Pergamon

Tetrahedron 58 (2002) 5927–5931

TETRAHEDRON

Synthesis of polycyclic xanthenes and furans via palladium-catalyzed cyclization of polycyclic aryltriflate esters

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Received 19 March 2002; accepted 21 May 2002

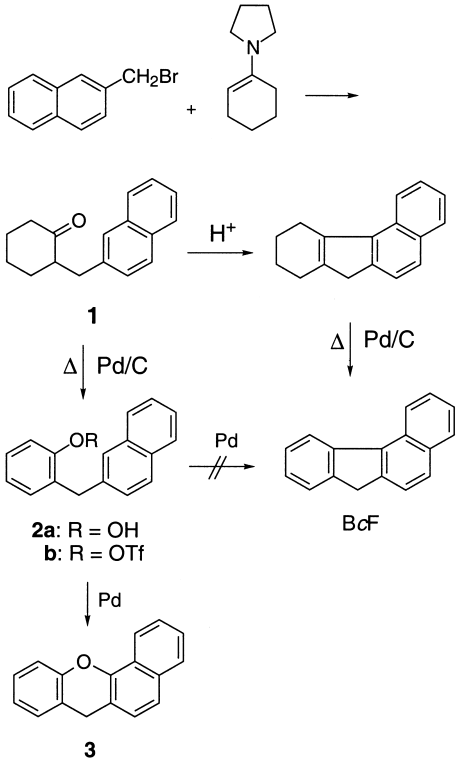
Abstract—Palladium-catalyzed cyclization of polycyclic aromatic *o*-(arylmethyl)phenol triflate esters takes place with unexpected sulfur–oxygen bond cleavage to furnish polycyclic xanthenes. These are the first examples of Pd-catalyzed cross-coupling of aryl triflate esters with arenes to form diaryl ethers. In contrast, analogous palladium-catalyzed cyclization of polycyclic *o*-(aryloxy)phenol triflate esters proceeds via a mechanism that involves conventional carbon–oxygen bond cleavage to furnish diaryl furans.

Administration of coal tar to mice in the diet results in the formation of DNA adducts in mouse lung and a high incidence of lung tumors.[1,2] A principal component of tar responsible for formation of the DNA adducts has recently been identified as 7*H*-benzo[*c*]fluorene (B*c*F).[3] This finding has important implications for cancer in human populations because B*c*F is a relatively common environmental pollutant produced by incomplete combustion of fossil fuels, and B*c*F is also a component of mainstream cigarette smoke.[4] In connection with studies to identify the active metabolites of B*c*F that bind to DNA,[5] we required practical syntheses of B*c*F and 3-methoxy-B*c*F.[6]

Synthesis of B*c*F was accomplished via alkylation of the enamine of cyclohexanone by 2-bromomethylnaphthalene (Scheme 1) to furnish 2-(2-naphthylmethyl)cyclohexanone (**1**), followed by acid-catalyzed cyclodehydration and dehydrogenation.[7,8] Because the yield in the cyclization step was only moderate, we investigated a modification of this method. The alternative approach entailed conversion of **1** to the corresponding phenol derivative (**2a**) and cyclization of its triflate ester derivative (**2b**) by palladium-catalyzed intramolecular coupling.

1. Results and discussion

Although palladium-catalyzed coupling of aryl halides with arenes has numerous synthetic applications,[9] analogous coupling of aryl triflates with arenes is less well known.[10] Intramolecular aryl triflate–arene coupling mediated by bis(triphenylphosphine)palladium(II) chloride was employed by Rice and Cai[11] as a key step in the synthesis of several benzofluoranthenes. Their synthesis resembles the proposed synthesis of B*c*F in that a five-membered ring is formed in the coupling step, but differs in that it entails cyclization to a peri ring position of an adjacent aromatic ring, whereas the synthesis of B*c*F involves reaction at an *ortho* position of the



Scheme 1.

Keywords: palladium-catalyzed coupling; polycyclic xanthenes; polycyclic furans.

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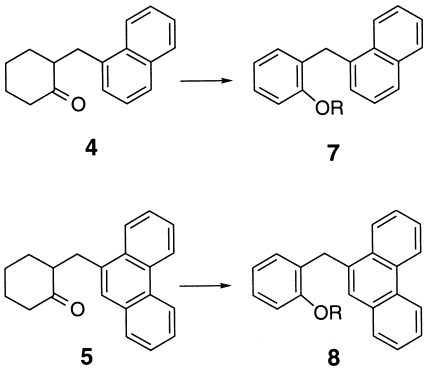
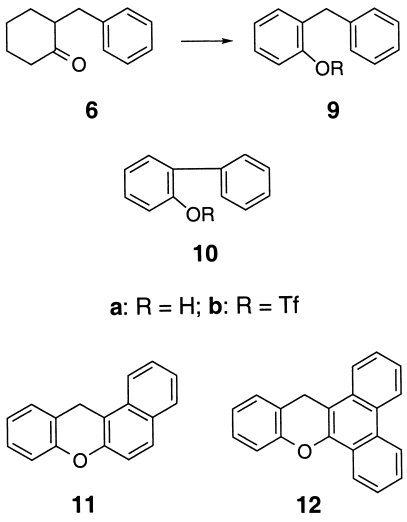
0040–4020/02/$ - see front matter
PII: S0040-4020(02)00534-3

same aromatic ring. The geometries of the five-membered rings that are formed in these cases are significantly different.

Dehydrogenation of 2-(2-naphthylmethyl)cyclohexanone (**1**) over a 10% palladium–charcoal catalyst in refluxing triglyme at 240°C gave 2-(2-naphthylmethyl)phenol (**2a**) (Scheme 1). The latter was converted to the corresponding triflate ester (**2b**) by treatment with trifluoromethanesulfonic acid anhydride and 2,6-lutidine. Reaction of **2b**, LiCl, and DBU with bis(triphenylphosphine)palladium(II) chloride (0.1 equiv.) in DMF at 145°C gave a white solid, mp 88–89°C, whose ^{1}H and ^{13}C NMR spectra and other properties were inconsistent with the structure of B*c*F, the expected product of palladium-catalyzed cyclization. The novel product was identified as 7*H*-benzo[*c*]xanthene (**3**), a polycyclic aromatic compound with one more oxygen atom [FAB MS *m/z* 232 (M^{+})]. The ^{1}H and ^{13}C NMR spectra of **3** were in agreement with this structural assignment as were its melting point (88–89°C; lit[12] 90–91°C) and elemental analysis. Evidently, cyclization of the triflate ester (**2b**) took place with cleavage of the sulfur–oxygen bond rather than the carbon–oxygen bond. This mode of bond cleavage was not observed previously in the analogous cyclization of triflate esters to form benzofluoranthenes.[11] As far as we are aware, this is the first example of palladium-catalyzed cross-coupling of an aryl triflate ester with an arene to form a diaryl ether product.

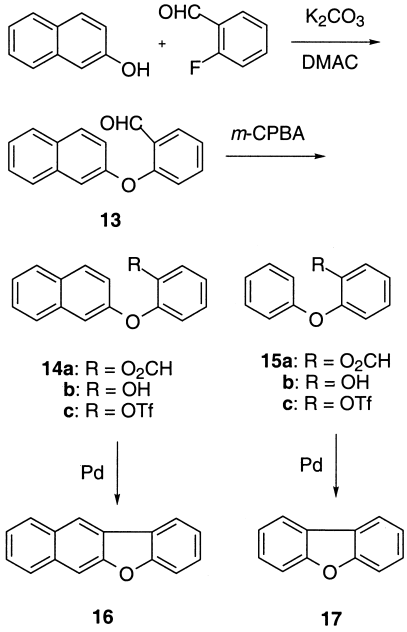
In view of the novelty of the synthesis of 7*H*-benzo[*c*]-xanthene, we investigated the utility of the method for the synthesis of other oxygen-containing heterocyclic polycyclic aromatic compounds. Ketones **4**–**6** were prepared by alkylation of the enamine of cyclohexanone by 2-bromomethylnaphthalene, 9-bromomethylphenanthrene, and benzyl bromide, respectively. The ketones **4**–**6** were converted to the corresponding triflate esters (**7b**–**9b**) via dehydrogenation over a 10% palladium–charcoal catalyst in triglyme followed by treatment of the phenolic products (**7a**–**9a**) with trifluoromethanesulfonic anhydride in the presence of 2,6-lutidine. Palladium-catalyzed reaction of triflate esters **7b** and **8b** under the same conditions as **2b** furnished as the principal products 12*H*-benzo[*a*]xanthene (**11**) and 14*H*-dibenzo[*a*,*c*]xanthene (**12**), respectively. However, analogous reaction of the triflate ester **9b** failed to afford xanthene or fluorene, the products anticipated to arise via either mode of cyclization. Instead, there was obtained an insoluble residue of indeterminate structure. Analogous reaction of 2-hydroxybiphenyl triflate (**10b**) also failed to afford cyclized products.





We also examined whether aryloxyphenol triflate esters might participate in palladium-catalyzed reactions to afford cyclized products with one or two oxygen atoms in the saturated ring. 2-(2-Naphthoxy)phenol triflate (**14c**) was prepared (Scheme 2) by base-catalyzed reaction of 2-fluorobenzaldehyde with 2-naphthol to yield the aryloxybenzaldehyde derivative (**13**), followed by Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid to furnish 2-(2-naphthyloxy)phenol formate (**14a**). The latter was hydrolyzed to the free phenol (**14b**) which was converted to the triflate ester (**14c**) by treatment with triflic acid anhydride in the presence of lutidine. The triflate ester of 2-(phenoxy)phenol (**15c**) was similarly prepared from analogous reaction of 2-fluorobenzaldehyde and phenol.

Palladium-catalyzed reaction of the triflate esters **14c** and **15c** under the same conditions employed for **2b** provided the corresponding polycyclic aromatic furan derivatives, benzo[*b*]naphtho[2,3-*d*]furan (**16**) and dibenzofuran (**17**), in yields of 96 and 80%, respectively. In both these



Scheme 2.

examples, cyclized products were formed via exclusive carbon–oxygen bond cleavage. The related polycyclic aromatic dioxanes expected to arise from the alternative mode of bond cleavage were not detected. It is also worthy of note that cyclization of **14c** took place regioselectively to the 3-position of the naphthalene ring rather than to the usually more reactive 1-position, as observed in cyclization of **2b**.

In summary, palladium-catalyzed cyclization of arylmethylphenol triflate esters (**2b**, **7**, **8**) takes place with preferential sulfur–oxygen bond cleavage to furnish polycyclic xanthene compounds, 7*H*-benzo[*c*]xanthene (**3**), 12*H*-benzo[*a*]xanthene (**11**) and 14*H*-dibenzo[*a*,*c*]xanthene (**12**). In contrast, analogous palladium-catalyzed reactions of the triflate esters of aryloxyphenols (**14c** and **15c**) occur with preferential carbon–oxygen bond cleavage to furnish polycyclic furans, benzo[*b*]naphtho[2,3-*d*]furan (**16**) and dibenzofuran (**17**). These reactions provide convenient synthetic access to polycyclic xanthenes and furan compounds.

Details of the mechanisms of these reactions are not known. We are grateful to a reviewer for pointing out that *ortho*-palladation of unsubstituted diary ethers is an established reaction[14] and the intermediates involved may be the same as in the synthesis of the furans whose synthesis is reported herein. More extensive investigation will be required to determine the details of the mechanisms and the roles of the factors involved in determining the mode of bond cleavage and the direction of cyclization.

2. Experimental

2.1. Materials and methods

2-(2-Naphthylmethyl)cyclohexanone (**1**) and 2-(1-naphthylmethyl)cyclohexanone (**4**) were synthesized by reaction of 2-bromomethylnaphthalene and 1-bromomethylnaphthalene, respectively, with 1-pyrrolidino-1-cyclohexene by the published method.[7] 9-Bromomethylphenanthrene was synthesized from 9-methylphenanthrene by bromination with *N*-bromosuccinimide in CCl_4 in the presence of benzoyl peroxide.[7] 2-Phenoxyphenol (**15b**) was prepared by the published method.[13] 1-Pyrrolidino-1-cyclohexene, 2-benzylphenol (**9a**), 2-hydroxybiphenyl (**10a**), and *m*-chloroperbenzoic acid (*m*-CPBA) were purchased from the Aldrich Chemical Co. (CAUTION: *m*-CPBA is potentially explosive when dry). 1-Pyrrolidino-1-cyclohexene and trifluoromethanesulfonic anhydride (Tf_2O) were purified by distillation. Dimethylformamide (DMF), dimethylacetamide (DMA), and 2,6-lutidine were dried over CaH_2 prior to use. 1,4-Dioxane and triglyme were freshly distilled from sodium/benzophenone ketal.

NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Integrations were consistent with all structural assignments. Mass spectra (MS) and HRMS were performed by the University of Illinois at Urbana-Champaign, School of Chemical Sciences. Microanalyses were conducted by Atlantic Microlab, Inc. Melting points are uncorrected.

2.1.1. 2-(9-Phenanthrylmethyl)cyclohexanone (5). To a solution of 9-(bromomethyl)phenanthrene (5.00 g, 18.4 mmol) in dry dioxane (30 mL) was added 1-pyrrolidino-1-cyclohexene (3.0 mL, 18.6 mmol). The solution was heated at reflux for 18 h. Then water (10 mL) was added, and refluxing was continued for another 2 h. After cooling to room temperature, the solution was transferred to a separatory funnel and ether (500 mL) and 5% HCl (300 mL) were added. The organic layer was washed with 5% HCl, 5% aqueous $NaHCO_3$ solution and water, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column eluted with benzene–hexane (1:1) to afford **5** (4.55 g, 86%) as a white solid, mp 100–101°C: ^{1}H NMR ($CDCl_3$) δ 8.72–8.75 (m, 1), 8.62–8.66 (m, 1), 7.98–8.02 (m, 1), 7.81–7.85 (m, 1), 7.56–7.68 (m, 5), 3.96 (dd, 1, J=10.42 Hz), 1.41–2.81 (m, 10); ^{13}C NMR ($CDCl_3$) δ 212.3, 134.2, 131.5, 131.0, 130.7, 129.6, 128.0, 127.7, 126.6, 126.5, 126.1, 126.0, 124.2, 123.3, 122.3, 50.7, 42.11, 33.8, 32.8, 27.9, 24.9; FAB MS *m*/*z* 288 (M^+). Anal. Calcd for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.74; H, 7.22.

2.1.2. 2-(2-Naphthylmethyl)phenol (2a). To a solution of **1** (1.00 g, 4.2 mmol) in dry triglyme (20 mL) was added 10% Pd/C (500 mg). The mixture was heated to 230°C under argon for 14 h. After cooling, the mixture was diluted with ether and filtered. The filtrate was washed three times with water. The ether layer was dried over $MgSO_4$, and evaporated to dryness. The crude product was purified by chromatography on a column of silica gel eluted with EtOAc–hexane (1:15) to afford **2a** (810 mg, 83%) as a white solid, mp 58–59°C: ^{1}H NMR ($CDCl_3$) δ 7.75–7.82 (m, 3), 7.66 (s, 1), 7.41–7.48 (m, 2), 7.37 (d, 1, J=8.45 Hz), 7.13–7.19 (m, 2), 6.91 (t, 1, J=7.42 Hz), 6.79 (d, 1, J=7.88 Hz), 4.76 (s, 1, OH), 4.16 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 153.7, 137.4, 133.6, 132.2, 131.0, 128.3, 127.9, 127.6, 127.5, 127.3, 126.8, 126.0, 125.4, 121.0, 115.7, 36.5; FAB MS *m*/*z* 234 (M^+). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.26; H, 6.22.

2.1.3. 2-(2-Naphthylmethyl)phenol triflate (2b). To a solution of **2a** (1.00 g, 4.3 mmol) and 2,6-lutidine (0.80 mL, 6.9 mmol) in dry CH_2Cl_2 (30 mL) was added triflic anhydride (0.90 mL, 5.4 mmol) in CH_2Cl_2 (20 mL) over 1 h under argon at −30°C. The cooling bath was changed to ice, and stirring was continued for an additional hour. Reaction was quenched by addition of water (50 mL), and the solution was allowed to warm to room temperature. Conventional workup followed by chromatography on a silica gel column eluted with EtOAc–hexane (1:15) gave **2b** (1.56 g, 100%) as a white solid, mp 50–51°C: ^{1}H NMR ($CDCl_3$) δ 7.76–7.85 (m, 3), 7.65 (s, 1), 7.43–7.50 (m, 2), 7.18–7.34 (m, 5), 4.27 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 147.9, 135.9, 133.9, 133.5, 132.2, 131.9, 128.4, 128.2, 127.7, 127.6, 127.3, 126.2, 125.7, 121.4, 118.6 (q, CF_3, J=320.0 Hz), 35.8; ^{19}F NMR ($CDCl_3$) δ −73.50; FAB MS *m*/*z* 366 (M^+). Anal. Calcd for $C_{18}H_{13}F_3O_3S$: C, 59.01; H, 3.58. Found: C, 59.02; H, 3.64.

2.1.4. 2-(1-Naphthylmethyl)phenol (7a). Dehydrogenation of **4** (3.07 g, 12.9 mmol) by the procedure employed for analogous reaction of **1** gave **7a** (2.43 g, 81%) as an oil: ^{1}H NMR ($CDCl_3$) δ 8.02–8.97 (m, 1), 7.84–7.90 (m, 1),

7.76 (d, 1, J=8.26 Hz), 7.45–7.50 (m, 2), 7.37–7.42 (m, 1), 7.22–7.26 (m, 1), 7.10–7.16 (m, 1), 6.95–7.00 (m, 1), 6.80–6.86 (m, 2), 4.82 (br s, 1, OH), 4.44 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 153.5, 135.4, 133.9, 132.1, 130.8, 128.7, 127.7, 127.3, 126.5, 126.2, 126.1, 125.7, 125.6, 124.0, 121.0, 115.5, 33.0.

2.1.5. 2-(1-Naphthylmethyl)phenol triflate (7b). Conversion of **7a** (2.37 g, 10 mmol) to a triflate ester by the method employed for **2b** gave **7b** (3.42 g, 92%) as an oil: ^1H NMR ($CDCl_3$) δ 7.86–7.91 (m, 1), 7.80–7.85 (m, 2), 7.42–7.51 (m, 3), 7.24–7.37 (m, 3), 7.11–7.17 (m, 1), 6.86–6.91 (m, 1), 4.54 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 147.8, 134.0, 133.9, 133.6, 132.0, 131.2, 128.8, 128.4, 128.1, 127.9, 127.8, 126.3, 125.8, 125.5, 123.9, 121.2, 118.6 (q, CF_3, J=319.55 Hz), 32.78; ^{19}F NMR ($CDCl_3$) δ −73.42; FAB HRMS Calcd for $C_{18}H_{13}F_3O_3S$: m/z 366.0538; Found: 366.0537. Anal. Calcd for $C_{18}H_{13}F_3O_3S$: C, 59.01; H, 3.58. Found: C, 59.29; H, 3.60.

2.1.6. 2-(9-Phenanthrylmethyl)phenol (8a). Catalytic dehydrogenation of **5** (2.00 g, 6.9 mmol) by the procedure employed for reaction of **1** gave **8a** (1.50 g, 76%) as a white solid, mp 165–166°C: ^1H NMR ($CDCl_3$) δ 8.75 (d, 1, J=8.43 Hz), 8.68 (d, 1, J=8.48 Hz), 8.10 (d, 1, J=8.44 Hz), 7.79 (d, 1, J=8.07 Hz), 7.54–7.70 (m, 4), 7.50 (s, 1), 7.14–7.20 (m, 1), 7.02–7.07 (m, 1), 6.83–6.90 (m, 2), 4.91 (br s, 1, OH), 4.47 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 153.5, 133.7, 131.7, 131.3, 130.8, 130.7, 129.9, 128.3, 127.7, 127.1, 126.7, 126.6, 126.4, 126.3, 125.9, 124.7, 123.1, 122.4, 121.1, 115.5; FAB MS m/z 284 (M^+). Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.48; H, 5.63.

2.1.7. 2-(9-Phenanthrylmethyl)phenol triflate (8b). Conversion of **8a** (1.00 g, 3.52 mmol) to its triflate ester by the method employed for **2b** gave **8b** (1.42 g, 97%) as a viscous oil: ^1H NMR ($CDCl_3$) δ 8.75 (d, 1, J=8.44 Hz), 8.69 (d, 1, J=8.24 Hz), 7.81–7.90 (m, 2), 7.53–7.70 (m,5), 7.38 (d, 1, J=8.18 Hz), 7.26–7.32 (m, 1), 7.10–7.16 (m, 1), 6.97 (d, 1, J=7.70 Hz), 4.57 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 147.8, 133.3, 132.1, 131.6, 131.2, 130.9, 130.8, 130.1, 128.7, 128.4, 128.3, 128.2, 126.9, 126.8, 126.6, 126.5, 124.7, 123.2, 122.5, 121.3, 118.7 (q, CF_3, J=320.60 Hz), 33.35; ^{19}F NMR ($CDCl_3$) δ −73.37; FAB HRMS Calcd for $C_{22}H_{15}F_3O_3S$: m/z 416.0694; Found: 416.0695. Anal. Calcd for $C_{22}H_{15}F_3O_3S$: C, 63.46; H, 3.63. Found: C, 63.31; H, 3.76.

2.1.8. 2-Benzylphenol triflate (9b). Analogous conversion of 2-benzylphenol (2.12 g, 11.5 mmol) to its triflate ester gave **9b** (3.51 g, 97%) as an oil: ^1H NMR ($CDCl_3$) δ 7.20–7.40 (m, 9), 4.13 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 147.9, 138.4, 134.0, 131.8, 129.1, 128.6, 128.4, 128.2, 126.6, 121.3, 118.6 (q, CF_3, J=319.40 Hz), 35.72; ^{19}F NMR ($CDCl_3$) δ −73.58; Anal. Calcd for $C_{14}H_{11}F_3O_3S$: C, 53.16; H, 3.51. Found: C, 53.26; H, 3.55.

2.1.9. 2-Hydroxybiphenyl triflate (10b). Analogous conversion of 2-hydroxybiphenyl (1.95 g, 11.5 mmol) to its triflate ester gave **10b** (3.20 g, 93%) as an oil: ^1H NMR ($CDCl_3$) δ 7.40–7.53 (m, 9); ^{13}C NMR ($CDCl_3$) δ 146.8, 135.5, 135.5, 131.9, 129.3, 129.0, 128.5, 128.5, 128.3, 122.1, 118.3 (q, CF_3, J=320.80 Hz); ^{19}F NMR ($CDCl_3$) δ −73.91; FAB MS m/z 302 (M^+). Anal. Calcd for $C_{13}H_9F_3O_3S$: C, 51.66; H, 3.00. Found: C, 51.74; H, 3.04.

2.1.10. 7*H*-Benzo[*c*]xanthene (3). A solution of **2b** (1.00 g, 2.7 mmol), $Pd(PPh_3)_2Cl_2$ (192 mg, 0.27 mmol), LiCl (347 mg, 8.2 mmol), and DBU (0.5 mL, 3.3 mmol) in dry DMF (30 mL), was heated at 145°C under argon for 18 h. After cooling, the dark brown solution was transferred to a separatory funnel. Water and ether were added. The ether layer was washed 3 times with water, dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a column of silica gel eluted with hexane to yield **3** (210 mg, 33%) as a white solid, mp 88–89°C (lit[12] 90–91°C): ^1H NMR ($CDCl_3$) δ 8.40 (d, 1, J=8.20 Hz), 7.80 (d, 1, J=7.95 Hz), 7.45–7.60 (m, 3), 7.20–7.29 (m, 4), 7.04–7.12 (m, 1), 4.19 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 151.7, 146.3, 133.3, 129.0, 127.6, 127.5, 126.6, 125.9, 125.8, 124.2, 123.2, 122.3, 121.4, 120.3, 116.6, 114.1, 28.0; FAB MS m/z 232 (M^+). Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 88.03; H, 5.18.

2.1.11. 12*H*-Benzo[*a*]xanthene (11). Analogous reaction of **7b** (3.35 g, 9.1 mmol) gave **11** (470 mg, 22%) as a white solid, mp 89–90°C (lit[15] 80°C): ^1H NMR ($CDCl_3$) δ 7.86 (d, 1, J=8.44 Hz), 7.82 (d, 1, J=8.11 Hz), 7.72 (d, 1, J=8.93 Hz), 7.54–7.59 (m, 1), 7.40–7.45 (m, 1), 7.29–7.32 (m, 1), 7.20–7.27 (m, 2), 7.05–7.10 (m, 2), 4.37 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 151.0, 148.6, 132.0, 130.1, 129.4, 128.5, 128.3, 127.7, 126.7, 124.1, 123.1, 122.2, 119.5, 117.9, 116.5, 111.6, 24.8; FAB MS m/z 232 (M^+). Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.81; H, 5.34.

2.1.12. 14*H*-Dibenzo[*a*,*c*]xanthene (12). Analogous reaction of **8b** (1.24 g, 3.0 mmol) gave **12** (480 mg, 57%) as a white solid, mp 186–188°C: ^1H NMR ($CDCl_3$) δ 8.61–8.67 (m, 2), 8.46–8.50 (m, 1), 7.84–7.87 (m, 1), 7.55–7.70 (m, 4), 7.22–7.34 (m, 3), 7.08–7.13 (m,1), 4.32 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 150.7, 144.0, 131.0, 130.4, 129.4, 127.3, 127.1, 126.81, 126.7, 124.7, 123.3, 122.8, 122.7, 122.4, 122.2, 119.5, 116.5, 107.9, 25.0; FAB MS m/z 282 (M^+). Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.26; H, 5.10.

2.1.13. 2-(2-Naphthoxy)phenol (14b). To a solution of 2-naphthol (5.48 g, 38 mmol) and 2-fluorobenzaldehyde (4.0 mL, 38 mmol) in dry DMA (40 mL) was added anhydrous K_2CO_3. The mixture was heated at reflux for 2 h, then allowed to cool. EtOAc was added, and the solution was washed with water and brine. The organic layer was dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a silica gel column. Elution with hexane–CH_2Cl_2 provided 2-(2-naphthoxy)-benzaldehyde (**13**) (7.94 g, 84%) as a pale yellow oil: ^1H NMR ($CDCl_3$) δ 10.56 (s, 1, C*H*O), 7.98 (d, 1, J=9.7 Hz), 7.84–7.89 (m, 2), 7.71 (m, 1), 7.45–7.51 (m, 3), 7.37 (s, 1), 7.28–7.31 (m, 1), 7.21 (m, 1), 6.94 (d, 1, J=10.3 Hz). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.12; H, 5.94.

To a solution of **13** (5.43 g, 22 mmol) in $CHCl_3$ (80 mL) was added *m*-CPBA (9.50 g). The solution was stirred at 30°C for 6 h then washed with dilute $NaHSO_3$, saturated $NaHCO_3$

(3X), and water. Evaporation of the solvent afforded crude 2-(2-naphthoxy)phenol formate (**14a**) as an oil. This compound was dissolved MeOH (100 mL), 2 drops of conc. HCl were added, and the solution was stirred at room temperature for 1 h. Reaction was quenched by addition of $NaCO_3$ (2 g), and the solution was filtered and evaporated to dryness. Chromatography of the residue on a silica gel column eluted with hexane–CH_2Cl_2 (2:1) afforded 2-(2-naphthoxy)phenol (**14b**) (2.73 g, 53%) as a white solid, mp 106–107°C: ^{1}H NMR ($CDCl_3$) δ 7.82 (t, 2, J=8.00 Hz), 7.69 (d, 1, J=8.50 Hz), 7.38–7.47 (m, 2), 7.23–7.30 (m, 2), 7.05–7.10 (m, 2), 6.94 (d, 1, J=8.50 Hz), 6.83–6.88 (m, 1), 5.62 (br s, 2, OH); ^{13}C NMR ($CDCl_3$) δ 154.5, 147.5, 143.4, 134.2, 130.3, 130.1, 127.8, 127.2, 126.7, 125.0, 124.9, 120.7, 119.1, 119.1, 116.3, 113.2; FAB MS m/z 236 (M^+). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.24; H, 5.10.

2.1.14. 2-(2-Naphthoxy)phenol triflate (14c). Conversion of **14b** (1.00 g, 4.2 mmol) to its triflate ester by the usual method gave **14c** (1.55 g, 100%) as a white solid, mp 52°C: ^{1}H NMR ($CDCl_3$) δ 7.82–7.92 (m, 2), 7.74 (d, 1, J= 7.80 Hz), 6.97–7.52 (m, 8); ^{13}C NMR ($CDCl_3$) δ 153.1, 149.4, 140.0, 134.1, 130.8, 130.3, 129.3, 127.8, 127.3, 126.8, 125.3, 123.7, 123.1, 119.7, 119.5, 118.7 (q, CF_3, J= 319.75 Hz); ^{19}F NMR ($CDCl_3$) δ −73.36. Anal. Calcd for $C_{17}H_{11}F_3O_4S$: C, 55.44; H, 3.01. Found: C, 55.54; H, 2.99.

2.1.15. 2-Phenoxyphenol triflate (15c). Conversion of 2-phenoxyphenol (**15b**) (2.14 g, 11.5 mmol) to its triflate ester by the usual method gave **15c** (3.41 g, 93%) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.35–7.44 (m, 3), 7.26–7.31 (m, 1), 7.20–7.25 (m, 1), 7.11–7.16 (m, 3), 6.98 (dd, 1, J= 1.50 Hz); ^{13}C NMR ($CDCl_3$) δ 155.4, 149.5, 140.0, 130.0, 129.2, 124.6, 123.4, 122.9, 119.4, 119.1, 118.8 (q, CF_3, J=320.50 Hz); ^{19}F NMR ($CDCl_3$) δ −73.54; FAB MS m/z 318 (M^+). Anal. Calcd for $C_{13}H_9F_3O_4S$: C, 49.06; H, 2.85. Found: C, 49.03; H, 2.74.

2.1.16. Dibenzofuran (17). Palladium-catalyzed reaction of **14c** (2.73 g, 8.6 mmol) by the procedure employed for the preparation of 7*H*-benzo[*c*]xanthene (**3**) furnished **17** (1.38 g, 96%) as a white solid, mp 81–82°C (lit[16] 83°C): ^{1}H NMR ($CDCl_3$) δ 7.99 (d, 2, J=7.69 Hz); 7.64 (d, 2, J=8.17 Hz); 7.99 (t, 2, J=7.39 Hz); 7.99 (t, 2, J= 7.54 Hz); the ^{1}H NMR spectrum of **17** matched that of a commercial sample.[17]

2.1.17. Benzo[*b*]naphtho[2,3-*d*]furan (16). Analogous reaction of **14c** (1.22 g, 3.3 mmol) by the same procedure gave **17** (580 mg, 80%) as a white solid, mp 202–204°C (lit[18] 207.5–209°C): ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 1), 7.99–8.12 (m, 2), 7.96 (d, 1, J=7.55 Hz), 7.91 (s, 1), 7.43–7.62 (m, 4), 7.32–7.42 (m, 1); ^{13}C NMR ($CDCl_3$) δ 157.6, 154.8, 133.0, 130.1, 128.3, 127.7, 125.8, 125.4, 124.3, 123.9, 122.7, 121.3, 119.2, 111.5, 106.9. Anal. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 88.14; H, 4.62.

Acknowledgements

This research was supported by contract EP-P2394/C1070 from the Electric Power Research Institute, Palo Alto, CA.

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