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 reactions[2] 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]
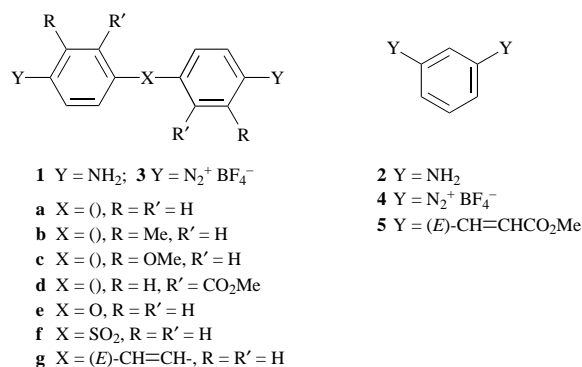
Although aryl halides (Br, I) and triflates are traditionally used for Heck and cross-coupling reactions, we[6] and others[7,8] have shown that arenediazonium salts are promising alternatives to these substrates and, in fact, hold several advantages over the aryl halides: ready availability of starting 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, we[9] and Genet and co-workers[10] 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 ester[11] *via* reduction of the nitro groups with $N_2H_4\cdot H_2O$/Pd–C. The diaminostilbene derivative **1g** was prepared according to a literature procedure *via* controlled reduction (Zn/NH$_4$Cl) 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]

1 Y = NH$_2$; **3** Y = N$_2^+$ BF$_4^-$

a X = (), R = R′ = H
b X = (), R = Me, R′ = H
c X = (), R = OMe, R′ = H
d X = (), R = H, R′ = CO$_2$Me
e X = O, R = R′ = H
f X = SO$_2$, R = R′ = H
g X = (E)-CH=CH-, R = R′ = H

2 Y = NH$_2$
4 Y = N$_2^+$ BF$_4^-$
5 Y = (E)-CH=CHCO$_2$Me

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

6 Z = CO$_2$Et
7 Z = Ph

8
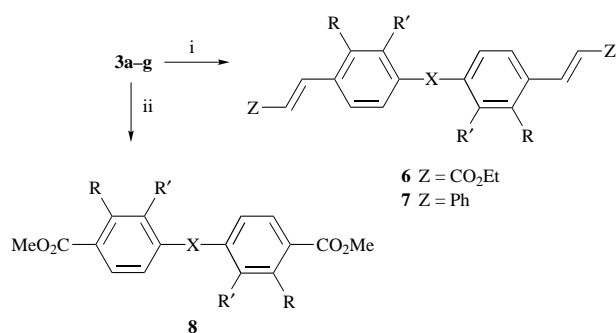
Scheme 1 *Reagents and conditions:* i, 2% Pd(OAc)$_2$, EtOH, CH$_2$=CHZ, 80 °C, 1 h; ii, 2% Pd(OAc)$_2$, MeOH, CO (1 atm.), 25 °C, 30 min

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-

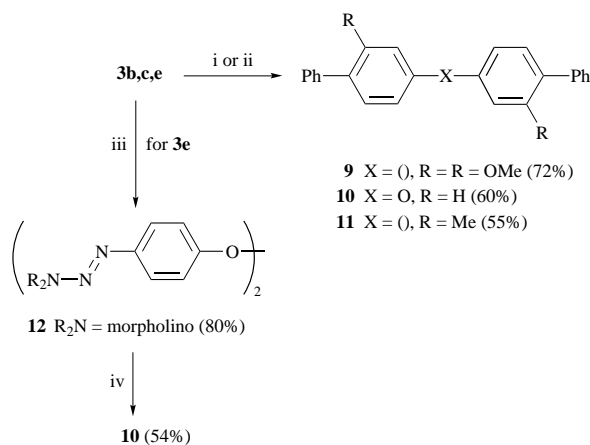**Table 1** Two-fold Heck reaction and carbonylation of bis-salts **3a–g**

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 CH_3CN 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 methanol[9] 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-

ture consisting of the desired product **11** together with side-products arising out of homocoupling and protodediazoniation 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 $PhBF_3K$, 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 tri-fluoroacetic acid (TFA) (4 mol equiv.) and a catalytic amount of I_2[18] 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

The bisarenediazonium salts **3a–g** were prepared, just prior to use, via standard tetrazotization ($NaNO_2$, conc. HCl, 0 °C, then $NaBF_4$ or $NaNO_2$, 42% HBF_4, 0 °C)[14] of the bisanilines **1a–g** whereas bis-salt **4** was prepared from m-phenylenediamine according to a literature procedure.[15] $PhBF_3K$ 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 Na_2SO_4. 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 CH_2Cl_2 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 $CHCl_3$–light petroleum); v_{max}(Nujol)/cm⁻¹ 1700, 1630 and 1460; δ_H($CDCl_3$)

3b,c,e →(i or ii) Ph—[ring]—X—[ring]—Ph (with R substituents)

iii | for **3e**

9 X = (), R = R = OMe (72%)
10 X = O, R = H (60%)
11 X = (), R = Me (55%)

12 R_2N = morpholino (80%)

iv

10 (54%)

Scheme 2 *Reagents and conditions:* i, 10% $Pd(OAc)_2$, $PhB(OH)_2$, MeOH, 60 °C, 1 h (for **3c,e**); ii, 10% $Pd(OAc)_2$, $PhBF_3K$, MeOH, 60 °C, 1 h (for **3b**); iii, excess of morpholine; iv, TFA (4 mol equiv.), I_2 (cat.), benzene, reflux

† dba = 1,3-dibenzylideneacetonato(1−).

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 CH$_2$Cl$_2$–light petroleum) (Found: C, 76.52; H, 6.70. C$_{24}$H$_{26}$O$_4$ requires C, 76.19; H, 6.87%); ν_{max}(Nujol)/cm^{-1} 1705, 1625, 1450, 1310 and 1173; δ_H(CDCl$_3$) 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 CH$_2$Cl$_2$–light petroleum) (Found: C, 69.99; H, 6.40. C$_{24}$H$_{26}$O$_6$ requires C, 70.24; H, 6.34%); ν_{max}(Nujol)/cm^{-1} 1685, 1595, 1440, 1380, 1270 and 1120; δ_H(CDCl$_3$) 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. C$_{26}$H$_{26}$O$_8$ requires C, 66.95; H, 5.58%); ν_{max}(Nujol)/cm^{-1} 1710, 1445, 1355 and 1175; δ_H(CDCl$_3$) 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. C$_{22}$H$_{22}$O$_5$ requires C, 72.13; H, 6.01%); ν_{max}(Nujol)/cm^{-1} 1700, 1620, 1580, 1490, 1355, 1230 and 1160; δ_H(CDCl$_3$) 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. C$_{22}$H$_{22}$O$_6$ requires C, 63.76; H, 5.31%); ν_{max}(Nujol)/cm^{-1} 2920, 2830, 1705, 1455, 1370, 1305 and 1150; δ_H(CDCl$_3$) 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 CH$_2$Cl$_2$–light petroleum); ν_{max}(KBr)/cm^{-1} 1705, 1630, 1300 and 1170; δ_H(CDCl$_3$) 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 CH$_2$Cl$_2$–light petroleum) (Found: C, 93.52; H, 6.68. C$_{30}$H$_{26}$ requires C, 93.26; H, 6.74%); ν_{max}(Nujol)/cm^{-1} 1590, 1545, 1285, 1205, 1030, 960 and 805; δ_H(CDCl$_3$) 2.63 (6 H, s) and 7.26–7.86 (20 H, m).

Compound **7c**: 75%; mp 195–196 °C (from CH$_2$Cl$_2$–light petroleum) (Found: C, 86.12; H, 6.22. C$_{30}$H$_{26}$O$_2$ requires C, 86.28; H, 6.38%); ν_{max}(Nujol)/cm^{-1} 1590, 1540, 1280, 1010, 950 and 800; δ_H(CDCl$_3$) 4.00 (6 H, s) and 6.15–6.7 (20 H, m).

Compound **7d**: 63%; mp 205–206 °C (from CH$_2$Cl$_2$–light petroleum); ν_{max}(Nujol)/cm^{-1} 1710, 1450, 1290, 1240 and 1080; δ_H(CDCl$_3$) 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 CH$_2$Cl$_2$–light petroleum) (lit.,[19a] >350 °C); δ_H(CDCl$_3$) 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(CDCl$_3$) 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 cm^3), and CO was passed through the mixture for 1 h. Standard work-up with CH$_2$Cl$_2$ followed by recrystallization gave the diesters **8c,e**.

Compound **8c**: 93%; mp 170–171 °C (from MeOH) (Found: C, 65.25; H, 5.49. C$_{18}$H$_{18}$O$_6$ requires C, 65.45; H, 5.45%); ν_{max}(Nujol)/cm^{-1} 1700, 1600, 1460, 1380, 1280, 1180 and 1020; δ_H(CDCl$_3$) 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(CDCl$_3$) 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 PhBF$_3$K (0.184 g, 1 mmol) (for **3b**) in MeOH (10 cm^3) and the

mixture was heated under reflux for 1 h. It was then cooled to room temp. and standard work-up with CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$–light petroleum) (lit.,[19c] 183–184 °C) (Found: C, 85.72; H, 6.12. C$_{26}$H$_{22}$O$_2$ requires C, 85.24; H, 6.01%); δ_H(CDCl$_3$) 3.92 (6 H, s) and 7.18–7.60 (16 H, m).

Compound **10**: 60%; mp 205–206 °C (from MeOH–CHCl$_3$) (Found: C, 89.02; H, 5.68. C$_{24}$H$_{18}$O requires C, 89.44; H, 5.59%); ν_{max}(Nujol)/cm^{-1} 1590, 1545, 1285, 1210, 1120, 960 and 810; δ_H(CDCl$_3$) 7.06–7.60 (18 H, m).

Compound **11**: 55%; mp 137–139 °C (from CH$_2$Cl$_2$–light petroleum) (lit.,[19d] 141 °C); δ_H(CDCl$_3$) 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 cm^3) in water (30 cm^3) and the mixture was stirred for 5 min at 25 °C. It was then cooled to 0 °C and treated dropwise with aq. NaNO$_2$ (0.703 g, 10.2 mmol in 4 cm^3). 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. NaHCO$_3$ 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(CDCl$_3$) 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 I$_2$ (5 mg) in benzene (20 cm^3). After the addition was complete, refluxing was continued for a further 3 h after which it was cooled, poured into 5% aq. Na$_2$CO$_3$ (10 cm^3) and extracted with CHCl$_3$ (3 × 10 cm^3). Removal of solvent followed by recrystallization from CHCl$_3$–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)$_2$.

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