# $I_2$-Catalyzed Divergent Regioselective Addition of Methoxybenzenes with Ethenylbenzenes under Microwave Irradiation

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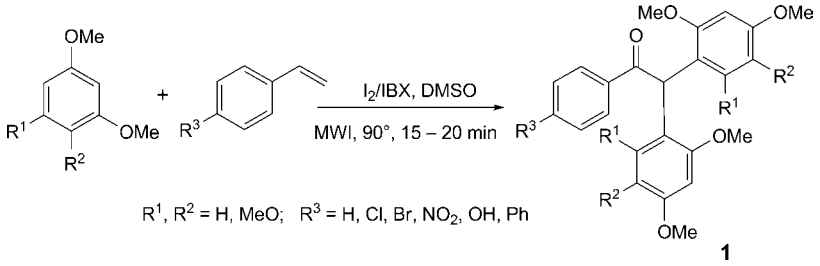
A highly efficient synthesis of 1,2,2-triarylethanones has been developed from simple and commercially available electron-rich arenes and styrenes (ethenylbenzenes).

**Introduction.** – The synthesis of diarylmethanes have attracted considerable attention due to their importance as the core structure in a multitude of biologically active compounds and pharmaceuticals such as anastrozol, avrainvilleol, beclobrate, letrozole, piritrexim, trimethoprim, and papaverine [1]. Diarylmethanes are key intermediates in the synthesis of such natural products and biologically relevant small molecules. In spite of their diverse medicinal features including antitubercular, anticancer, and antiproliferative activities, an efficient and general protocol for the synthesis of diarylmethanes is still highly desirable [2]. Consequently, several elegant methods have been reported for the synthesis of diarylmethane derivatives, which were mainly focused on *Friedel–Crafts* alkylation of electron-rich arenes with carbonyl compounds and their imines using a *Lewis* or a protic acid [3]. Various Pd-catalyzed coupling methods have also been developed for the synthesis of diarylmethanes from aryl methyl ketones [4]. *Myrboh* and co-workers also proposed a regioselective diarylation of aromatic ketones in the presence of $SeO_2$ and $BF_3 \cdot Et_2O$ [5]. Recently, *A.-X. Wu* and co-workers reported excellent methods for the oxidation aryl methyl ketones or terminal alkenyl-arenes to $\alpha$-oxoaldehydes and subsequent reactions with various nucleophiles [6]. On the basis of these reports, we found that a wide range of terminal ethenyl-arenes could easily be converted to $\alpha$-iodoacetophenone in the presence of $I_2$/2-iodoxybenzoic acid (IBX) in DMSO [7] and $\alpha$-iodoacetophenone was easily converted to $\alpha$-oxoaldehyde in DMSO *via Kornblum* oxidation [8].

In view of this and in continuation of our work on microwave-promoted reactions [9], we herein report on a protocol under microwave irradiation (MWI) for the diarylation of aromatic arenes with electron-rich arenes such as 1,3-dimethoxybenzene 1,3,5-trimethoxybenzene, and 1,2,4-trimethoxybenzene to afford 1,2,2-triarylethanones **1** (*Scheme 1*).

**Results and Discussion.** – The initial reaction of styrene with 1,3-dimethoxybenzene was examined under MWI with different oxidants and $I_2$ in DMSO. Surprisingly, all of

Scheme 1. *Synthesis of 1,2,2-Triarylethanones from Methoxybenzenes and Styrenes*




the oxidants including oxone, $PhI(OAc)_2$, DMP, TBHP, TEMPO, DDQ, and *m*CPBA were ineffective. Gratifyingly, the reaction proceeded in good yield by using 2-iodoxybenzoic acid (IBX) as an oxidant and $I_2$ as an additive in DMSO under MWI. Different temperatures were also tested to improve the yield, and 90° was found to be the most optimal temperature for the domino reaction. Finally, from the above results, the optimal reaction conditions for the domino reaction turned out to be styrene (ethenylbenzene; $R^3 = H$; 0.5 mmol) and 1,3-dimethoxybenzene ($R^1 = R^2 = H$; 1.2 mmol), at 90° with $I_2$/IBX (0.8 mmol/0.6 mmol) in DMSO (3 ml) under MWI.

With the optimized reaction conditions in hand, the scope of the reaction was investigated (*Table*). Both electron-donating and electron-withdrawing groups ($R^3$; see *Scheme 1*) attached to etheyl-arenes were all suitable for this protocol. Ethenyl-arenes with different substituents, such as Br, Cl, $NO_2$, and OH could all provide the corresponding products with yields in the range of 50–75% (*i.e.*, **1b**, **1c**, **1d**, **1h**, **1i**, **1j**, **1k**, and **1l**). Simple styrenes also gave good yields with electron-rich arenes (*Table*; **1a**, **1f**, and **1j**). In addition, 4-phenylstyrene also reacted with 1,3-dimethoxybenzene ($R^1 = R^2 = H$) to give the desired products **1e** in 65% yield. Then, we turned our attention to the methoxybenzenes, and found all the electron-rich arenes gave good yields (*i.e.*, **1a**–**1l**). There had been no steric influence of different electron-rich arenes on the reaction. Next, an attempt was undertaken to examine the reactivity of 1,2-, 1,4-dimethoxybenzene and catechols. They, however, failed to give the desired products. All the compounds were characterized by their IR, $^1$H- and $^{13}$C-NMR, and MS data.

A possible reaction mechanism is shown in *Scheme 2*. Initially, the substrate styrene is converted into phenacyl iodide, **A**, by $I_2$/IBX. Subsequently, phenylglyoxal is formed *via Kornblum* oxidation in the presence of DMSO. The $\alpha$-keto aldehyde **B** is attacked by 1,3-dimethoxybenzene in the presence of formed HI, which then undergoes a *Friedel–Crafts*-like alkylation with the diarylmethanes (*Scheme 2*).

**Conclusion.** – We have developed a highly efficient, microwave-assisted synthesis of diarylmethanes by domino oxidative *Friedel–Crafts* reaction of styrenes with methoxybenzenes.

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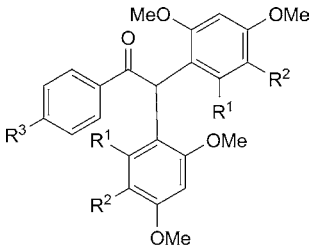
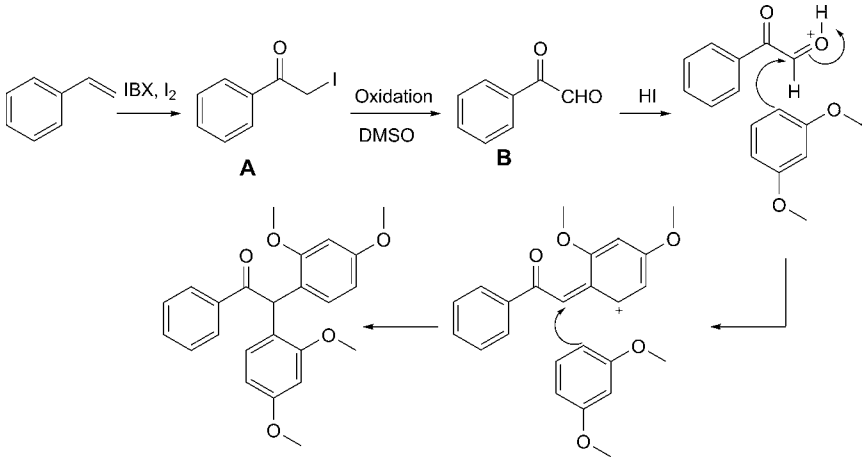
Table. *Synthesis of Diarylmethanes from Methoxybenzenes and Styrenes with $I_2$/IBX in DMSO under Microwave Irradiation*




**1**

| *Entry* | $R^1$ | $R^2$ | $R^3$ | Product | Yield [%] |
|---|---|---|---|---|---|
| *1* | H | H | H | **1a** | 65 |
| *2* | H | H | Br | **1b** | 75 |
| *3* | H | H | $NO_2$ | **1c** | 50 |
| *4* | H | H | OH | **1d** | 60 |
| *5* | H | H | Ph | **1e** | 65 |
| *6* | MeO | H | H | **1f** | 65 |
| *7* | MeO | H | Br | **1g** | 70 |
| *8* | MeO | H | $NO_2$ | **1h** | 50 |
| *9* | MeO | H | OH | **1i** | 55 |
| *10* | H | MeO | H | **1j** | 65 |
| *11* | H | MeO | Cl | **1k** | 70 |
| *12* | H | MeO | Br | **1l** | 70 |

Scheme 2. *A Plausible Mechanism of the Reaction Leading to 1,2,2-Triarylethanones*



## Experimental Part

*General*. The chemicals, $I_2$, styrenes (*Aldrich*), IBX (prepared), and all the solvents were obtained from local suppliers. Column chromatography (CC): silica gel ($SiO_2$; 60–120 mesh). M.p.: *Mettler-Temp* apparatus; uncorrected. IR Spectra: *PerkinElmer-1600* FT-IR spectrometer; in KBr; $\tilde{\nu}$ in $cm^{-1}$. $^1$H- and $^{13}$C-NMR spectra: *Bruker-Avance-300* spectrometer; in $CDCl_3$; $\delta$ in ppm rel. to $Me_4Si$ as internal standard; *J* in Hz. ESI-MS: *VG Micromass 7070 H* spectrometer with a direct inlet system; in *m*/*z* (rel. %), and *Agilent 6510 Q-TOF* LC/MS instrument. Microwave irradiation (MWI): *CEM™ Discover Microwave* instrument.

*General Procedure:* Freshly prepared IBX (0.6 mmol) and $I_2$ (0.8 mmol) were added to a well-stirred soln. of styrene (0.5 mmol) and 1,3-dimethoxybenzene (1.2 mmol) in anh. DMSO (3 ml). The mixture was stirred for 5–10 min at r.t., then placed in the cavity of a MW reactor, and irradiated for 15–20 min, at 90° (temp. monitored by built-in infrared sensor) with a power of 150 W. After cooling to r.t. by an air-flow, the tube was removed from the rotor. The mixture was diluted with $H_2O$ and extracted with AcOEt. The combined extracts were then dried ($Na_2SO_4$), and, after removal of the solvent, the mixture was purified by CC ($SiO_2$, 60–120 mesh; hexane/AcOEt 4:1) to give the pure product **1a**.

*2,2-Bis(2,4-dimethoxyphenyl)-1-phenylethanone* (**1a**). White solid. M.p. 145–146°. IR: 2959, 2836, 1680, 1610, 1212, 1038. $^1$H-NMR: 7.99 (*d*, *J* = 7.9, 2 H); 7.46 (*t*, *J* = 7.4, 1 H); 7.37 (*t*, *J* = 7.4, 2 H); 6.87 (*d*, *J* = 8.3, 2 H); 6.49 (*d*, *J* = 2.4, 2 H); 6.48 (*s*, 1 H); 6.41 (*d*, *J* = 2.4, 1 H); 6.39 (*d*, *J* = 2.4, 1 H); 3.78 (*s*, 6 H); 3.75 (*s*, 6 H). $^{13}$C-NMR: 199.6; 159.9; 157.6; 137.0; 132.2; 130.2; 128.4; 128.2; 119.4; 103.8; 98.7; 55.5; 55.2; 45.0. ESI-MS: 393 ($[M+H]^+$).

*1-(4-Bromophenyl)-2,2-bis(2,4-dimethoxyphenyl)ethanone* (**1b**). Pale-orange color solid. M.p. 110–112°. IR: 3155, 2961, 2835, 1720, 1610, 1587, 1503, 1466, 1271, 1210, 1135, 810. $^1$H-NMR: 7.86 (*d*, *J* = 8.5, 2 H); 7.50 (*d*, *J* = 8.5, 2 H); 7.50 (*d*, *J* = 8.5, 2 H); 6.85 (*d*, *J* = 8.5, 2 H); 6.49 (*d*, *J* = 2.4, 2 H); 6.41 (*d*, *J* = 2.4, 2 H); 6.40 (*s*, 1 H); 3.78 (*s*, 6 H); 3.75 (*s*, 6 H). $^{13}$C-NMR: 198.4; 160.0; 157.5; 135.8; 131.5; 130.2; 129.9; 127.2; 119.0; 104.0; 98.7; 55.4; 55.2; 45.0. ESI-MS: 471 ($[M+H]^+$).

*2,2-Bis(2,4-dimethoxyphenyl)-1-(4-nitrophenyl)ethanone* (**1c**). Pale-yellow solid. M.p. 179–180°. IR: 2930, 2833, 1694, 1592, 1530, 1505, 1344, 1210, 834. $^1$H-NMR: 8.22 (*d*, *J* = 9.0, 2 H); 8.12 (*d*, *J* = 9.0, 2 H); 6.86 (*d*, *J* = 8.5, 2 H); 6.50 (*d*, *J* = 2.4, 2 H); 6.43 (*d*, *J* = 2.4, 1 H); 6.42 (*s*, 1 H); 6.41 (*d*, *J* = 2.4, 1 H); 3.78 (*s*, 6 H); 3.76 (*s*, 6 H). $^{13}$C-NMR: 198.0; 159.5; 157.7; 153.1; 145.8; 130.1; 129.5; 123.2; 122.9; 103.5; 98.5; 55.3; 55.0; 42.3. ESI-MS: 438 ($[M+H]^+$).

*2,2-Bis(2,4-dimethoxyphenyl)-1-(4-hydroxyphenyl)ethanone* (**1d**). Ash-colored solid. M.p. 147–148°. IR: 3269, 2930, 2827, 1640, 1599, 1472, 1222, 1121, 810. $^1$H-NMR: 7.93 (*d*, *J* = 8.8, 2 H); 6.87 (*d*, *J* = 8.5, 2 H); 6.79 (*d*, *J* = 8.6, 2 H); 6.48 (*d*, *J* = 2.4, 2 H); 6.42 (*s*, 1 H); 6.40 (*d*, *J* = 2.4, 1 H); 6.38 (*d*, *J* = 2.4, 1 H); 6.32 (*s*, 1 H); 3.77 (*s*, 6 H); 3.74 (*s*, 6 H); $^{13}$C-NMR: 198.1; 159.0; 157.9; 153.3; 136.5; 132.2; 130.1; 125.6; 114.7; 103.4; 98.7; 55.6; 55.2; 41.2. ESI-MS: 409 ($[M+H]^+$).

*1-(1,1′-Biphenyl-4-yl)-2,2-bis(2,4-dimethoxyphenyl)ethanone* (**1e**). Pale yellow solid. M.p. 140–142°. IR: 3034, 3100, 2924, 1697, 1602, 1487, 1198, 1125, 824. $^1$H-NMR: 8.68 (*d*, *J* = 8.4, 2 H); 7.56–7.61 (*m*, 4 H); 7.40–7.46 (*m*, 2 H); 6.90 (*d*, *J* = 8.3, 2 H); 6.52 (*s*, 1 H); 6.50 (*d*, *J* = 2.2, 2 H); 6.43 (*d*, *J* = 2.4, 1 H); 6.40 (*d*, *J* = 2.2, 1 H); 3.78 (*s*, 6 H); 3.77 (*s*, 6 H). $^{13}$C-NMR: 199.0; 159.9; 157.6; 144.7; 139.9; 135.7; 130.2; 129.6; 128.9; 128.8; 128.7; 127.8; 127.1; 127.0; 126.8; 119.4; 103.9; 98.7; 55.4; 55.1; 45.0. ESI-MS: 469 ($[M+H]^+$).

*1-Phenyl-2,2-bis(2,4,6-trimethoxyphenyl)ethanone* (**1f**). Sandy-brown colored solid. M.p. 75–77°. IR: 2996, 2936, 1693, 1593, 1461, 1225, 1205, 1120, 813. $^1$H-NMR: 7.86 (*d*, *J* = 8.5, 2 H); 7.38 (*t*, *J* = 7.4, 2 H); 7.30 (*d*, *J* = 7.8, 2 H); 6.29 (*s*, 1 H); 6.07 (*s*, 4 H); 3.75 (*s*, 6 H); 3.55 (*s*, 12 H). $^{13}$C-NMR: 198.0; 159.5; 158.9; 137.7; 131.1; 127.7; 127.4; 110.7; 91.2; 55.8; 55.0; 41.4. ESI-MS: 453 ($[M+H]^+$).

*1-(4-Bromophenyl)-2,2-bis(2,4,6-trimethoxyphenyl)ethanone* (**1g**). Light-brown solid. M.p. 111–113°. IR: 3055, 2972, 2824, 1730, 1605, 1499, 1309, 1133, 823. $^1$H-NMR: 7.71 (*d*, *J* = 8.4, 2 H); 7.42 (*d*, *J* = 7.4, 2 H); 6.22 (*s*, 1 H); 6.07 (*s*, 4 H); 3.77 (*s*, 6 H); 3.56 (*s*, 12 H). $^{13}$C-NMR: 197.1; 159.7; 158.8; 136.6; 131.7; 131.0; 130.9; 129.0; 125.8; 110.2; 91.1; 55.8; 55.0; 41.5. ESI-MS: 531 ($[M+H]^+$).

*1-(4-Nitrophenyl)-2,2-bis(2,4,6-trimethoxyphenyl)ethanone* (**1h**). Burly wood-colored solid. M.p. 153–155°. IR: 2929, 2833, 1694, 1612, 1532, 1345, 1211, 834. $^1$H-NMR: 8.15 (*d*, *J* = 8.8, 2 H); 7.98 (*d*, *J* =

8.6, 2 H); 6.28 (*s*, 1 H); 6.07 (*s*, 4 H); 3.77 (*s*, 6 H); 3.58 (*s*, 12 H). $^{13}$C-NMR: 197.9; 160.2; 157.5; 130.2; 129.2; 128.2; 123.4; 118.2; 104.0; 98.7; 55.7; 55.4; 55.2; 45.6. ESI-MS: 498 ($[M+H]^+$).

*1-(4-Hydroxyphenyl)-2,2-bis(2,4,6-trimethoxyphenyl)ethanone* (**1i**). Burly wood-colored solid. M.p. 210–211°. IR: 3259, 2934, 2839, 1669, 1603, 1458, 1225, 1115, 813. $^1$H-NMR: 7.75 (*d*, $J=8.8$, 2 H); 6.68 (*s*, 2 H); 6.25 (*s*, 1 H); 6.06 (*s*, 4 H); 3.76 (*s*, 6 H); 3.54 (*s*, 12 H). $^{13}$C-NMR: 198.2; 159.6; 159.0; 132.1; 129.8; 116.3; 115.5; 114.7; 114.6; 91.3; 55.8; 55.6; 55.1; 42.3. ESI-MS: 469 ($[M+H]^+$).

*1-Phenyl-2,2-bis(2,4,5-trimethoxyphenyl)ethanone* (**1j**). Pale-orange solid. M.p. 128–129°. IR: 2934, 2832, 1680, 1517, 1205, 1033. $^1$H-NMR: 8.02 (*d*, $J=7.1$, 2 H); 7.48 (*d*, $J=7.1$, 1 H); 7.39 (*d*, $J=7.1$, 2 H); 6.59 (*d*, $J=10$, 4 H); 6.54 (*s*, 1 H); 3.89 (*s*, 6 H); 3.75 (*s*, 6 H); 3.75 (*s*, 6 H). $^{13}$C-NMR: 199.3; 150.7; 148.4; 142.2; 136.6; 132.0; 127.9; 117.9; 113.5; 97.3; 56.1; 55.9; 55.5; 44.9. ESI-MS: 453 ($[M+H]^+$).

*1-(4-Chlorophenyl)-2,2-bis(2,4,5-trimethoxyphenyl)ethanone* (**1k**). Brick-red solid. M.p. 129–130°. IR: 3032, 2839, 1670, 1601, 1452, 1235, 1123, 817. $^1$H-NMR: 7.96 (*d*, $J=8.5$, 2 H); 7.36 (*d*, $J=8.5$, 2 H); 6.57 (*s*, 4 H); 6.46 (*s*, 1 H); 3.88 (*s*, 6 H); 3.75 (*s*, 6 H); 3.69 (*s*, 6 H). $^{13}$C-NMR: 198.5; 151.1; 148.8; 142.9; 138.7; 135.3; 129.8; 128.6; 118.0; 113.8; 97.7; 56.5; 56.4; 56.0; 45.3. ESI-MS: 487 ($[M+H]^+$).

*1-(4-Bromophenyl)-2,2-bis(2,4,5-trimethoxyphenyl)ethanone* (**1l**). White solid. M.p. 112–114°. IR: 3055, 2945, 2830, 1745, 1609, 1588, 1500, 1210, 1135, 810. $^1$H-NMR: 7.88(*d*, $J=8.6$, 2 H); 7.52 (*d*, $J=8.6$, 2 H); 6.57 (*d*, $J=8.2$, 2 H); 6.45 (*s*, 1 H); 3.88 (*s*, 6 H); 3.74 (*s*, 6 H); 3.68 (*s*, 6 H). $^{13}$C-NMR: 198.6; 151.0; 148.8; 142.9; 135.7; 131.5; 129.9; 127.4; 117.9; 113.8; 97.7; 56.5; 56.4; 56.0; 45.2. ESI-MS: 531 ($[M+H]^+$).

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