Indian Journal of Chemistry
Vol. 62, August 2023, pp. 823-826
DOI: 10.56042/ijc.v62i8.736

A green protocol for the base, ligand, and phase transfer catalyst free coupling of terminal acetylenes in water

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Received 20 April 2023; accepted (revised) 6 July 2023

A green reaction methodology has been developed for the homocoupling / heterocoupling of terminal alkynes to construct the building block 1,4-diarylbuta-1,3-diyne. The coupling reaction occurs in an aqueous medium in absence of any additional base, ligand, or phase transfer catalyst. Water extract of banana peel ash (WEB) plays a magical role in performing the palladium catalyzed coupling reactions of non-polar organic molecules in polar aqueous medium.

Keywords: WEB, $PdCl_2$, Coupling, Terminal alkyne, 1,3-Diyne

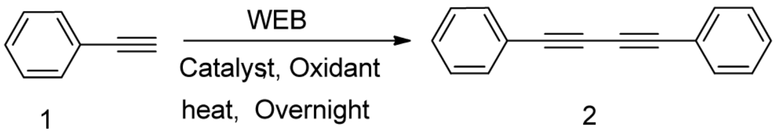
Copper-catalyzed ethylenic coupling reactions have a long history of about 150 years. In 1869, Carl Glaser observed that oxidation of Cu(1) phenyl acetylide led to diphenyldiacetylene *via* dimerisation[1-3]. However, recently, Glaser reactions have been employed in the synthesis of sharp persistent macrocycles, molecular recognition processes, conjugated ethylenic polymers, *etc*.[4,5] Jia and co-workers have reported a facile CuI/I_2 mediated methodology for synthesizing 1,3-diynes *via* coupling between terminal alkyne carbons in DMF solvent at 80°C, here Iodine acts as the oxidizing agent[6]. Jiang *et al*. have synthesized 1,3-diynes *via* homocoupling of terminal acetylenes by using CuAL-LDH complex and TMDEA acts as the ligand in acetonitrile solvent[7]. Recently Kesavan *et al*. have developed a room temperature homocoupling process for terminal acetylenes in presence of $Cu(OAc)_2$ catalyst and piperidine base in dichloromethane solvent[8,9].

Nowadays, green chemistry is the sustainable and eco-friendly usage of scientific protocols. The conventional protocols are modified to newer ones, to increase sustainability on technological and economical grounds. The chemical synthesis can be made in the one principle of green chemistry[10]. Sarma and co-workers utilized the water extract of banana peel ash (WEB) as solvents for Suzuki-Miyaura cross-coupling[11]. Bananas are one of the most abundant fruits. Their waste peels are biodegradable and can be used as a fertilizer for growing plants. Water extract of banana peel ash (WEB), which can be employed in organic transformations[12].

WEB is obtained by mixing ashes of dry banana peels (*Musa balbisiana* Colla, family: Musaceae) with water, followed by filtration to obtain the required extract (filtrate). It contains sodium ions, hydroxide ions, and chloride ions (*p*H=12.8). WEB = Ca (14.98%),Mg (9.33%), K (32.54%), Na (0.37%), Fe (33.9%), Mn (4.16%)[13]. Herein, we have developed an environmentally friendly green reaction methodology for the coupling of terminal acetylenes in WEB solvent extract in presence of palladium chloride ($PdCl_2$) catalyst and oxidizing agent $Cu(OAc)_2$ at 70°C temperature.

At first, we have chosen phenylacetylene as a model substrate and performed the reaction in water extract of banana peel ash (WEB) solvent in presence of palladium chloride ($PdCl_2$) catalyst and copper bromide CuBr as the oxidising agent and we have isolated the coupling product in 40% yield. Then we have used different oxidising agents to improve the reaction yield (Table 1, Entry 2-5). We found that oxidising agent $CuCl_2$, $CuSO_4$ (Table 1, Entry 2,3) gave poor yields whereas the highest yield was obtained from copper acetate with WEB solvent (Entry 4). When we performed the reaction at room temperature in presence of $PdCl_2$ catalyst and $Cu(OAc)_2$, the yield was decreased to 45%. We also observed that the product was not formed in absence of either the catalyst $PdCl_2$ or the oxidizing agent $Cu(OAc)_2$.

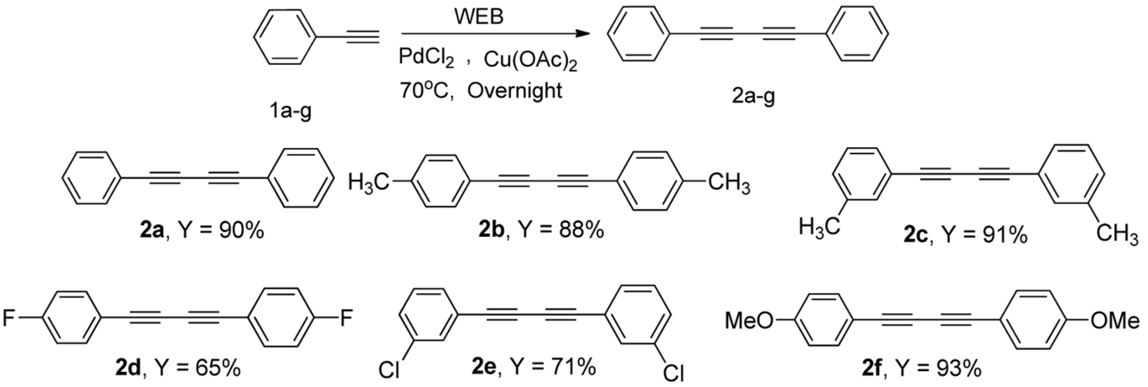
Table 1 — Optimisation of reaction parameters [a]



S. No.	Catalyst	Oxidising agent	Solvent mixture	Temperature (°C)	Time (h)	Yield (%) [b]
1	$PdCl_2$	CuBr	WEB	70	24	40
2	$PdCl_2$	$CuCl_2$	WEB	70	24	20
3	$PdCl_2$	$CuSO_4$	WEB	70	24	25
4	$PdCl_2$	$Cu(OAc)_2$	WEB	70	24	90
5	$PdCl_2$	$Cu(OAc)_2$	WEB	RT	24	45
6	$PdCl_2$	−	WEB	RT	24	Trace
7	$PdCl_2$	−	WEB	70	24	No reaction
8	−	$Cu(OAc)_2$	WEB	70	24	No reaction
9	$Pd(OAc)_2$	$Cu(OAc)_2$	WEB	70	24	82

[a] Reaction Conditions: Substrate (0.1 mL), Pd-cat. Oxidizing agent (1 mmol) and 5 mL of WEB solvent (water extract of banana peel ash) stirred at 70°C. [b] Isolated yield.

Table 2 — Examination of the substrate scope



Reaction conditions: Substrate (1 mmol), $PdCl_2$. Oxidizing agent: $Cu(OAc)_2$, (1 mmol) and 5 mL of solvent (water extract of banana peel ash) stirred at 70°C.

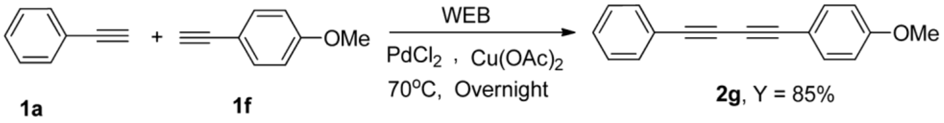
Hence, the optimized reaction conditions are phenylacetelene (0.1 mL), $PdCl_2$-catalyst, Oxidizing agent $Cu(OAc)_2$ (1 equiv.), and 5 mL of WEB (water extract of banana peel ash) solvent stirred at 70°C.

After getting the optimized reaction conditions we employed it on various substituted phenyl acetylenes and the results are shown in Table 2. We have observed that the substrate containing the electron releasing group (Table 2, entry-2b, 2c, 2f) gives better yield than the electron deficient substrates (2d, 2e). This is because the electron rich substrate can easily loose electrons to get oxidation to form the oxidative coupling product 1,4-diarylbuta-1,3-diyne derivative. The coupling of non-polar acetylenes in polar aqueous solvent becomes possible because of some phase transferring activities of WEB. The overall yields of the reactions were good to excellent.

After getting the homo-coupling products, we tried to apply this methodology to the heterocoupling synthesis. We have performed the reaction between 1-ethynyl-4-methoxybenzene with phenyl acetylene in 1:4 ratio and the yield of the hetero-coupling product 1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene was 85% (Scheme 1).

Experimental Section

High quality reagents were purchased from Sigma Aldrich. Analytical grade commercial reagents and solvents were purified by standard procedures prior to use. Chromatographic purification was done



Scheme 1 —

with 60-120 mesh silica gel (Merck). For reaction monitoring, pre-coated silica gel 60 F254 sheets (Merck) were used. NMR spectra were recorded on a BRUKER-AC 400 MHz spectrometer. Chemical shifts are reported in δ (ppm) with reference to tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz).

Procedure for the preparation of WEB

At first banana peel was dried in sunlight and then burned using a Bunsen Burner. The 5 g of burned ash was taken in 200 mL water, stirred for 10 min and then filtered. A straw yellow coloured clear filtrate was collected and used as the solvent for the organic reactions (Fig. 1).


Dry peels of banana plant **Ashes of banana parts** **Water extract of banana (WEB)**

Fig. 1

General reaction procedure for the synthesis of 1,4-diarylbuta-1,3-diyne

In a two neck flask, the substrate 0.5 mmol of aryl acetylene was taken and then 5 mL of WEB (water extract of banana peel ash) solvent was added to it. Then catalyst $PdCl_2$ and $Cu(OAc)_2$ (1 equivalent) were added to the reaction vessel and stirred at 70°C with continuous air bubbling through a syringe. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (3×20 mL). Thereafter, the combined organic layer was washed with brine, dried over anhyd. Na_2SO_4 and concentrated at reduced pressure. Finally, the crude product was purified by column chromatography over silica gel (60-120 mesh) as stationary phase and 2% ethyl acetate in hexane as the eluent.

Spectral data of the compounds

1,4-Diphenyl-1,3-butadiyne, 2a: White solid. m.p.85-86°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 - 7.40 (6H, m), 7.52-7.54 (4H, m); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 76.6, 81.8, 121.9, 128.6, 129.4, 132.7.

The spectral data are in well agreement with the literature reported data.

1,4-Bis(4-methylphenyl)-1,3-butadiyne, 2b: White solid. m.p.183-184°C. ^{1}H NMR (200MHz, $CDCl_3$): δ 2.36 (6H, s), 7.14 (4H, d, J = 8.0 Hz) 7.41 (4H, d, J = 8.0Hz); ^{13}C NMR ($CDCl_3$, 50MHz): δ 21.8 (2C), 73.7 (2C), 81.8 (2C), 119.0 (2C), 129.4 (4C), 132.6 (4C), 139.7 (2C).

1,4-Bis(3-methylphenyl)-1,3-butadiyne, 2c: Pale yellow solid compound; mp: 73-74°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.34 (6H, s) 7.17-7.24 (4H, m), 7.33-7.35(4H, m). ^{13}C NMR ($CDCl_3$, 50MHz) δ: 21.4 (2×CH_3), 73.9 (2×C), 81.8 (2×C), 121.8 (2×C), 128.5 (2×CH), 129.8 (2×CH), 130.3 (2×CH), 133.2 (2×CH), 138.3 (2×C).

1,4-Bis(4-Fluorophenyl)-1,3-butadiyne, 2d: White solid. m.p.190-191°C. ^{1}H NMR (200MHz, $CDCl_3$): δ 6.99-7.00 (4H, m), 7.48-7.55 (4H, m); ^{13}C NMR ($CDCl_3$, 50MHz): δ 73.7 (2×C), 80.6 (2×C), 116.1 (4×CH, d, J = 22.0Hz), 118.0 (2×C), 134.7 (4×CH, d, J = 8.5Hz), 163.3(2×CF, d, J = 250.0Hz).

1,4-Bis(3-chlorophenyl)buta-1,3-diyne, 2e: White solid. m.p.72-73°C. ^{1}H NMR ($CDCl_3$, 200MHz): δ 7.23-7.44 (6H, m), 7.50-7.51 (2H, m); ^{13}C NMR ($CDCl_3$, 50MHz): δ 74.9 (2×C), 80.7(2×C), 123.5 (2×C), 129.9 (4×CH), 130.8 (2×CH), 132.4 (2×CH), 134.5 (2×C).

1,4-Bis(4-methoxyphenyl)-1,3-butadiyne, 2f: Yellow solid. m.p.139-140°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.82(6H, s), 6.85 (4H, d, J = 8.8 Hz), 7.46 (4H, d, J = 8.8Hz), ^{13}C NMR ($CDCl_3$, 50MHz): δ 55.4 (2×C), 73.0 (2×C), 81.3 (2×C), 113.9, 114.2, 134.1, 160.3.

1-Methoxy-4-(4-phenyl-buta-1,3-diynyl)-benzene, 2g: White solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.86 (3H, s), 6.88-6.93 (2H, m), 7.37-7.42 (3H, m), 7.50-7.52 (1H, m), 7.54-7.60 (3H, m); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 55.5, 73.0, 74.4, 81.2, 82.0, 113.9, 114.4, 122.2, 128.6, 129.2, 132.6, 134.3, 160.6.

Conclusion

In conclusion, we have developed a green, efficient and ecofriendly approach for the construction of 1,3-diynes *via* homocoupling and heterocoupling of terminal acetylenes to construct the building block 1,4-diarylbuta-1,3-diynes. Water extract of banana peel ash (WEB) provides an electrolytic solvent to promote the reaction and it also acts as the phase transfer catalyst to perform the coupling of nonpolar phenyl acetylenes in highly polar aqueous solvent. The coupling reaction also occurs in absence of any ligand, base and phase transfer agents. The yield of the reaction was good to excellent.

Acknowledgement

The Authors thank DST-SERB, New Delhi, GoI for financial assistance (ECR/2017/000396) and DST-FIST (SR/FST/College-295, 18th November, 2015), New Delhi, Govt. of India for sponsoring college research facilities.

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