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WEPA: a bio-derived medium for added base, π -acid and ligand free Ullmann coupling of aryl halides using Pd(OAc)₂⁺

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A bio-derived sustainable medium based on water extract of pomegranate ash (WEPA) has, for the first time, been developed for the homocoupling of aryl halides under palladium-assistance. Avoiding the requirement of an external base, ligand and π -acid, the use of the proposed renewable medium offers remarkable attributes like wide substrate scope, good to nearly quantitative yields of biphenyls with exceptional chemoselectivity and scale up viability.

Biaryls constitute an important category of organic compounds and are emerging structural motifs of pharmaceuticals, ligands, energy based materials, agrochemicals, dyes and bio-active natural products.¹ Homocoupling (Ullmann coupling) of aryl halides is a simple and convenient technique to access biaryls, and aryl halides are the most elementary, stable and readily available substrates.² Ullmann coupling has long been known $(about a century ago)^3$ for the synthesis of biaryls and was initially reported by the use of a stoichiometric amount of copper catalyst at elevated temperatures (>200 °C). However, the requirement of excess amounts of copper, high temperature, slow rate of reaction (due to the low solubility of copper in organic solvents), and low tolerance to functional groups restricted the widespread use of copper catalysis.⁴ Many dedicated efforts have been focused on finding alternative catalysts operable under less-vigorous conditions. In connection with this, various transition metals such as nickel,⁵ palladium,^{4b,6-9} zinc,¹⁰ iron¹¹ and cobalt¹² based catalysts have been developed as an alternative to copper. In particular, palladium holds great prominence because it enables coupling at low to moderate temperature (rt – 120 °C) besides offering high reaction rates and huge substrate scope.^{4,6–9} Most of the palladium based homocoupling reactions of aryl halides require the use of organic solvents^{4b,6} and external bases.^{4b,6c–k,7} In addition, phosphine based ligands,^{6a–e} reducing agents^{7a,b,8} and (or) π -acids^{6a,f,g,8c,9} are often required.

Despite the increasing number of reports on ligand and (or) base-promoted Ullman couplings, a very small number of methods have been reported by the application of pure water/ aqueous solvents as reaction media.^{7*a*-*f*,8*a*-*c*,9*a*} Nevertheless, these reported protocols also suffer from certain drawbacks like the requirement of π -acids such as CO₂,^{8*b*,9*a*} paraformaldehyde^{8*c*} reducing agents like zinc,^{8*a*,*b*} magnesium^{8*c*} and ascorbic acid^{7*a*,*b*} and an external base.^{7*a*-*f*}

Green chemistry concerns the sustainability of human life and the environment, and also redesigning the materials and processes which are the basis of our life and economy, making them as safe as possible.¹³ In this context, the use of non-toxic solvents and renewable feedstocks are two of the twelve principles by which green chemistry was constituted. A considerable number of reports have appeared in the literature using bio-based solvents including ethyl acetate, glycerol, cyrene, γ -valerolactone and 2-methyltetrahydrofuran for organic synthesis.¹⁴ There are very few reports in the literature on the use of nature derived aqueous bases for organic synthesis, which can address several principles of green chemistry, in particular, the use of safer solvents and renewable feedstocks.^{14b,15} Inspired by the advantages of the nature derived aqueous feedstocks (base), we report here a convenient and sustainable method for the synthesis of biaryls via the Ullmann coupling of aryl halides catalyzed by Pd(OAc)₂ in WEPA under aerobic conditions. To the best of our knowledge, this is the first report to use WEPA as an effective (basic) medium by the successful utilization of agro waste such as pomegranate peel.

Herein, the potentiality of WEPA as a renewable medium is systematically investigated using 4-iodoanisole (1a) as a model substrate. Initially, 1 mol% of Pd(OAc)₂ in WEPA (0.5 mL) and 1a (1 mmol) was heated at 80 °C (which was found to be effective after screening at different temperatures) and led to the

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[†] Electronic supplementary information (ESI) available: Comparative analysis of the reported Pd catalyzed Ullmann couplings of aryl halides, procedure for the preparation of WEPA, general experimental procedure, recyclability, compound characterization data, copies of ¹H & ¹³C NMR, XPS and EDS spectra, SEM image, CV data and particle size analysis. See DOI: 10.1039/c8cc06940a

Table 1 Optimization of the reaction conditions^a

M	leO ^r 1a 80) °C	2a		
S. no.	Catalyst (mol%)	Medium (mL)	Co-solvent (mL)	Time (h)	Yield ^b (%)
1	$Pd(OAc)_2(1)$	WEPA (0.5)	_	12	42
2	$Pd(OAc)_{2}$ (1)	WEPA (0.5)	EtOH (0.5)	10	73
3	$Pd(OAc)_2$ (2)	WEPA (0.5)	EtOH (0.5)	5	81
4	$Pd(OAc)_2$ (2)	WEPA (1)	EtOH (0.5)	5	88
5	$Pd(OAc)_2$ (3)	WEPA (1)	EtOH (0.5)	4	99
6	$Pd(OAc)_2(4)$	WEPA (1)	EtOH (0.5)	4	99
7	$Pd(OAc)_2$ (3)	_ ()	EtOH (0.5)	12	_
8	$Pd(OAc)_{2}$ (3)	Water	EtOH (0.5)	12	_
9	_	WEPA (1)	EtOH (0.5)	12	_
10	$PdCl_2$ (3)	WEPA (1)	EtOH (0.5)	5	93
11	$Pd(PPh_3)Cl_2(3)$	WEPA (1)	EtOH (0.5)	5	91 ^c
12	$Pd(dba)_3(3)$	WEPA (1)	EtOH (0.5)	5	68
13	$Pd(dppf)Cl_2(3)$	WEPA (1)	EtOH (0.5)	5	60
14	$Pd(OAc)_2$ (3)	WEB (1)	EtOH (0.5)	5	81
15	$Pd(OAc)_2$ (3)	WERSA (1)	EtOH (0.5)	5	48
16	$Pd(OAc)_2$ (3)	WEPBA (1)	EtOH (0.5)	5	83
17	$Pd(OAc)_2$ (3)	WELFSA (1)	EtOH (0.5)	5	56
18	CuCl (3)	WEPA (1)	EtOH (0.5)	12	_
19	$Cu(OAc)_2$ (3)	WEPA (1)	EtOH (0.5)	12	_
20	CuÌ (3)	WEPA (1)	EtOH (0.5)	12	_
21	$CuSO_4 \cdot 5H_2O(3)$	WEPA (1)	EtOH (0.5)	12	_
22	$\operatorname{CoCl}_2(3)$	WEPA (1)	EtOH (0.5)	12	_

formation of biphenyl (2a) in 42% isolated yield in 12 h (Table 1, entry 1). Upon addition of 0.5 mL of ethanol to the reaction mixture, the yield of 2a was increased to 73% in 10 h (Table 1, entry 2) and an increase in catalyst loading to 2 mol% enhanced the yield to 81% in 5 h (Table 1, entry 3). At this stage, the increase of the WEPA (basic medium) to 1 mL formed 2a in 88% yield in 5 h (Table 1, entry 4) and an enhancement of Pd(OAc)₂ to 3 mol% improved the yield of 2a to nearly quantitative in 4 h (Table 1, entry 5). Further increase of the catalyst amount to 4 mol% does not show any significant effect on the reaction progress (Table 1, entry 6). The reaction was then studied independently, in the absence of WEPA and Pd(OAc)₂ and no reaction was found (Table 1, entries 7-9), indicating that the use of Pd(OAc)₂ and WEPA (basic medium) is crucial for the present conversion. We then screened other Pd-based catalysts such as PdCl₂, Pd(PPh₃)Cl₂, Pd(dba)₃ and Pd(dppf)Cl₂, under similar reaction conditions and found the formation of 2a in 93%, 91%, 68%, and 60% yields, respectively, in 5 h (Table 1, entries 10-13), indicating Pd(OAc)₂ as the best among the screened catalysts. Moreover, the formation of phosphine oxide as the byproduct was observed when Pd(PPh₃)Cl₂ was used (Table 1, entry 11). The scope of the reaction was also studied further by using transition-metal based salts such as CuCl, Cu(OAc)₂, CuI, CuSO₄·5H₂O and CoCl₂ under the present experimental conditions and no progress was found (Table 1, entries 18-22).

Furthermore, this method was investigated with other bioderived aqueous extracts such as water extract of banana (WEB),¹⁶ water extract of rice straw ash (WERSA),¹⁷ water extract

of papaya bark ash (WEPBA)¹⁸ and water extract of lemon fruit shell ash (WELFSA),¹⁹ and the formation of 2a was observed in 81%, 48%, 83%, and 56% yields, respectively in 5 h (Table 1, entries 14-17). This observation supports our assumption that the pomegranate peel may be an effective medium for Pdcatalyzed Ullman coupling. We speculate that the basic nature of WEPA might be due to the presence of significant amounts of nutrients. It was reported in the literature that pomegranate peel was approved as a nutritious feed to cattle.²⁰ To assess the presence of nutrients in WEPA, X-ray photoelectron spectroscopy (XPS) of ash and energy-dispersive X-ray spectroscopy (EDS) analysis of the extract (a white solid formed after the evaporation of water) were carried out and the corresponding spectra are provided in the ESI.[†] As can be seen, the presence of K, Mg, Ca, C, O and Cl is evident from these spectra. Furthermore, these spectra indicate the presence of a high amount (51.54 wt%) of K which is higher than that of other extracts, WEB,¹⁶ WERSA¹⁷ and WEPBA.¹⁸ The presence of oxygen and chlorine suggests that K, Mg and Ca may exist in the form of the corresponding carbonates, oxides, and chlorides and impart basicity to the WEPA and play a key role in the formation of products. In addition, the pH of WEPA was found to be between 11.7 and 12.1 upon several repetitions, further supporting its basic nature.

Under the successful optimized conditions, we tested the applicability of this method to various aryl halides including aryl iodides, aryl bromides and aryl chlorides and the results are listed in Table 2. Aryl iodides are found to be more reactive than bromides, which are in turn more reactive than aryl chlorides.

Aryl iodides with both electron releasing (ER) (methoxy and methyl) and electron withdrawing (EW) (chloro, acetyl, formyl and nitro) groups are found to form Ullmann coupling products (2) in excellent yields (85–95%) (Table 2, entries 1, 2 and 4–8). Unsubstituted aryl iodide, iodobenzene (**1d**), was also found as a good substrate for the present conversion which formed nearly quantitative yield of **2d** (Table 2, entry 3). Mixed aryl halide, 4-chloro-1-iodobenzene (**1f**), formed **2f** in 95% yield with excellent chemoselectivity (Table 2, entry 5), *i.e.*, the priority for iodine in the presence of chlorine. Formation of the coupling product related to chlorine is not at all observed.

We then investigated the influence of this method on aryl/ heteroaryl bromides and found the formation of biaryls in good to high yields (73-93) (Table 2, entries 9-27). High conversion of arene bromides into biaryls was observed with ER (methoxy, methyl and tert-butyl) (73-91%) as well as EW (phenyl, chloro, fluoro, acetyl and formyl) (80–87%) groups (Table 2, entries 9–22), however, a protodebrominated product was formed as a minor product with 2-bromoanisole (11), a major product with 2-bromotoluene (1n) (o-cresol, 4 is the minor one) and exclusively in the case of 2-bromobiphenyl (1q) and 2-bromobenzaldehyde (1v). Bromobenzene (1x) was found to be the best substrate among the aryl bromides to give 2d in 93% yield in 3 h (Table 2, entry 23). 9-Bromophenanthrene (1y) provided very good yield of biaryl, 2n (86%) (Table 2, entry 24), while, 9-bromoanthracene (1z) gave the protodebromination product, 7 (Table 2, entry 25).



S. no.	Aryl halide (1)	Time (h)	Product (2)	Yield ^b (%)		
1	3-Iodoanisole (1b)	4	2b	93		
2	2-Iodoanisole (1c)	5	2c	89		
3	Iodobenzene (1d)	2	2d	99		
4	4-Iodotoluene (1e)	3	2e	94		
5	4-Chloro-1-iodobenzene (1f)	4	2f	95		
6	4-Iodoacetophenone (1g)	4	2g	87		
7	4-Iodobenzaldehyde (1h)	4	2h	89		
8	4-Nitroiodobenzene (1i)	4	2i	85		
9	4-Bromoanisole (1j)	6	2a	88		
10	3-Bromoanisole (1k)	6	2b	82		
11	2-Bromoanisole (11)	6	2c + 3	73 & 11		
12	4-Bromotoluene (1m)	6	2e	91		
13	2-Bromotoluene (1n)	3	4 + 5	35 & 61		
14	4-Bromo-4-tert-butylbenzene (10)	6	2j	84		
15	4-Bromobiphenyl (1p)	6	2k	83		
16	2-Bromobiphenyl (1q)	3	2d	95		
17	1-Bromo-4-chlorobenzene (1r)	6	2f	83		
18	1-Bromo-4-fluorobenzene (1s)	6	21	80		
19	4-Bromoacetophenone (1t)	6	2g	83		
20	4-Bromobenzaldehyde (1u)	6	2h	87		
21	2-Bromobenzaldehyde (1v)	3	6	94		
22	3-Bromoacetophenone (1w)	6	2m	81		
23	Bromobenzene (1x)	3	2d	93		
24	9-Bromophenanthrene (1y)	12	2n	86		
25	9-Bromoanthracene (1z)	10	7	90		
26	3-Bromopyridine (1aa)	10	20	80		
27	2-Bromopyridine (1ab)	10	2p	81		
28	4-Chloroanisole (1ac)	12	2a	32		
29	Chlorobenzene (1ad)	12	2d	35		
30	4-Chlorobenzaldehyde (1ae)	12	2h	25		
31	1-Chloro-2,4-dinitrobenzene	4	8	89		
	(1af)					
^a Reaction conditions: 1 (1 mmol), WEPA (1 mL), EtOH (0.5 mL)						
Pd(OA	c) ₂ (3 mol%) at 80 °C. ^b Isolated	vield.		. ,		

Moreover, the efficiency of the present method was also tested with the heteroaryl bromides, 3-bromopyridine (**1aa**) and 2-bromopyridine (**1ab**) and good yields (80% and 81%) of the coupled products were found. High chemoselectivity over the halogens (*i.e.*, bromine over chlorine and fluorine) was observed

when 1-bromo-4-chlorobenzene (1r) and 1-bromo-4-fluorobenzene (1s) were used as substrates (Table 2, entries 17 & 18).

Furthermore, this method was extended to aryl chlorides (**1ac-1af**) and it was found that the corresponding reaction proceeds with a long reaction time (12 h) and produced low yields (25–35%) of products **2a**, **2d** and **2h** (Table 2, entries 28–30). 1-Chloro-2,4-dinitrobenzene (1af) formed only the protodechlorination product, *m*-dinitrobenzene (8), in 89% yield in 4 h (Table 2, entry 31). In one instance, the controlled reductive dechlorination of **1af** was reported with H₂-Pd(PPh₃)₄-DMF,²¹ and copper powder-benzoic acid at > 200 °C,²² but, this method is rather simple, benign and promises higher yields.

The present method was also tested and its successful applicability for the multi-gram (up to 3 g) scale synthesis of biaryl **2a** (find at ESI[†]) was found. Additionally, the recyclability tests are discussed in the ESI.[†]

The plausible mechanism of the present conversion is exemplified in the following scheme (Scheme 1). The mechanism of the palladium-catalyzed Ullmann coupling in WEPA (catalytic cycle 1) is believed to be similar to the mechanism proposed by Nadri *et al.*^{6d} Initially, the reduction (I) of $Pd(OAc)_2$ in WEPA forms an active Pd^0 species (A) (evidenced by EDS and cyclic voltammetric analysis, ESI[†]) and it adds two aryl halides in two consecutive oxidative additions (*viz.*, II and III) to form a Pd^{IV} species, C. The intermediate C participates in reductive elimination (IV) to give products, 2 and $Pd^{II}X_2$ (D) and D may be finally reduced (V) to active Pd^0 species, A, in WEPA (base). In another possibility (catalytic cycle 2) the inter exchange of the Ar and X groups (VI) between B generates dicoordinated palladium intermediates, E and D. Finally, E may undergo reductive elimination (VII) to generate A.

In summary, we have developed an effective and benign method for the synthesis of biaryls from abundant aryl halides *via* the application of novel renewable media, WEPA, in the presence of Pd(OAc)₂. The present protocol avoids the use of toxic solvents, external bases, phosphine ligands, π -acids and harsh reducing agents. To the best of our knowledge, the present development is the first report highlighting the use of naturederived basic media for Ullmann coupling. Furthermore, formation



Scheme 1 Plausible mechanism of Ullmann coupling in WEPA.

of biaryls in good to nearly quantitative yields, utilization of agro waste, inherent safeness associated with the usage of an aqueous medium, excellent chemoselectivity, scale up feasibility and broad substrate scope make the present method most attractive for Ullmann coupling. Interestingly, substrates with a variety of reactive functional groups, nitro, chloro, fluoro, acetyl, formyl and amino, were tolerated under the present conditions. This methodology largely relied on the application of agro wastederived aqueous (basic) media along with the few existing and demonstrated examples, and may open up new avenues in the development of green and sustainable protocols in organic synthesis.

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Conflicts of interest

There are no conflicts to declare.

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