Organolead-Mediated Arylations: 2-(3,3-Diphenylallyloxy)phenyllead Triacetate as an Internal Free-Radical-Trap-Containing Reagent

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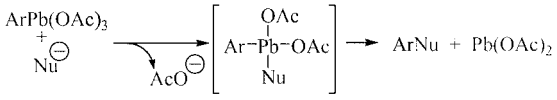
Keywords: Arylation / Copper / Radicals / Organolead / Radical trap

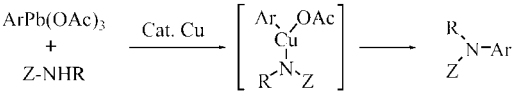
2-(3,3-Diphenylprop-2-enyloxy)phenyllead triacetate, an arylating reagent containing an internal free radical trap, was synthesised and its behaviour studied in base-catalysed *C*-arylation reactions and in copper-catalysed *N*-arylation reactions. The absence of benzofuran derivatives among the products of *C*- and *N*-arylation reactions excludes the involvement of radical species in these two processes.

Introduction

Aryllead triacetates, diaryl-λ^3-iodanes and pentavalent triarylbismuth derivatives are versatile and highly reactive reagents for nucleophilic aromatic substitutions taking place by the ligand-coupling mechanism.[1] These reactions occur regioselectively at the *ipso* position leading to *C*-arylation with soft carbon nucleophiles under basic conditions[1,2] and to the modified Ullmann *N*-arylation with amines under copper catalysis.[3,4] In the case of aryllead triacetates, the *C*-arylation, known as the Pinhey arylation reaction,[5] was discovered and developed by Pinhey and his group[6] and the *N*-arylation was discovered by Barton et al.[7,8] (Schemes 1 and 2).



Scheme 1. Base-catalysed *C*-arylation with aryllead triacetate



Scheme 2. Copper-catalysed *N*-arylation with aryllead triacetate

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These reactions are believed to take place through arylheteroatom-substrate or oxidized arylcopper intermediates, respectively, which subsequently undergo a reductive elimination-type reaction to afford the final products.[9] The intervention of a free radical species has sometimes been invoked to explain the reactions with diaryliodonium salts[10] and the copper-catalysed *N*-arylation with triarylbismuth diacetate.[11] However, use of the well-established intramolecular free radical probe [(*o*-allyloxy)phenyl radical][12] excluded the participation of free radical species in *C*-arylation with aryllead triacetates,[13] diaryl-λ^3-iodanes[14] and pentavalent triarylbismuth derivatives,[15] as well as in the copper-catalysed *N*- and *O*-arylation with triarylbismuth diacetates.[15] The same conclusion was reached from experiments with 1,1-diphenylethylene as an intermolecular free radical trap.[7c,16,17] However, these experiments with either external or internal free radical traps are not definitive proof of the exclusion of a homolytic pathway, as the trapping of aryl radicals with short lifetimes reacting within the coordination sphere of the heteroatom may be too slow.

The efficiency of intramolecular radical clocks can be improved by incorporation of a radical-stabilizing group, such as a phenyl, into the skeleton of the internal radical clock, leading to a 10-fold increase in the cyclisation rate.[18] For example, the reaction of active magnesium with a 2-bromophenyl 3′-phenylprop-2′-enyl ether trap ($k_{cycl} \approx 10^{10}$ s^{-1}) allowed Chanon et al. to isolate the cyclisation products in high yields.[18] In contrast, the hex-5-enylalkyl halides ($k_{cycl} = 10^5$ s^{-1})[19] and 2-(3-butenyl)phenyl halides ($k_{cycl} = 5.3 \times 10^8$ s^{-1})[20] did not afford any cyclisation product in similar experiments.

We considered that combining the concept of an internal trap with a 1,1-diphenylethene moiety as the trapping centre should constitute a highly efficient system to trap aryl radicals. Examples of internal trapping of free-radical species on such a *gem*-diphenylethene group have been reported

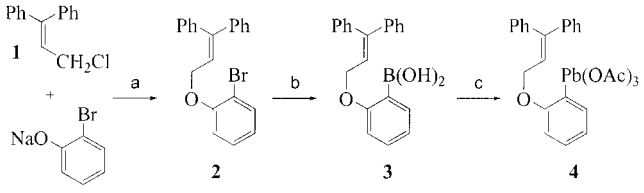
  DOI: 10.1002/ejoc.200300784

by Newcomb et al. in the case of α-ethoxycarbonyl and α-cyano free radicals,[21] nitrogen-centred radicals[22] and more recently by Ozaki et al.[23] in the case of electrochemically generated acyl radicals. Kinetic studies showed a rate constant of 4.5×10^7 s^{-1} for the cyclisation of the 6,6-diphenylhex-5-enyl radical[24] compared to a rate of 2.7×10^5 s^{-1} for the cyclisation of the unsubstituted hex-5-enyl radical.[25]

We now report the synthesis of an aryllead triacetate, containing a 2-(3,3-diphenylprop-2-enyloxy)phenyl group acting as the intramolecular trap, and its application to the search for free radical species in aryllead triacetate mediated arylation reactions under base- and copper-catalysed conditions. The presence of the two radical-stabilizing phenyl groups[26] in the allyloxy moiety of **4** should lead to a higher intramolecular rate of cyclisation for the radical species derived from **4** compared to the rate constants observed with the analogous non-stabilized precursor[27] [k_{cycl} of 2-(prop-2-enyloxy)phenyl radical = $5.2-6.3 \times 10^9$ s^{-1}] or having only one stabilizing phenyl group[18] [k_{cycl} of 2-(3-phenylprop-2-enyloxy)phenyl radical ≈ 10^{10} s^{-1}].

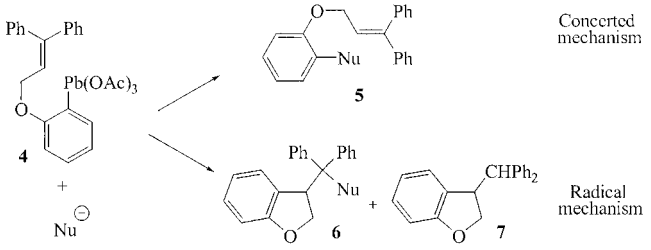
Results and Discussion

The aryllead triacetate derivative **4** was prepared in three steps from the known 3,3-diphenylprop-2-enyl chloride (**1**).[28] Reaction of this allyl chloride **1** with sodium 2-bromophenoxide in THF under reflux in the presence of a catalytic amount (10%) of sodium iodide led to the ether **2** in 89% yield. Ether **2** was treated with 1 equiv. of *n*-butyllithium to realize the bromine/lithium exchange, and subsequent treatment with triisopropyl borate[13] afforded the arylboronic acid **3** in a 36% yield. The modest yield of the boronation step (36%) may be due, in part, to a competitive cyclisation of the aryllithium intermediate.[29] Finally, the arylboronic acid **3** was converted into the corresponding aryllead triacetate derivative **4** by boron/lead exchange.[30] Thus, treatment of the arylboronic acid **3** with 1 equiv. of lead tetraacetate in the presence of a catalytic amount (10%) of mercuric acetate in anhydrous chloroform afforded the lead derivative **4** in 56% yield (Scheme 3).



Scheme 3. Synthesis of aryllead triacetate **4**; reagents and conditions: a) cat. NaI, THF, reflux, 6 h, 89%; b) (i) BuLi, THF, −78 °C, 10 min, (ii) $B(OCHMe_2)_3$, −78 °C, 1.5 h, then −78 °C to room temp., overnight, (iii) 10% aqueous HCl, 36%; c) $Pb(OAc)_4$, cat. $Hg(OAc)_2$, $CHCl_3$, 45 °C, 2 h, then room temp., 10 h, 56%

The involvement of radical or heterolytic routes in reductive coupling reactions with **4** could be distinguished by the nature of the products formed in the radical or the concerted non-synchronous coupling process (Scheme 4). The possibility of cyclisation of the 2-(3,3-diphenylprop-2-enyloxy)phenyl radical was confirmed by the reaction of **2** with Bu_3SnH in the presence of AIBN, which afforded the 3-substituted benzofuran derivative **7** in good yield (81%).



Scheme 4. Possible evolution of the reaction of organolead reagent **4** with a nucleophile

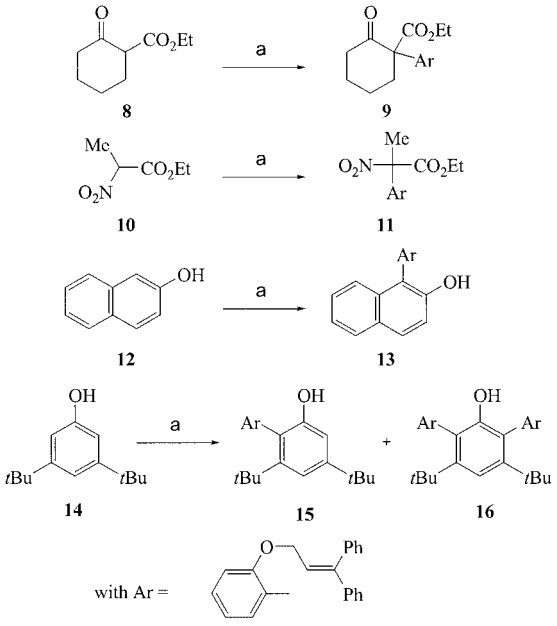
Four substrates (β-oxo ester **8**, nitro ester **10**, 2-naphthol **12** and the sterically hindered 3,5-di-*tert*-butylphenol **14**) were selected to test the behaviour of **4** in the *C*-arylation reactions. In all these reactions, the substrates were treated with 1.1 equiv. of the lead reagent **4** and 3.3 equiv. of pyridine in anhydrous chloroform at 45 °C. *C*-Arylation of the two esters, ethyl 2-oxocyclohexanecarboxylate (**8**) and ethyl 2-nitropropionate (**10**), with the aryllead triacetate **4** afforded the corresponding non-cyclized derivatives **9** and **11**, respectively, in good to high yields (Table 1). In the case of the nitro ester **10**, a significant amount of unchanged substrate was isolated (21%). Similarly, the reactive 2-naphthol (**12**) gave a high yield of the linear arylation product **13** together with a small amount (7%) of unchanged substrate. On the other hand, the sterically hindered phenol **14** afforded only a moderate yield (47%) of the monoarylated phenol **15**, as well as traces (5%) of the diarylated product **16**. In all these reactions, a mass balance was achieved (Table 1). However, formation of cyclisation products could not be detected in any of the four cases, leading to the conclusion that an aryl radical is not found in these processes.

Table 1. *C*-Arylation reactions performed under base-catalysed conditions

Substrate[a]	Products (%)
8	**9** (85)
10	**11** (73), **10** (21)
12	**13** (91), **12** (7)
14	**15** (47), **16** (5), **14** (48)

[a] Aryllead **4** (1.1 equiv.) pyridine (3.3 equiv.), $CHCl_3$, 45 °C, 2 h, then room temp., overnight.

In the copper-catalysed *N*-arylation reactions, transmetallation between the organolead reagent and a copper species has been putatively suggested to lead to a hypervalent



Cu^{III} intermediate. In a second step, these Cu^{III} species undergo a reductive elimination to afford the modified Ullmann-condensation-type products (Scheme 2).[3,4,7c] To investigate the formation of free radicals in these reactions, the two substrates [3,4-dimethylaniline (**17**) and benzimidazole (**19**)] were treated with 1.1 equiv. of the lead reagent in the presence of a catalytic amount of copper diacetate (0.1 equiv.) in anhydrous chloroform at 45 °C (Table 2). The aniline **17** afforded the *N*-arylated compound **18** in high yield (79%); side products were not detected. Interestingly, the modified Ullmann-type arylation of benzimidazole gave the arylation product **20** in 64% yield as well as compound **21**, derived from the aryl group acetoxylation reaction, isolated in a moderate yield (24%).

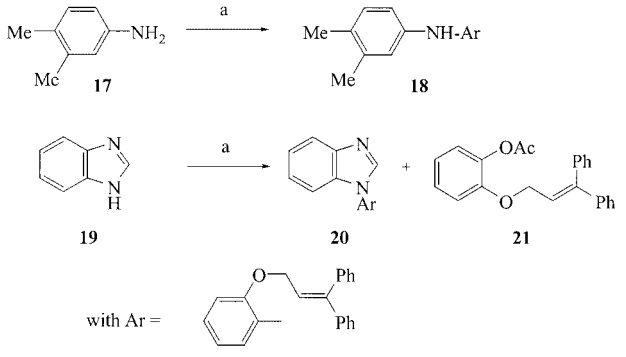


Table 2. Copper-catalysed *N*-arylation reactions

Substrate[a]	Products (%)
17	**18** (79), **17** (16)
19	**20** (64), **21** (24), **19** (23)

[a] Aryllead **4** (1.1 equiv.), $Cu(OAc)_2$ (0.11 equiv.), $CHCl_3$, 45 °C, 2 h, then room temp., overnight.

Conclusion

In conclusion, application of the new designed radical clock **4**, containing a 2-(3′,3′-diphenylprop-2′-enyloxy)-phenyl group, to the mechanistic study of the *C*- and *N*-arylation reactions mediated by aryllead triacetates did not reveal the formation of any radical adducts. This conclusion agrees with the previous studies of Morgan and Pinhey who used the less efficient 2-allyloxyphenyl trap in the *C*-arylation reactions.[13] In the copper-catalysed *N*-arylation, the present reagent, containing an internal trap, was used for the first time with organolead reagents. The intervention of transient free-radical species in the mechanism of this *N*-arylation reaction was also excluded. As unlikely as it may seem, it could, however, still be argued that, under the present sets of reaction conditions, the arylation reaction is still faster than the radical trap reaction. On the other hand, the synthesis of radical clock **4** involves a transmetallation of the arylboronic acid **3**. This boronic acid can be a useful free radical trap for mechanistic studies of different types of reactions involving arylboronic acids (Suzuki *C*-arylations[31] or Chan *O*- and *N*-arylations[32]). More generally, this new type of radical trap should be useful in mechanistic studies not only of arylation but also of various reactions thought to involve free radicals.

Experimental Section

General Remarks: Melting points were recorded with a Büchi capillary apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC 300 spectrometer. Chemical shifts (δ) are reported in ppm for a solution of the compound in $CDCl_3$ with $SiMe_4$ as internal reference. In the description of the NMR spectroscopic data of the compounds, A refers to atom A of the substrate, A′ to atom A of the aryl group derived from the aryllead reagent and A′′ and A′′′ to atom A of the respective phenyl group of the diphenylallyl group. In the case of compounds **8** and **10**, A refers to atom A of the aryl group derived from the aryllead reagent and A′ and A′′ to atom A of the respective phenyl group of the diphenylallyl group. Combustion analyses were performed at the "Laboratoire de Microanalyse de l'Université d'Aix-Marseille 3". Separations by column chromatography were performed using Merck Kieselgel 60 (70−230 mesh). All solvents were purified by standard techniques.

Synthesis of 1-Bromo-2-(3,3-diphenylprop-2-enyloxy)benzene (2): Sodium hydride (0.67 g of a 60% emulsion in oil, 16.8 mmol) was added to a cooled (between −5 and 0 °C) solution of 2-bromophenol (2.7 g, 15.8 mmol) in THF (50 mL). Then 3,3-diphenylprop-2-enyl chloride[28] (3.5 g, 15.8 mmol) and NaI (0.23 g, 1.6 mmol) were added and the mixture was refluxed for 6 h. The solvent was distilled under reduced pressure and the crude product was purified by column chromatography (CC) on silica gel (pentane/diethyl ether, 49:1) to afford **2** (5 g, 89%) as an oil. ^1H NMR: δ = 4.66 (d, J = 6.6 Hz, 2 H, OCH_2CH), 6.35 (t, J = 6.6 Hz, 1 H, OCH_2CH), 6.73 [dd, J_1 = 8.3 and J_2 = 1.4 Hz, 1 H, C(3)-H], 6.80 [dt, J_1 = 7.3 and J_2 = 1.3 Hz, 1 H, C(5)-H], 7.16−7.40 (m, 11 H, Ar-H) and 7.53 [dd, J_1 = 8.0 and J_2 = 1.5 Hz, 1 H, C(6)-H] ppm. ^{13}C NMR: δ = 67.2 (OCH_2CH), 113.8 (OCH_2CH), 141.4 ($OCH_2CH=C$), 112.4, 138.8, 145.9 and 154.9 (C-Ar, tertiary), 121.9, 123.3, 127.8

and 128.3 (C-3, C-4, C-5, C-6, interchangeable assignments), 133.4 (C-4′ and C-4′′), 127.7, 128.2, 128.3 and 129.7 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′ and C-6′′, interchangeable assignments) ppm. $C_{21}H_{17}BrO$ (365.26): calcd. C 69.05, H 4.69; found C 69.01, H 4.53.

Synthesis of 2-(3,3-Diphenylprop-2-enyloxy)phenylboronic Acid (3): *n*BuLi (4.7 mL of a 1.6 M solution in hexanes, 7.52 mmol) was added to a solution of **2** (2.5 g, 6.85 mmol) in THF (30 mL) at −78 °C under an inert gas. The solution was stirred for 10−15 min, then triisopropyl borate (1.8 mL, 7.53 mmol) was added. The mixture was stirred at −78 °C for 2 h, and then warmed to room temperature overnight. Diethyl ether (100 mL) was added and the mixture was shaken with 10% aqueous HCl (3 × 50 mL), washed with water and dried with Na_2SO_4. The solvent was distilled under reduced pressure. The crude product was stirred in pentane (30 mL) in an ice bath for 1 h. The insoluble residue was decanted, dissolved in a small volume of diethyl ether and precipitated by addition of pentane to afford the boronic acid **3** (0.8 g, 36%) as a white powder, m.p. 118 °C. ^{1}H NMR: δ = 4.69 (d, *J* = 6.8 Hz, 2 H, O*CH*$_2$CH), 6.18 (s, 2 H, BOH), 6.31 (t, *J* = 6.8 Hz, 1 H, OCH$_2$*CH*), 6.75 (d, *J* = 8.1 Hz, 1 H, 3-H), 7.01 [t, *J* = 7.4 Hz, 1 H, C(5)-H], 7.18−7.44 (m, 11 H, Ar-H) and 7.85 [dd, *J* = 7.4 and *J* = 1.9 Hz, 1 H, C(6)-H] ppm. ^{13}C NMR: δ = 66.4 (O*CH*$_2$CH), 111.3 (OCH$_2$*CH*), 121.4, 122.2, 128.0, 128.1, 132.7 and 136.9 (C-3, C-4, C-5, C-6, C-4′ and C-4′′, interchangeable assignments), 127.7, 128.3, 128.4 and 129.6 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′ and C-6′′, interchangeable assignments), 141.2 (OCH$_2$CH=*C*), 138.6 and 147.2 (C-1′ and C-1′′) and 163.6 (C-2), (C-1 could not be detected due to the expected 5 lines coupling C-B pattern) ppm. $C_{21}H_{19}BO_3$ (330.18): calcd. C 76.39, H 5.80; found. C 76.01, H 5.87.

Synthesis of 2-(3,3-Diphenylprop-2-enyloxy)phenyllead Triacetate (4): A solution of the boronic acid **3** (0.3 g, 0.91 mmol) in anhydrous chloroform (1.5 mL) was added to a mixture of $Pb(OAc)_4$ (0.42 g, 0.91 mmol) and $Hg(OAc)_2$ (0.029 g, 0.091 mmol) in chloroform (1.5 mL) at 45 °C. The mixture was stirred at 45 °C for 1.5 h, then at the room temperature overnight. The mixture was filtered through Celite, the volume of the filtrate was reduced to one third by distillation under reduced pressure and pentane was then added to induce crystallisation to afford **4** (0.34 g, 56%) as a light-yellow powder, m.p. 159.5 °C. ^{1}H NMR: δ = 2.04 (s, 9 H, CH_3), 4.69 (d, *J* = 6.8 Hz, 2 H, O*CH*$_2$CH), 6.33 (t, *J* = 6.8 Hz, 1 H, OCH$_2$*CH*), 6.85 [d, *J* = 8.0 Hz, 1 H, C(3)-H], 7.13−7.46 (m, 12 H, Ar-H) and 7.81 [d, *J* = 7.5 Hz, 1 H, C(6-H)] ppm. ^{13}C NMR: δ = 20.5 (CH_3), 67.3 (O*CH*$_2$CH), 113.5 (OCH$_2$*CH*), 122.0, 123.5, 128.0, 128.1, 131.9 and 133.0 (C-3, C-4, C-5, C-6, C-4′ and C-4′′), 127. 8, 128.3, 128.5 and 129.6 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′ and C-6′′), 138.5, 146.7, 151.1 and 156.6 (C-1, C-2, C-1′ and C-1′′), 141.1 (OCH$_2$CH=*C*) and 180.0 [*C*(O)OCH$_2$) ppm. $C_{27}H_{26}PbO_7$ (669.69): calcd. C 48.42, H 3.91; found C 48.35, H 3.88.

Synthesis of the Radical Cyclisation Product 7: A mixture of **2** (0.540 g, 1.48 mmol), tributyltin hydride (0.520 g, 1.77 mmol) and AIBN (0.024 g, 0.18 mmol) was refluxed in anhydrous benzene for 3 h. The solution was then cooled to room temperature, KF (0.3 g, 5.31 mmol) was added and the mixture was stirred vigorously for 24 h. The solution was filtered and the solvent was distilled under reduced pressure. The crude product was purified by CC (eluent: diethyl ether/pentane, 3:97) to afford the cyclisation product **7** (0.34 g, 81%) as a white powder, m.p. 150 °C. ^{1}H NMR: δ = 4.02 (d, *J* = 11.1 Hz, 1 H, Ph$_2$*CH*CHCH$_2$), 4.18−4.24 (m, 1 H, Ph$_2$CHCH*CH*$_2$), 4.32−4.41 (m, 1 H, Ph$_2$CH*CH*CH$_2$), 4.51−4.57 (m, 1 H, Ph$_2$CHCH*CH*$_2$), 6.15 [d, *J* = 7.6 Hz, 1 H, C(6)-H], 6.57 [dt, *J* = 7.6 and *J* = 0.7 Hz, 1 H, C(5)-H], 6.77 [d, *J* = 8.1 Hz, 1 H, C(3)-H], 7.06 [dt, *J* = 8.1 and *J* = 0.7 Hz, 1 H, C(4)-H] and 7.20−7.32 (m, 10 H, Ar-H) ppm. ^{13}C NMR: δ = 45.9 (Ph$_2$*CH*CHCH$_2$), 56.8 (Ph$_2$CH*CH*CH$_2$), 75.8 (Ph$_2$CHCH*CH*$_2$), 109.5, 119.8, 125.7, 126.7, 126.8, 128.4 (C-3, C-4, C-5, C-6, C-4′, C-4′′), 127.9, 128.5, 128.6 and 128.8 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′ and C-6′′), 128.9, 143.0, 143.1 and 160.3 (C-1, C-2, C-1′ and C-1′′) ppm. $C_{21}H_{18}O$ (286.37): calcd. C 88.08, H 6.34; found C 87.83, H 6.18.

Typical Procedure for the Base-Catalysed Arylation with 4. Arylation of 2-Naphthol: A mixture of the aryllead triacetate **4** (0.210 g, 0.31 mmol), 2-naphthol (0.041 g, 0.29 mmol) and pyridine (0.071 g, 0.94 mmol) in anhydrous chloroform (1.5 mL) was stirred at 45 °C for 2 h and at room temperature overnight . The solvent was distilled under reduced pressure and the residue was purified by column chromatography (CC) on silica gel (pentane/diethyl ether/EtOH, 83:15:2) to afford 1-[2-(3,3-diphenylprop-2-enyloxy)phenyl]-2-naphthol (**13**) (0.111 g, 91%) and 2-naphthol (**12**) (0.003 g, 7%).

1-[2-(3,3-Diphenylprop-2-enyloxy)phenyl]-2-naphthol (13): White powder, m.p. 68 °C. ^{1}H NMR: δ = 4.48−4.60 (m, 2 H, O*CH*$_2$CH), 5.42 (s, 1 H, OH), 6.03 (t, *J* = 6.6 Hz, 1 H, OCH$_2$*CH*), 6.90−7.43 (m, 18 H, Ar-H) and 7.80−7.85 (m, 2 H, Ar-H) ppm. ^{13}C NMR: δ = 66.8 (O*CH*$_2$CH), 114.2 (OCH$_2$*CH*), 141.3 (OCH$_2$CH=*C*), 118.1, 123.4, 129.2, 138.7, 145.8, 150.7 and 156.6 (tertiary Ar-C), 117.9, 121.8, 123.1, 123.4, 124.9, 126.2, 128.0, 129.5, 129.9 and 133.5 (C-3, C-4, C-5, C-6, C-7, C-8, C-3′, C-4′, C-5′ and C-6′), 129.6 (C-4′′ and C-4′′′), 127.6, 127.7, 128.1 and 128.2 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′) ppm. $C_{31}H_{24}O_2$ (428.52): calcd. C 86.89, H 5.65; found C 86.51, H 5.54.

Ethyl 1-[2-(3,3-Diphenylprop-2-enyloxy)phenyl]-2-oxocyclohexanecarboxylate (9): Under the same conditions, reaction of **4** with ethyl 2-oxocyclohexanecarboxylate (**8**) (0.069 g, 0.41 mmol) led to **9** (0.150 g, 85%), CC (diethyl ether/pentane, 1:4); colourless oil. ^{1}H NMR: δ = 1.18 (t, *J* = 6.4 Hz, 3 H, *CH*$_3$CH$_2$O), 1.64−1.78 (m, 2 H, CH$_2$-4), 1.84−1.95 (m, 2 H, CH$_2$-5), 2.49−2.67 (m, 4 H, CH$_2$-3 and CH$_2$-6), 4.11−4.25 (m, 2 H, CH$_3$*CH*$_2$O), 4.56−4.59 (m, 2 H, O*CH*$_2$CH), 6.24 (t, *J* = 6.6 Hz, 1 H, OCH$_2$*CH*), 6.76 [d, *J* = 8.1 Hz, 1 H, C(6′)-H], 6.95 [t, *J* = 7.8 Hz, 1 H, C(4′)-H], 7.15 [d, *J* = 7.8 Hz, 1 H, C(3)-H] and 7.20−7.40 (m, 11 H, Ar-H) ppm. ^{13}C NMR: δ = 14.0 (*CH*$_3$CH$_2$O), 22.0, 27.1, 35.2 and 40.7 (CH$_2$ cyclic), 61.3 (CH$_3$*CH*$_2$O), 66.7 (O*CH*$_2$CH), 113.0 (OCH$_2$*CH*), 128.1, 138.9, 144.9 and 156.3 (C-Ar tertiary), 120.8, 123.6, 127.4, 127.7 and 128.7 (C-3′, C-4′, C-5′, C-6′, C-4′′, C-4′′′), 127.7, 128.2, 128.3 and 129.6 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′), 141.6 (OCH$_2$CH=*C*), 171.4 (*C*O$_2$CH$_2$) and 205.9 (C-1) ppm. $C_{30}H_{30}O_4$ (454.56): calcd. C 79.27, H 6.65; found C 79.03, H 6.55.

Ethyl 2-[2-(3,3-Diphenylprop-2-enyloxy)phenyl]-2-nitropropionate (11): Under the same conditions, reaction of **4** with ethyl 2-nitropropionate (**10**) (0.050 g, 0.34 mmol) led to **11** (0.103 g, 73%) and recovered **10** (0.0105 g, 21%), CC (diethyl ether/pentane, 1:19); colourless oil. ^{1}H NMR: δ = 1.23 (t, *J* = 7.1 Hz, 3 H, *CH*$_3$CH$_2$O), 2.27 (s, 3 H, CH$_3$), 4.30 (m, *J* = 7.1 Hz, 2 H, CH$_3$*CH*$_2$O), 4.60−4.64 (m, 2 H, O*CH*$_2$CH), 6.20 (t, *J* = 6.6 Hz, 1 H, OCH$_2$*CH*), 6.79 [d, *J* = 8.1 Hz, 1 H, C(6)-H], 6.95 [t, *J* = 7.7 Hz, 1 H, C(3)-H], 7.15 [dt, J_1 = 7.7 and J_2 = 0.9 Hz, 1 H, C(4)-H] and 7.18−7.43 (m, 11 H, Ar-H) ppm. ^{13}C NMR: δ = 13.8 (*CH*$_3$CH$_2$O), 23.0 (CH$_3$), 62.9 (CH$_3$*CH*$_2$O), 66.7 (O*CH*$_2$CH), 94.3 (CH$_3$*C*NO$_2$), 113.0 (OCH$_2$*CH*), 141.3 (OCH$_2$CH=*C*), 124.6, 138.7, 145.9, 156.2 (C-Ar tertiary), 120.6, 122.7, 127.2 and 130.9 (C-3, C-4, C-5 and C-6), 127.7, 128.2, 128.4, and 129.6 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′, C-6′′) and 128.9 (C-4′ and C-4′′) ppm. $C_{26}H_{25}NO_5$

(431.48): calcd. C 72.37, H 5.84, N 3.25; found C 72.02, H 5.91, N 3.11.

Under the same conditions, reaction of **4** with 3,5-di-*tert*-butylphenol (**14**) (0.050 g, 0.54 mmol) led to **15** (0.0946 g, 47%), **16** (0.015 g, 4.7%) and recovered **14** (0.0395 g, 48%).

2-[2-(3,3-Diphenylprop-2-enyloxy)phenyl]-3,5-di-*tert*-butylphenol (15): CC (diethyl ether/pentane, 1:19); colourless powder, m.p. 51 °C. ^{1}H NMR: δ = 1.17 and 1.35 (2 s, 18 H, CMe_3), 4.40 (s, 1 H, OH), 4.59 (d, J = 6.6 Hz, 2 H, OCH_2CH), 6.11 (t, J = 6.6 Hz, 1 H, OCH_2CH), 6.78 [d, J = 7.3 Hz, 1 H, C(6′)-H], 6.89 [d, J = 1.9 Hz, 1 H, C(6)-H], 7.00 [dt, J = 7.6 and J = 1.2 Hz, 1 H, C(4′)-H] and 7.12−7.47 (m, 13 H, Ar-H) ppm. ^{13}C NMR: δ = 32.0 and 32.7 (CMe_3), 34.8 and 36.8 (CMe_3), 65.8 (OCH_2CH), 109.6 (OCH_2CH), 141.5 (OCH_2CH=C), 120.7, 126.0, 138.9, 145.3, 148.6, 151.1, 152.9 and 156.8 (C-Ar tertiary), 112.7, 116.1, 124.2, 128.3, 128.6, 128.7, 130.7 and 133.8 (C-4, C-6, C-3′, C-4′, C-5′, C-6′, C-4′′ and C-4′′′), 127.3, 128.2, 128.6 and 129.7 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′) ppm. $C_{35}H_{38}O_2$ (490.68): calcd. C 85.67, H 7.81; found C 85.49, H 7.42.

2,6-Bis-[2-(3,3-diphenylprop-2-enyloxy)phenyl]-3,5-di-*tert*-butylphenol (16): CC (diethyl ether/pentane, 1:19); colourless oil. ^{1}H NMR: δ = 1.24 (s, 18 H, CMe_3), 4.34 (s, 1 H, OH), 4.44 (d, J = 6.6 Hz, 4 H, OCH_2CH), 6.05 (t, J = 6.6 Hz, 2 H, OCH_2CH), 6.62 (d, J = 7.3 Hz, 2 H, C(6′)-H] and 6.97−7.37 (m, 27 H, Ar-H) ppm. ^{13}C NMR: δ = 32.0 (CMe_3), 36.8 (CMe_3), 65.7 (OCH_2CH), 112.8 (OCH_2CH), 141.5 (OCH_2CH=C), 121.3, 128.4, 138.9, 144.4, 147.4 and 151.1 (C-Ar tertiary), 117.0, 120.3, 125.1, 127.5, 128.8, 130.1 and 133.1 (C-4, C-3′, C-4′, C-5′, C-6′, C-4′′ and C-4′′′), 127.6, 128.1, 128.2 and 129.7 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′) ppm. $C_{56}H_{54}O_3$ (775.03): calcd. C 86.78, H 7.02; found C 86.61, H 6.88.

Typical Procedure for the Copper-Catalysed Arylation with 4. *N*-Arylation of 3,4-Dimethylaniline: A mixture of the aryllead triacetate **4** (0.400 g, 0.598 mmol), 3,4-dimethylaniline (0.066 g, 0.543 mmol) and copper diacetate (0.012 g, 0.060 mmol) in anhydrous chloroform (2 mL) was stirred at 45 °C for 2 h and at room temperature overnight. The solvent was distilled under reduced pressure and the residue was purified by CC (diethyl ether/pentane, 3:97) to afford **18** (0.170 g, 79%) as a light yellow oil. ^{1}H NMR: δ = 2.22 and 2.23 (2 s, 6 H, CH_3), 4.65 (d, J = 6.6 Hz, 2 H, OCH_2CH), 6.09 (s, 1 H, NH), 6.35 (t, J = 6.6 Hz, 1 H, OCH_2CH), 6.70−6.74 (m, 2 H, Ar-H), 6.80−6.85 (m, 1 H, Ar-H), 6.90−6.98 (m, 2 H, Ar-H), 7.05 (d, J = 7.9 Hz, 1 H, Ar-H) and 7.20−7.40 (m, 11 H, Ar-H) ppm. ^{13}C NMR: δ = 19.0 and 19.9 (CH_3), 66.6 (OCH_2CH), 112.1 (OCH_2CH), 141.5 (OCH_2CH=C), 113.8, 117.1, 118.9, 121.1, 121.2, 123.8 and 130.2 (C-2, C-5, C-6, C-3′, C-4′, C-5′and C-6′), 127.8 (C-4′′ and C-4′′′), 127.7, 128.2, 128.4 and 129.6 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′), 129.8, 134.3, 137.4, 138.9, 140.2, 145.7 and 146.7 (C-Ar tertiary) ppm. $C_{29}H_{27}NO$ (405.53): calcd. C 85.89, H 6.71, N 3.45; found C 85.71, H 6.59, N 3.41.

Under the same conditions, benzimidazole **19** (0.065 g, 0.55 mmol) gave **20** (0.140 g, 64%), **21** (0.050 g, 24%) and recovered **19** (0.021 g, 33%).

***N*-[2-(3,3-Diphenylprop-2-enyloxy)phenyl]benzimidazole (20):** CC (diethyl ether/EtOH/pentane, 2:1:17), colourless powder, m.p. 135 °C. ^{1}H NMR: δ = 4.59 (d, J = 6.6 Hz, 2 H, OCH_2CH), 6.07 (t, J = 6.6 Hz, 1 H, OCH_2CH), 7.01 [d, J = 8.3 Hz, 1 H, C(6′)-H], 7.08−7.38 (m, 16 H, Ar-H), 7.88 [dd, J_1 = 7.6 and J_2 = 1.5 Hz, 1 H, C(3′)-H] and 8.17 (s, 1 H, H-2) ppm. ^{13}C NMR: δ = 66.7 (OCH_2CH), 110.9 (OCH_2CH), 141.0 (OCH_2CH=C), 114.1, 119.9, 121.2, 122.5, 122.6, 123.3, 125.0, 127.8 and 129.5 (C-4, C-5, C-6, C-7, C-3′, C-4′, C-5′, C-6′, C-4′′ and C-4′′′), 127.5, 128.1, 128.3 and 129.5 (C-2′′, C-3′′, C-5′′, C-6′′, C-2′′′, C-3′′′, C-5′′′ and C-6′′′), 134.2 138.6, 142.5, 143.7, 146.1 and 152.7 (C-Ar tertiary) and 174.5 (C-2) ppm. $C_{28}H_{22}N_2O$ (402.49): calcd. C 83.56, H 5.51, N 6.96; found C 83.42, H 5.50, N 6.96.

[2-(3,3-Diphenylprop-2-enyloxy)phenyl] Acetate (21): CC (diethyl ether/EtOH/pentane, 2:1:17), colourless oil. ^{1}H NMR: δ = 2.32 (s, 3 H, $COOCH_3$), 4.61 (d, J = 6.6 Hz, 2 H, OCH_2CH), 6.27 (t, J = 6.6 Hz, 1 H, OCH_2CH), 6.86 [dd, J_1 = 8.2 and J_2 = 1.5, 1 H, C(3)-H], 6.97 [dd, J_1 = 7.9 and J_2 = 1.6 Hz, 1 H, C(6)-H], 7.21−7.26 [m, 2 H, C(4)-H and C(5)-H] and 7.27−7.40 (m, 10 H, Ar-H) ppm. ^{13}C NMR: δ = 20.7 ($COOCH_3$), 66.7 (OCH_2CH), 114.0 (OCH_2CH), 141.5 (OCH_2CH=C), 120.9, 121.6, 122.8, 123.5, 127.77 and 127.81 (C-3, C-4, C-5, C-6, C-4′ and C-4′′), 127.7, 128.2, 128.3 and 129.7 (C-2′, C-3′, C-5′, C-6′, C-2′′, C-3′′, C-5′′ and C-6′′), 138.8, 140.2, 145.8 and 150.1 (C-1, C-2, C-1′ and C-1′′) and 163.0 (COMe) ppm. $C_{23}H_{20}O_3$ (344.40): calcd. C 80.21, H 5.85; found C 80.35, H 6.04.

Acknowledgments

A. Yu. F. thanks INTAS for the award of a YSF-2002-122 fellowship, the Russian Foundation for Basic Research (RFBR grant no. 02-0333021) and the St. Petersburg Competitive Centre for Fundamental Research (grant no. PD 02-1.3-443) for financial support.

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Received December 16, 2003

