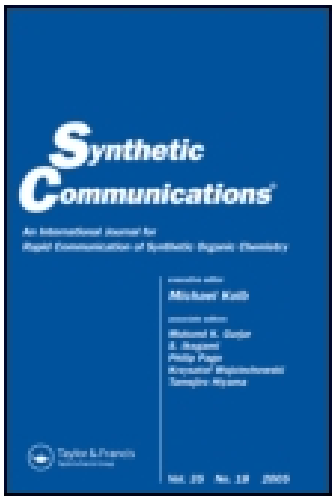

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A Simple Preparation of Diarylmethanes by Oxidative Friedel-Crafts Reaction of Methyl-Substituted Benzenes with *o*-Chloranil

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ABSTRACT

The reaction of *o*-chloranil with some methyl-substituted benzenes at elevated temperature was found to be a simple and selective route toward diarylmethanes without need for prior preparation of benzyl halides.

Diarylmethanes have been widely utilized as raw materials for fragrance,[1] polyurethane resins,[2–4] and medicines.[5–9] A promising synthetic pathway toward diphenylmethane derivatives is the Friedel-Crafts type alkylation of aromatic compounds with benzyl halides.[10] Previously, we eventually found that 1,3-benzodixoles were

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formed by the reaction of *o*-chloranil and methyl-substituted benzenes in refluxing tetrachloroethylene albeit in low yields.[11] When we investigated a similar reaction with the methyl-substituted benzenes as the solvents, diarylmethanes were obtained in acceptable yields. Thus, we wish to describe here the synthesis of diarylmethanes without need for prior preparation of benzyl halides.

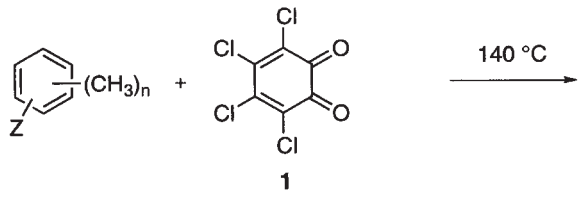
A solution of *o*-chloranil in *p*-xylene as the solvent was refluxed for 24 h to give 2,4′,5-trimethyldiphenylmethane (**2**) in 71% yield. The formation of tetrachlorocatechol was also detected by GLC analysis. Similarly, the reactions of mesitylene and durene with *o*-chloranil at 140°C provided 2,3′,4,5′,6-pentamethyldiphenylmethane (**3**) and 2,2′,3,4′,5,5′,6-heptamethyldiphenylmethane (**4**) in 94 and 89% yields, respectively. Treatment of *p*-methylanisole with *o*-chloranil afforded 2,4′-dimethoxy-5-methyldiphenylmethane (**5**) in 74% yield, accompanied by the formation of 2,2′,4″-trimethoxy-4,4′-dimethyltriphenylmethane (**6**) in 24% yield. In contrast, the reaction of toluene with *o*-chloranil under reflux resulted in the formation of a 1:1 mixture of 4-methyldiphenylmethane (**7**) and 2-methyldiphenylmethane (**8**) only in 9% yield, along with the formation of 4,5,6,7-tetrachloro-2-phenyl-1,3-benzodioxole (**9**) in 30% yield. The attempted reactions with *o*-xylene, *N*,*N*-dimethyl-*p*-toluidine, *p*-bromotoluene, and 4-methylbenzonitrile resulted in the formation of a complex mixture.

The formation of diarylmethanes would be explained by the intermediacy of benzyl cations and the subsequent Friedel-Crafts type alkylation. Previously, triarylmethanes were described to give triarylmethyl cations on treatment with quinones such as DDQ.[12] *p*-Chloranil was also reported to abstract a hydride from *p*-xylene under the dehydrogenation conditions of cholesterin.[13] However, the use of DDQ or *p*-chloranil instead of *o*-chloranil for the present trans-

Table 1. Products and yields of the oxidative Friedel-Crafts reaction of methyl-substituted benzenes.

Substrate	Products yield[a] (%)
p-Xylene	**2** (71%)
Mesitylene	**3** (94%)
Durene	**4** (89%)
p-Methylanisole	**5** (74%), **6** (24%)
Toluene	**7** + **8** (1:1, 9%), **9** (30%)

[a]Yields are based on *o*-chloranil (**1**). The yields of **6** and **9** are calculated based on the assumption that two molar equivalents of **1** are required.



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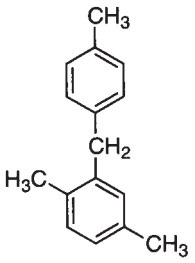

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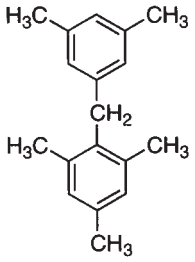

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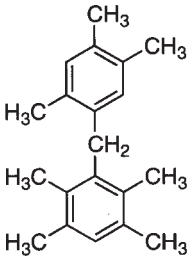

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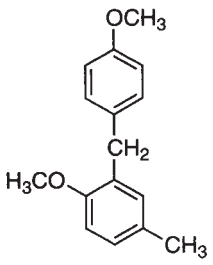

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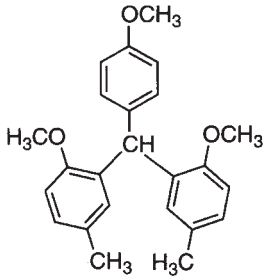

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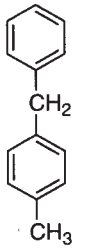

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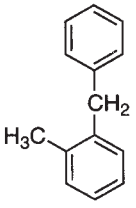

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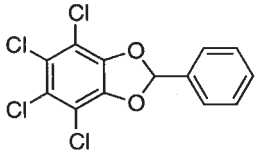

9

formation resulted in the formation of an inseparable mixture, and the use of *o*-chloranil is requisite. Oxidative Friedel-Crafts reactions of methyl-substituted benzenes were widely investigated with Fe(III),[14–17] Cu(II),[18] Pd(II),[19] Mn(III) and Mn(IV),[20,21] and NO_2^+ speices.[22] Unfortunately, these reactions seem not always useful for the synthesis of diarylmethanes due to the formation of by-products such as biaryls and the requirement of acidic conditions. Thus, the present method would provide one of simple and selective routes to some diarylmethanes under neutral conditions, without need for prior preparation of the corresponding benzyl halides.

EXPERIMENTAL

General

All mps were determined with a Yanagimoto hot-stage apparatus. Infrared spectra were obtained with a JEOL Diamond-20 spectrometer. NMR spectra were recorded with a JEOL JNM-LA400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) spectrometer using TMS as internal standard. Assignments of the ^{1}H and ^{13}C signals are based on DEPT, H-H COSY, and C-H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron impact mode (70 eV). Elemental analyses were performed with a Perkin–Elmer Model 240 apparatus. The GLC analyses were carried out on a Shimadzu GC-12A (FID) instrument equipped with a 10%-SE30 column at 180°C column temperature using nitrogen as the carrier gas. Solvents were dried and purified by standards methods. Yields are based on the isolated products with sufficient purity.

General procedure. A mixture of *o*-chloranil (**1**) (246 mg, 1 mmol) and a methyl-substituted benzene (5 cm^3) was heated at 140°C (bath temperature) for 24 h. The excess aromatic compound was recovered by vacuum distillation, and the residue was separated by column chromatography (silica gel, hexane-ethyl acetate 10/1) to give a diphenylmethane derivative and other products if available. The remaining parts of the fractions collected after chromatography was subjected to GLC analyses, which detected the presence of tetrachlorocatechol.

2,4′,5-Trimethyldiphenylmethane[15,23,24] (2). 71%; a colorless oil; bp 130–135°C/2 Torr (bath temp, cold-finger trap distillation). IR (neat) 3045, 3018, 3001, 2972, 2943, 2920, 2861, 1514, 1502, 1444, 1379, 1117, 1038, 1022 cm^{-1}. ^{1}H NMR ($CDCl_3$) $\delta = 2.17$ (3H, s, CH_3), 2.26 (3H, s, CH_3), 2.28 (3H, s, CH_3), 3.88 (2H, s, CH_2) 6.90–7.05 (7H, m). ^{13}C NMR

($CDCl_3$) $\delta = 19.2$ (CH_3), 21.0 (CH_3), 39.0 (CH_2), 127.0, 128.6, 129.0, 130.1, 130.7, 133.4, 135.2, 135.3, 137.4, 138.9, 1C (CH_3) missing. MS *m*/*z* (rel. intensity) 210 (M^+, 70), 195 (M-CH_3, 100), 118 (63), 91 ($PhCH_2$, 13). Found: C, 91.63; H, 8.69%. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63%.

2,3′,4,5′,6-Pentamethyldiphenylmethane (3). 94%; colorless plates (from chloroform–methanol 1/2). M.p. 68–69°C (Lit.[25] m.p. 67°C). IR (KBr) 3012, 2964, 2935, 2916, 2858, 2729, 1603, 1579, 1508, 1485, 1454, 1442, 1421, 1373, 1036, 1014 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.20$ (6H, s, CH_3), 2.22 (6H, s, CH_3), 2.29 (3H, s, CH_3), 3.94 (2H, s, CH_2), 6.62 (2H, s), 6.78 (1 H, s), 6.88 (2H, s). ^{13}C NMR ($CDCl_3$) $\delta = 20.2$ (CH_3), 20.9 (CH_3), 21.3 (CH_3), 34.6 (CH_2), 125.7, 127.4, 128.8, 133.9, 135.5, 137.0, 137.8, 140.0. MS *m*/*z* (rel. intensity) 238 (M^+, 100), 223 (M-CH_3, 93), 208 (M-2Me, 31), 132 (M-$Me_2C_6H_4$, 74). Found: C, 90.65; H, 9.30%. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30%.

2,2′,3,4′,5,5′,6-Heptamethyldiphenylmethane (4). 89%; colorless plates (from chloroform–methanol 1/1). M.p. 153–154°C (Lit.[16] m.p. 154–155°C, Lit[22] m.p. 144.6–145.2°C). IR (KBr) 2997, 2960, 2939, 2918, 2862, 2729, 2360, 2341, 1500, 1473, 1460, 1381, 1373, 1020, 1001 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.04$ (3H, s, CH_3), 2.06 (6H, s, CH_3), 2.18 (3H, s, CH_3), 2.26 (6H, s, CH_3), 2.36 (3H, s, CH_3), 3.87 (2H, s, CH_2), 6.28 (1H, s), 6.93 (1H, s), 6.96 (1H, s). ^{13}C NMR ($CDCl_3$) $\delta = 15.7$ (CH_3), 19.1 (CH_3), 19.2 (CH_3), 19.3 (CH_3), 20.6 (CH_3), 32.7 (CH_2), 127.9, 129.8, 131.2, 133.2, 133.5, 133.8, 135.3, 136.7, 2C missing. MS *m*/*z* (rel. intensity) 266 (M^+, 53), 251 (M-CH_3, 32), 146 (M-$Me_3C_6H_3$, 100). Found: C, 90.30; H, 9.93%. Calcd. for $C_{20}H_{26}$: C, 90.16; H, 9.84%.

2 4′-Dimethoy-5-methyldiphenylmethane[20,21] (5). 74%; colorless needles (from methanol). M.p. 72–73°C (Lit.[26] m.p. 74°C). IR (KBr) 3032, 2997, 2958, 2854, 1610, 1583, 1512, 1466, 1441, 1429, 1300, 1292, 1277, 1248, 1227, 1176, 1120, 1032 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.22$ (3H, s, CH_3), 3.76 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 3.87 (2H, s, CH_2), 6.74 (1H, d, $J = 8$ Hz, 3-H), 6.80 (2H, d, J = 9 Hz, 3′-H and 5′-H), 6.86 (1H, d, $J = 2$ Hz, 6-H), 6.96 (1 H, dd, $J = 8$ Hz and 2 Hz, 3-H), 7.12 (2H, d, $J = 9$ Hz, 2′-H and 6′-H). ^{13}C NMR ($CDCl_3$) $\delta = 20.5$ (CH_3), 34.9 (CH_2), 55.2 (OCH_3), 55.5 (OCH_3), 110.4, 113.6, 127.5, 129.6, 129.8, 130.9, 133.2, 155.2, 157.7, 1C missing. MS *m*/*z* (rel. intensity) 242 (M^+, 100), 227 (M-CH_3, 49), 211 (M-OCH_3, 59), 121 ($OCH_3C_6H_4CH_2$, 50). Found: C, 79.40; H, 7.33%. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

2,2′,4″-Trimethoxy-4,4′-dimethyltriphenylmethane (6). 24%; colorless needles (from methanol). M.p. 154–155.0°C. IR (KBr) 2999, 2956, 2941, 2908, 2837, 1608, 1558, 1541, 1510, 1496, 1458, 1436, 1321, 1290, 1238,

1178, 1119, 1107, 1032 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 2.18$ (6H, s, CH_3), 3.66 (6H, s, OCH_3), 3.77 (3H, s, OCH_3), 6.09 (1H, s, CH), 6.60 (2H, d, $J = 2$ Hz), 6.75 (2H, d, $J = 8$ Hz), 6.78 (2H, d, $J = 8$ Hz), 6.95–6.98 (4H, m). ^{13}C NMR ($CDCl_3$) $\delta = 20.8$ (CH_3), 42.2 (CH), 55.1 (OCH_3), 56.0 (OCH_3), 111.0, 113.3, 127.4, 129.2, 130.3, 130.7, 132.9, 136.1, 155.3, 157.5. MS *m/z* (rel. intensity) 362 (M^+, 88), 347 (M-CH_3, 45), 331 (M-OCH_3, 100), 241 (M-$CH_3C_6H_3OCH_3$, 14), 121 ($CH_3C_6H_3OCH_3$, 62). Found: C, 79.48; H, 7.02%. Calcd. For $C_{24}H_{26}O_3$: C, 79.53; H, 7.23%.

A 1:1 mixture of 4-methyldiphenylmethane (7) and 2-methyldiphenylmethane[18] (8). 9%; b.p. 108–115°C/2 Torr (bath temp., cold-finger trap distillation). IR (neat) 3060, 3026, 2918, 1601, 1514, 1495, 1462, 1452, 1107, 1074, 1030 cm^{-1}. ^1H NMR (CDCl3) $\delta = 2.23$ (1.5H, s, CH_3), 2.30 (1.5H, s, CH_3), 3.93 (1H, s, CH_2), 3.98 (1H, s, CH_2), 7.08–7.28 (9H, m). ^{13}C NMR ($CDCl_3$) $\delta = 19.7$ (CH_3), 21.0 (CH_3), 39.4 (CH_2), 41.5 (CH_2), 125.9, 126.0, 126.5, 128.3, 128.4, 128.7, 128.8, 128.9, 129.1, 130.0, 130.3, 135.5, 136.6, 138.1, 138.9, 140.4, 141.4, 1C missing. MS *m/z* (rel. intensity) 182 (M^+, 78), 167 (M-CH_3, 100), 165 (53), 104 (23). Found: C, 92.14; H, 7.72%. Calcd. for $C_{14}H_{14}$: C, 92.26; H, 7.74%.

4,5,6,7-Tetrachloro-2-phenyl-1,3-benzodioxole (9). 30%; m.p. and mixed m.p. 113.5–115°C (Lit.[11] m.p. 115°C).

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