

Palladium-catalyzed reactions of bisarenediazonium salts: two-fold Heck reaction, carbonylation and cross-coupling regimen

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Two-fold Heck reaction, carbonylation and cross-coupling reactions of bisarenediazonium salts have been carried out in high yields under mild, aqueous alcoholic conditions to provide a new synthetic repertoire for tetraaryls and other aromatic derivatives having extended conjugation.

Introduction

Palladium-catalyzed vinylation (the Heck reaction)¹ and cross-coupling reactions² of aryl halides are powerful synthetic methodologies for new carbon-carbon-bond formation in aromatic domains. Extensive methodological refinements over the last decade, particularly with regard to solvents, catalysts and additives, have greatly improved the synthetic efficacy of these reactions, as a result of which they are now finding almost routine use in complex organic synthesis.³ Recently, asymmetric versions of the Heck reaction have also emerged,⁴ which have opened a whole new vista in enantiomerically pure compound (EPC) synthesis. Increasing applications of Heck and cross-coupling reactions are also evident in macromolecular synthesis, especially in the field of poly-(*p*-phenylenevinylene) and poly-(*p*-phenylene) types of conjugated polymers.⁵

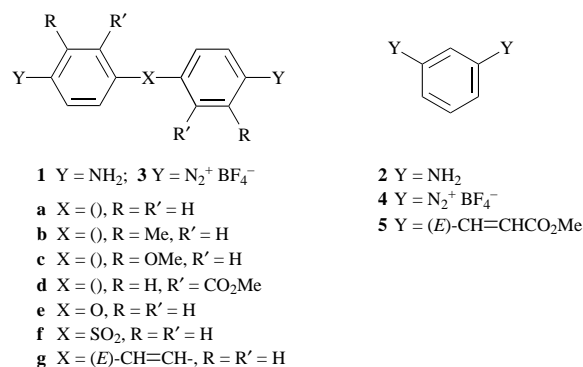
Although aryl halides (Br, I) and triflates are traditionally used for Heck and cross-coupling reactions, we⁶ and others^{7,8} have shown that arenediazonium salts are promising alternatives to these substrates and, in fact, hold several advantages over the aryl halides: ready availability of starting materials (anilines are cheaper than aryl halides), short reaction times (15 min to 1 h), high yields under mild conditions (room temp. to 80 °C) and operational simplicity including the option of using aqueous reaction media.^{6,8} In a recent development, we⁹ and Genet and co-workers¹⁰ have independently reported the successful cross-coupling of arenediazonium salts with arylboronic acids in a new synthesis of unsymmetrical biaryls. Most significantly, in all these reactions the diazonium nucleofuge has been found to be far more reactive than the corresponding aryl bromide, triflate or even the iodide, as shown by intramolecular competition experiments.

Palladium-catalyzed reactions of bisarenediazonium salts were a rational extension of the above studies. Since two-fold Pd-catalyzed reactions on dibromo- and diiodo-arenes have been intensively pursued in recent times, it was imperative on our part to study and compare the reactivity of bisarenediazonium salts in such reactions. With an ultimate goal towards using them in the synthesis of conjugated aromatic polymers via poly-Heck and poly-cross-coupling reactions,⁵ we thus undertook a study of two-fold Heck, carbonylation and cross-coupling reactions of a number of bisarenediazonium salts, and in this paper we describe our results towards these ends.

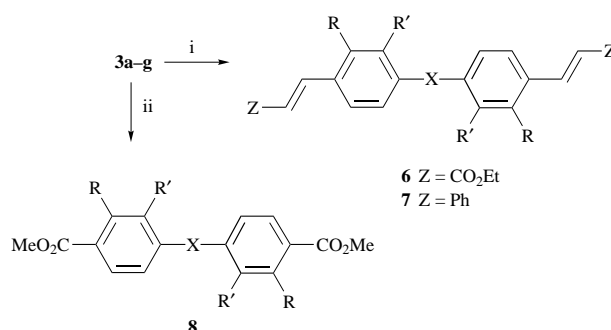
Results and discussion

In this study, the bisanilines **1a–g** and **2** were chosen as substrate precursors to the bisarenediazonium salts. They ranged from substituted benzidine derivatives **1a–d** to those where the two aniline rings are separated by spacer atoms (as in compounds **1e,f**) or by a vinyl group (as in compound **1g**). *m*-Phenylenediamine **2** was the only example of a homonuclear

diamine used in this work. While compounds **1a–c,e,f** and **2** were commercially available, compound **1d** was prepared from 4,4'-dinitrodiphenic acid dimethyl ester¹¹ via reduction of the nitro groups with N₂H₄·H₂O/Pd–C. The diaminostilbene derivative **1g** was prepared according to a literature procedure via controlled reduction (Zn/NH₄Cl) of 4,4'-dinitrostilbene.¹² The latter, in turn, was prepared in high yield via our recently disclosed stilbene synthesis involving a double Heck reaction of *p*-nitrobenzenediazonium salt with triethoxy(vinyl)silane.¹³ Once in hand, these bisanilines were converted into the respective bisarenediazonium tetrafluoroborates **3a–g** by using standard diazotization procedures.¹⁴



Two-fold Heck reaction was first studied with the bisdiazonium salts. Thus, the bis-salts **3a–g** were subjected to Pd-catalyzed [1–2% Pd(OAc)₂] vinylation with ethyl acrylate or styrene (4 mol equiv. each) in refluxing ethanol,⁶ which smoothly produced the bis-Heck products **6** and **7** in 60–80% yield (Scheme 1, Table 1). The bisdiazonium salt **4**¹⁵ derived



Scheme 1 Reagents and conditions: i, 2% Pd(OAc)₂, EtOH, CH₂=CHZ, 80 °C, 1 h; ii, 2% Pd(OAc)₂, MeOH, CO (1 atm.), 25 °C, 30 min

from *m*-phenylenediamine **2** also underwent two-fold Heck reaction with methyl acrylate in refluxing methanol to produce the *m*-phenylenediacrylate **5** in 83% yield. Several of these bis-

Table 1 Two-fold Heck reaction and carbonylation of bis-salts **3a–g**

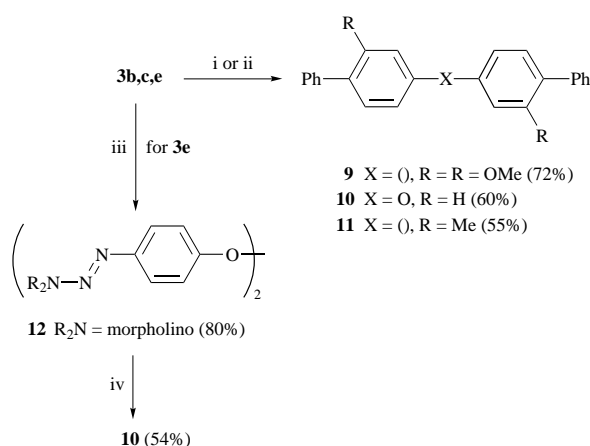
Entry	Bisdiazonium salt 3	Olefin ^a /CO	Products 6–8	Yield (%)
1	3a	A	6a	70
2	3b	A	6b	73
3	3b	B	7b	60
4	3c	A	6c	80
5	3c	B	7c	75
6	3c	CO	8c	93
7	3d	A	6d	70
8	3d	B	7d	63
9	3e	A	6e	80
10	3e	CO	8e	76
11	3f	A	6f	60
12	3g	A	6g	60
13	3g	B	7g	60

^a A = ethyl acrylate, B = styrene.

Heck reactions were also performed directly on the bisanilines **1** via our 'one-pot diazotization–Heck reaction' protocol^{6f} which gave very similar yields to those obtained through Heck reaction of the isolated salts **3**. In either case, the reactions were typified by short reaction times (45 min to 1 h), mild conditions and advantageous use of aqueous alcoholic media which greatly simplified isolation procedures. However, attempted synthesis of unsymmetrical bisvinylated products by employing one mol equiv. each of two different olefins has so far been unsuccessful, resulting in complex product mixtures.

Pd-catalyzed carbonylation of the bis-salts was also investigated. Thus, compounds **3c** and **3e** were carbonylated (1 atm. of CO) in methanol at room temp. to produce the dimethyl esters **8c** and **8e** in high yield, respectively (Scheme 1, Table 1). It may be mentioned here that carbonylations of (mono)arenediazonium salts have previously been reported in CH₃CN with Pd(dba)₂[†] as catalyst which, however, required 10 kg/cm² pressure of CO gas and a special autoclave device in order to conduct the reactions.¹⁶ In contrast, our methanolic reaction conditions are operationally much simpler, and our method merely involves passing CO gas through the reaction mixture at ambient temperature.

Two-fold cross-coupling of the bis-diazonium salts was briefly studied. Thus, reaction of the salts **3c** and **3e** with two mol equiv. of PhB(OH)₂ in refluxing methanol⁹ gave rise to the *p*-tetraaryl derivatives **9** and **10** in 72 and 60% yield, respectively (Scheme 2). Cross-coupling of the *o*-toluidine derived bis-salt **3b** with PhB(OH)₂, however, led to an inseparable product mix-



Scheme 2 Reagents and conditions: i, 10% Pd(OAc)₂, PhB(OH)₂, MeOH, 60 °C, 1 h (for **3c, e**); ii, 10% Pd(OAc)₂, PhBF₃K, MeOH, 60 °C, 1 h (for **3b**); iii, excess of morpholine; iv, TFA (4 mol equiv.), I₂ (cat.), benzene, reflux

[†] dba = 1,3-dibenzylideneacetone(1-).

ture consisting of the desired product **11** together with side-products arising out of homocoupling and protodediazotization of substrate **3b**. This was utterly surprising since the (mono)-diazonium salt derived from *o*-toluidine, upon cross-coupling with PhB(OH)₂, gave a 90% yield of 2-methylbiphenyl under identical reaction conditions.⁹ Nevertheless, these side-reactions could ultimately be eliminated by replacing PhB(OH)₂ with PhBF₃K, according to the recently reported Genet protocol,^{10a} which then produced the desired product **11** in 55% isolated yield. Interestingly, two-fold arylation of the bis-salts could also be achieved by a Gomberg–Bachmann procedure,¹⁷ which to the best of our knowledge has never been explored before with bisarenediazonium salts. Towards this end, the bis-salt **3e** was first converted into the bistriazene **12** (80%).^{6d} The latter was then decomposed in refluxing benzene in the presence of trifluoroacetic acid (TFA) (4 mol equiv.) and a catalytic amount of I₂¹⁸ to produce the di(biphenyl) ether **10** in 54% yield (Scheme 2), quite comparable to that obtained via two-fold boronic acid cross-coupling of bis-salt **3e** (*vide supra*). Despite the fact that biaryl syntheses via Gomberg–Bachmann procedures have their limitations (poor yields with *ortho*-substituted diazonium salts, and regiorandom for unsymmetrically substituted arenes), the above two-fold Gomberg–Bachmann protocol appears to hold much promise for the synthesis of relatively simple, symmetrically substituted *p*-tetraaryls.

In summary, the readily available bisarenediazonium salts, *in lieu* of the conventional but often difficult-to-prepare aromatic dihalides and ditriflates, have been established as novel substrates for two-fold Heck reaction, carbonylation and cross-coupling reactions. Pd-catalyzed reactions on bisarenediazonium salts provide good to excellent yields under conditions that are mild and operationally simple, thus providing an excellent repertoire for the synthesis of a wide variety of substituted tetraaryls and other extended conjugated systems. Application of this repertoire towards the synthesis of conjugated aromatic polymers is currently under investigation.

Experimental

All mps were measured on a Toshniwal 301 melting point apparatus and are uncorrected. IR spectra were taken in a Perkin-Elmer R-297 spectrometer. ¹H NMR spectra were recorded in CDCl₃–SiMe₄ on Varian EM-360 (60 MHz), JEOL FX-100 (100 MHz) and Varian XL-200 (200 MHz) instruments. *J*-Values are given in Hz. Column chromatography was performed on silica gel (60–120 mesh). The bisarenediazonium salts **3a–g** were prepared, just prior to use, via standard tetrazotization (NaNO₂, conc. HCl, 0 °C, then NaBF₄ or NaNO₂, 42% HBF₄, 0 °C)¹⁴ of the bisanilines **1a–g** whereas bis-salt **4** was prepared from *m*-phenylenediamine according to a literature procedure.¹⁵ PhBF₃K was prepared from PhB(OH)₂ as described in the literature.^{10a} Standard work-up refers to concentration of the reaction mixture under reduced pressure, dilution with an organic solvent, filtration through Celite, washing of the filtrate with water, and drying over anhydrous Na₂SO₄. Light petroleum refers to the fraction with distillation range 60–80 °C.

General procedure for two-fold Heck reaction of bis-salts **3a–g** and **4**

Pd(OAc)₂ (5 mg) was added to a mixture of the bisdiazonium salt **3** or **4** (1 mmol) and the appropriate olefin (4 mmol) in EtOH (MeOH for **4**) (10 cm³) and the mixture was heated under reflux for 1 h. It was then cooled to room temp. and standard work-up with CH₂Cl₂ followed by chromatography on silica gel (10% EtOAc in light petroleum) (for **6a–g**) or precipitation with light petroleum (for **5, 7b–d, 7g**) gave the respective bisvinylated products. They were further purified by recrystallization from appropriate solvents.

Compound 6a: 70%; mp 143–144 °C (from CHCl₃–light petroleum); ν_{max}(Nujol)/cm^{−1} 1700, 1630 and 1460; δ_H(CDCl₃)

1.35 (6 H, t, *J* 7.2), 4.30 (4 H, q, *J* 7.2), 6.47 (2 H, d, *J* 16) and 7.20–7.83 (10 H, m).

Compound 6b: 73%; mp 137–138 °C (from CH₂Cl₂–light petroleum) (Found: C, 76.52; H, 6.70. C₂₄H₂₆O₄ requires C, 76.19; H, 6.87%); ν_{\max} (Nujol)/cm^{−1} 1705, 1625, 1450, 1310 and 1173; δ_{H} (CDCl₃) 1.34 (6 H, t, *J* 7.5), 2.50 (6 H, s), 4.25 (4 H, q, *J* 7.5), 6.35 (2 H, d, *J* 15), 7.37 (4 H, s), 7.58 (2 H, d, *J* 7.5) and 7.93 (2 H, d, *J* 15).

Compound 6c: 80%; mp 155–156 °C (from CH₂Cl₂–light petroleum) (Found: C, 69.99; H, 6.40. C₂₄H₂₆O₆ requires C, 70.24; H, 6.34%); ν_{\max} (Nujol)/cm^{−1} 1685, 1595, 1440, 1380, 1270 and 1120; δ_{H} (CDCl₃) 1.35 (6 H, t, *J* 7.5), 3.98 (6 H, s), 4.26 (4 H, q, *J* 7.5), 6.52 (2 H, d, *J* 16), 7.04 (2 H, s), 7.15 (2 H, d, *J* 8), 7.54 (2 H, d, *J* 8) and 7.95 (2 H, d, *J* 16).

Compound 6d: 70%; mp 122–123 °C (from MeOH) (Found: C, 66.82; H, 5.55. C₂₆H₂₆O₈ requires C, 66.95; H, 5.58%); ν_{\max} (Nujol)/cm^{−1} 1710, 1445, 1355 and 1175; δ_{H} (CDCl₃) 1.35 (6 H, t, *J* 8), 3.66 (6 H, s), 4.30 (4 H, q, *J* 8), 6.52 (2 H, d, *J* 16), 7.24 (2 H, d, *J* 8), 7.68–7.84 (4 H, m) and 8.22 (2 H, d, *J* 3).

Compound 6e: 80%; mp 77–78 °C (from MeOH) (Found: C, 71.67; H, 6.07. C₂₂H₂₂O₅ requires C, 72.13; H, 6.01%); ν_{\max} (Nujol)/cm^{−1} 1700, 1620, 1580, 1490, 1355, 1230 and 1160; δ_{H} (CDCl₃) 1.36 (6 H, t, *J* 7), 4.26 (4 H, q, *J* 7), 6.34 (2 H, d, *J* 16), 7.02 (4 H, d, *J* 8), 7.52 (4 H, d, *J* 8) and 7.64 (2 H, d, *J* 16).

Compound 6f: 60%; mp 155–156 °C (from MeOH) (Found: C, 63.23; H, 5.34. C₂₂H₂₂O₆ requires C, 63.76; H, 5.31%); ν_{\max} (Nujol)/cm^{−1} 2920, 2830, 1705, 1455, 1370, 1305 and 1150; δ_{H} (CDCl₃) 1.33 (6 H, t, *J* 7.2), 4.27 (4 H, q, *J* 7.2), 6.49 (2 H, d, *J* 16), 7.65 (6 H, m) and 7.95 (4 H, d, *J* 7).

Compound 6g: 60%; mp 180–181 °C (from CH₂Cl₂–light petroleum); ν_{\max} (KBr)/cm^{−1} 1705, 1630, 1300 and 1170; δ_{H} (CDCl₃) 1.32 (6 H, t, *J* 8), 4.27 (4 H, q, *J* 8), 6.44 (2 H, d, *J* 16), 7.16 (2 H, s), 7.56 (8 H, s) and 7.73 (2 H, d, *J* 16).

Compound 7b: 60%; mp 165–166 °C (from CH₂Cl₂–light petroleum) (Found: C, 93.52; H, 6.68. C₃₀H₂₆ requires C, 93.26; H, 6.74%); ν_{\max} (Nujol)/cm^{−1} 1590, 1545, 1285, 1205, 1030, 960 and 805; δ_{H} (CDCl₃) 2.63 (6 H, s) and 7.26–7.86 (20 H, m).

Compound 7c: 75%; mp 195–196 °C (from CH₂Cl₂–light petroleum) (Found: C, 86.12; H, 6.22. C₃₀H₂₆O₂ requires C, 86.28; H, 6.38%); ν_{\max} (Nujol)/cm^{−1} 1590, 1540, 1280, 1010, 950 and 800; δ_{H} (CDCl₃) 4.00 (6 H, s) and 6.15–6.7 (20 H, m).

Compound 7d: 63%; mp 205–206 °C (from CH₂Cl₂–light petroleum); ν_{\max} (Nujol)/cm^{−1} 1710, 1450, 1290, 1240 and 1080; δ_{H} (CDCl₃) 3.65 (6 H, s), 7.20–7.76 (18 H, m) and 8.16 (2 H, d, *J* 3).

Compound 7g: 60%; mp >300 °C (from CH₂Cl₂–light petroleum) (lit.,^{19a} >350 °C); δ_{H} (CDCl₃) 7.08–7.38 (24 H, m).

Compound 5: 83%; mp 126–127 °C (from acetone–light petroleum); ν_{\max} (Nujol)/cm^{−1} 1730, 1645 and 1460; δ_{H} (CDCl₃) 3.83 (6 H, s), 6.45 (2 H, d, *J* 16), 7.40 (1 H, d, *J* 8), 7.55 (2 H, d, *J* 8), 7.65 (2 H, d, *J* 16) and 7.70 (1 H, s).

General procedure for two-fold carbonylation of bis-salts 3c and e Pd(OAc)₂ (5.5 mg) was added to a mixture of the salt **3c** or **3e** (0.5 mmol) in dry MeOH (10 cm³), and CO was passed through the mixture for 1 h. Standard work-up with CH₂Cl₂ followed by recrystallization gave the diesters **8c,e**.

Compound 8c: 93%; mp 170–171 °C (from MeOH) (Found: C, 65.25; H, 5.49. C₁₈H₁₈O₆ requires C, 65.45; H, 5.45%); ν_{\max} (Nujol)/cm^{−1} 1700, 1600, 1460, 1380, 1280, 1180 and 1020; δ_{H} (CDCl₃) 3.92 (6 H, s), 3.98 (6 H, s), 7.16–7.28 (4 H, m) and 7.92 (2 H, d, *J* 8).

Compound 8e: 76%; mp 153–154 °C (from MeOH) (lit.,^{19b} 153–155 °C); ν_{\max} (KBr)/cm^{−1} 1710, 1590, 1500, 1430, 1275, 1160, 1185 and 1100; δ_{H} (CDCl₃) 3.92 (6 H, s), 7.02–7.14 (4 H, m) and 8.04–8.12 (4 H, m).

General procedure for two-fold cross-coupling of bis-salts 3b,c,e Pd(OAc)₂ (13 mg) was added to a mixture of the bisdiazonium salt (0.6 mmol) and PhB(OH)₂ (0.122 g, 1 mmol) (for **3c,e**) or PhBF₃K (0.184 g, 1 mmol) (for **3b**) in MeOH (10 cm³) and the

mixture was heated under reflux for 1 h. It was then cooled to room temp. and standard work-up with CH₂Cl₂ followed by precipitation with light petroleum (for **9** and **10**) or preparative TLC (light petroleum, for **11**) gave the respective tetraaryl products, which were further purified by recrystallization from appropriate solvents.

Compound 9: 72%; mp 160–162 °C (from CH₂Cl₂–light petroleum) (lit.,^{19c} 183–184 °C) (Found: C, 85.72; H, 6.12. C₂₆H₂₂O₂ requires C, 85.24; H, 6.01%); δ_{H} (CDCl₃) 3.92 (6 H, s) and 7.18–7.60 (16 H, m).

Compound 10: 60%; mp 205–206 °C (from MeOH–CHCl₃) (Found: C, 89.02; H, 5.68. C₂₄H₁₈O requires C, 89.44; H, 5.59%); ν_{\max} (Nujol)/cm^{−1} 1590, 1545, 1285, 1210, 1120, 960 and 810; δ_{H} (CDCl₃) 7.06–7.60 (18 H, m).

Compound 11: 55%; mp 137–139 °C (from CH₂Cl₂–light petroleum) (lit.,^{19d} 141 °C); δ_{H} (CDCl₃) 2.46 (6 H, s) and 7.23–7.70 (16 H, m).

Preparation and two-fold Gomberg–Bachmann reaction of the bistriazene **12**

4,4'-Diaminodiphenyl ether **1e** (1.0 g, 5.0 mmol) was added to a solution of conc. HCl (2.6 cm³) in water (30 cm³) and the mixture was stirred for 5 min at 25 °C. It was then cooled to 0 °C and treated dropwise with aq. NaNO₂ (0.703 g, 10.2 mmol in 4 cm³). After 30 min at 0 °C the mixture was treated dropwise with morpholine (0.940 g, 10.8 mmol) and stirring was continued for a further 15 min. It was then basified with aq. NaHCO₃ and the separated solid was filtered off, washed with water, and dried in air. Recrystallization gave the bistriazene **12** as a crystalline solid (1.60 g, 80%), mp 141–142 °C (from light petroleum); ν_{\max} (Nujol)/cm^{−1} 1450, 1370, 1230 and 1100; δ_{H} (CDCl₃) 3.78 (16 H, m), 7.20 (4 H, d, *J* 8) and 7.62 (4 H, d, *J* 8).

TFA (0.456 g, 4.0 mmol) was added dropwise to a refluxing solution of the bistriazene **12** (0.396 g, 1.0 mmol) and I₂ (5 mg) in benzene (20 cm³). After the addition was complete, refluxing was continued for a further 3 h after which it was cooled, poured into 5% aq. Na₂CO₃ (10 cm³) and extracted with CHCl₃ (3 × 10 cm³). Removal of solvent followed by recrystallization from CHCl₃–MeOH gave compound **10** (0.174 g, 54%), identical in all respects with the product obtained from two-fold cross-coupling of bis-salt **3e** with PhB(OH)₂.

Acknowledgements

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