination, Corey-Fuchs reaction, and Sonogashira couplings in one-pot.[15]



Scheme 5. Synthesis of internal alkyne from aldehyde and iodobenzene

Conclusion

The described one-pot procedure allowed *in situ* formation of 1,1-dibromoalkenes at 0 °C to RT followed by the formation of 1-bromoalkynes or terminal alkynes at RT. Various substrates with different electronic properties are tolerated in this protocol. Additive NaOH beneficial in not only the exclusive synthesis of terminal alkynes but also for enhancing the rate of reaction to completion in 4 h. In contrast, 16 h is required for the synthesis of terminal alkynes from isolated 1,1-dibromoalkenes without using additive NaOH.[6] Additives NaOH and H_2O played a pivotal role as a switch for the selective synthesis of terminal alkynes and 1-bromoalkynes, respectively. DBU and additives NaOH and H_2O are relatively safe reagents compared to pyrophoric reagents such as n-BuLi or Ohira-Bestman reagent for the generation of alkyne functionality. Importantly, the use of acetonitrile as solvent is found to be highly efficient as a substitute for the harmful chlorinated solvent CH_2Cl_2 generally used in Ramirez olefination. We believe these developed protocols may useful and find immediate applications in a wide range of synthetic applications, especially in pharmaceutical, material and fine chemical industries.

Experimental Section

Representative experimental procedure for preparation of terminal alkynes from aldehydes: Synthesis of 5-ethynyl-1,2,3-trimethoxybenzene (3a): To a stirred solution of 3,4,5-trimethoxybenzaldehyde 1a (196 mg, 1.0 mmol) and tetrabromomethane (498 mg, 1.5 mmol) in anhydrous CH_3CN (2 mL), triisopropyl phosphite (0.49 mL, 2 mmol, 2 equiv) was added drop wise over a period of 5 min at 0 °C. After 10 min, DBU (0.59 mL, 4.0 mmol) was added to the reaction mixture drop wise over a period of 5 min at same temperature 0 °C. The reaction mixture was then allowed to reach ambient temperature over 30 min under stirring. Powdered sodium hydroxide (5-10 mmol) was added to the reaction mixture and allowed to stir for 4 h at ambient temperature. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with 10 mL of water. The reaction mixture was extracted with EtOAc (2 X 25 mL) and the organic layers were washed with brine solution (10 mL). The organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude residue. This crude residue was purified on SiO_2 (60-120 mesh) column using hexanes/EtOAc (95:5) as eluents to afford the analytically pure terminal alkyne 3a as a white solid (182 mg, 95 % yield).

Representative experimental procedure for the synthesis of 1-bromo alkynes from aldehydes: Synthesis of 5-(bromoethynyl)-1,2,3-trimethoxybenzene (4a): To a stirred solution of 3,4,5-trimethoxybenzaldehyde **1a** (196 mg, 1.0 mmol) and tetrabromomethane (498 mg, 1.5 mmol) in anhydrous CH_3CN (2 mL), triisopropyl phosphite (0.49 mL, 2 mmol, 2 equiv) was added drop wise over a period of 5 min at 0 °C. After 10 min, DBU (0.59 mL, 4.0 mmol) was added to the reaction mixture drop wise over a period of 5 min at 0 °C. The reaction mixture was then allowed to reach ambient temperature during 30 min under stirring. Water H_2O (1 mL) was added to the reaction mixture and allowed to stir for 3 h at ambient temperature. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with 10 mL of water. The reaction mixture was extracted with EtOAc (2 X 25 mL) and the organic layers were washed with brine solution (10 mL). The organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude residue. This crude residue was purified on SiO_2 (60-120 mesh) column using hexanes/EtOAc (95:5) as eluents to afford the analytically pure 1-bromo alkyne **4a** as a colorless solid (253 mg, 94 % yield).

Experimental procedure for preparation of internal alkyne: 1,2,3-trimethoxy-5-(phenylethynyl)benzene: To a stirred solution of 3,4,5-trimethoxybenzaldehyde **1a** (196 mg, 1.0 mmol) and tetrabromomethane (498 mg, 1.5 mmol) in anhydrous CH_3CN (2 mL), triisopropyl phosphite (0.49 mL, 2 mmol, 2 equiv) was added drop wise over a period of 5 min at 0 °C. After 10 min, DBU (0.59 mL, 4.0 mmol) was added to the reaction mixture drop wise over a period of 5 min at 0 °C. The reaction mixture was then allowed to reach ambient temperature during 30 min under stirring. Powdered sodium hydroxide (5-10 mmol) was added to the reaction mixture and allowed to stir for 4 h at ambient temperature. Subsequently, $PdCl_2$ (0.05 mmol), iodobenzene 6 (0.14 mL, 1.0 mmol), and CuI (0.05 mmol) were added to the reaction mixture. The reaction mixture was allowed to stir at ambient temperature for 14 h under inert atmosphere. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by water (10 mL) and stirred for 5 mins. The reaction mixture was extracted with EtOAc (30 mL) and the organic layers were washed with brine (10 mL). The organic layers were dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to afford a crude residue. This crude residue was purified on SiO_2 (60-120 mesh) column using Hexanes/EtOAc (95:5) as eluents to afford the analytically pure **5** as a colorless liquid (241 mg, 90 % yield).

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FULL PAPER

DBU-Mediated Synthesis of Aryl Acetylenes or 1-Bromoethynylarenes from Aldehydes

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