Superacid-Catalyzed Reaction of Substituted Benzaldehydes with Benzene

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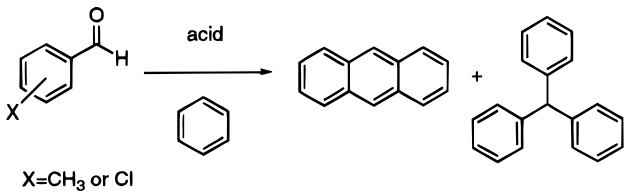
Benzaldehydes bearing an electron-withdrawing group reacted with 2 equiv of benzene in the presence of a superacid, trifluoromethanesulfonic acid, to give substituted triphenylmethane in good yields. On the other hand, benzaldehydes bearing an electron-donating or a neutral group reacted under the similar conditions to give *unsubstituted* diphenylmethane and triphenylmethanol, together with substituted benzene. We propose a new mechanism of this reaction, which involves transalkylation as the key step.

Since the discovery of the reaction in 1886,[1] the Friedel−Crafts-type reaction of benzaldehydes with benzene or various aromatic compounds has been studied by several research groups.[2−5] From the mechanistic point of view, interpretation of the results is not simple. Except for nitro-substituted benzaldehydes, substituted benzaldehydes react with an excess of benzene to give products which *do not* contain the aromatic ring of the aldehyde (Scheme 1).[3−5] Furthermore, unsubstituted benzaldehyde reacts with an excess of substituted benzenes to give phenylated products and substituted anthracene which contain only the aromatic ring of the substituted benzene, not that of benzaldehyde.[3−6] Anthracene formation is more pronounced when the concentration of the reactants is high, which usually makes this reaction messy.

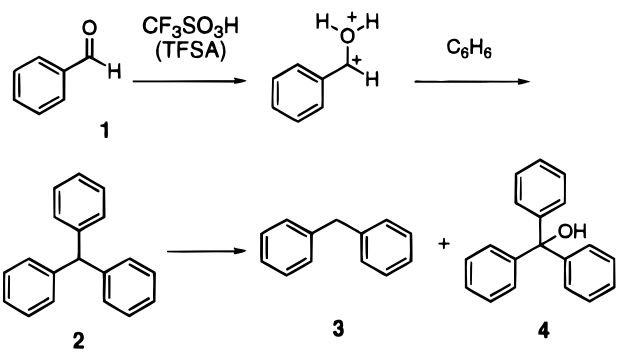
The results show that the [aromatic-C]−[formyl-C] bond is broken during the reaction. Hey has studied this reaction in detail.[3] He reported that carbon monoxide was formed in the reaction and concluded that carbon monoxide liberated from benzaldehyde is the key intermediate, which is protonated to react with benzene. However, the yield in the reaction of benzaldehyde with benzene is generally higher than that in the reaction of carbon monoxide with benzene, and the mechanism of the reaction of substituted benzaldehydes with benzene remains to be clearly established.

Olah *et al.*[7] and we[8] have recently studied the reaction of benzaldehyde with benzene in detail and concluded that diprotonated benzaldehyde is the key intermediate in the reaction. We have now investigated the reaction of substituted benzaldehydes with benzene in the presence of a protic superacid, trifluoromethanesulfonic acid (TFSA), in order to understand the mechanism of the reaction.

Scheme 1



Scheme 2



Results

We have already shown[8] that, in the presence of TFSA, benzaldehyde (**1**) reacted with a large excess of benzene (500 equiv) to give triphenylmethane (**2**) as the initial intermediate, followed by disproportionation to afford a 1:1 mixture of diphenylmethane (**3**) and triphenylmethanol (**4**) as the final products (Scheme 2).

We applied the optimized conditions (50 °C, 19 h) to the reaction of substituted benzaldehydes. 4-Fluorobenzaldehyde (**5**, $\sigma^+ = -0.07$[9]) reacted with benzene to give diphenylmethane (**3**, 36%) and triphenylmethanol (**4**, 29%) (Scheme 3). Fluorobenzene could be detected by GC in the reaction mixture. The rate of the reaction was not significantly affected by the 4-fluoro group. On the other hand, unsubstituted benzaldehyde, fluorotriphenylmethane, and fluorotriphenylmethanol were not detected, even when the reaction mixture of **5** was worked up at an earlier time.

Biphenyl-4-carboxyaldehyde (**6**, $\sigma_{Ph}^+ = -0.18$[9]) reacted more slowly than benzaldehyde. When the reaction was conducted at 70 °C for 16 h, some starting material still remained, and again **3** and **4** were obtained as major

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(1) Griepentrog, H. *Ber. Dtsh. Chem. Ges.* **1886**, *19*, 1876−1877. For review, see *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1964: vol. II, Chapter XIX (Hofmann, J. E., Schriesheim, A.) pp 616−621.

(2) Schaarschmidt, A.; Hermann, L.; Szemzo, B. *Ber. Dtsh. Chem. Ges.* **1925**, *58*, 1914−1916.

(3) Hey, D. H. *J. Chem. Soc.* **1935**, 72−75.

(4) Ellison, H.; Hey, D. H. *J. Chem. Soc.* **1938**, 1847−1853.

(5) Ungnade, H. E.; Crandall, E. W. *J. Am. Chem. Soc.* **1949**, *71*, 2209−2210.

(6) Ungnade, H. E.; Kline, E. F.; Crandall, E. W. *J. Am. Chem. Soc.* **1953**, *75*, 3333−3336.

(7) Olah, G. A.; Rasul, G.; York, C.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 11211−11214.

(8) Saito, S.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 11081−11084.

(9) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

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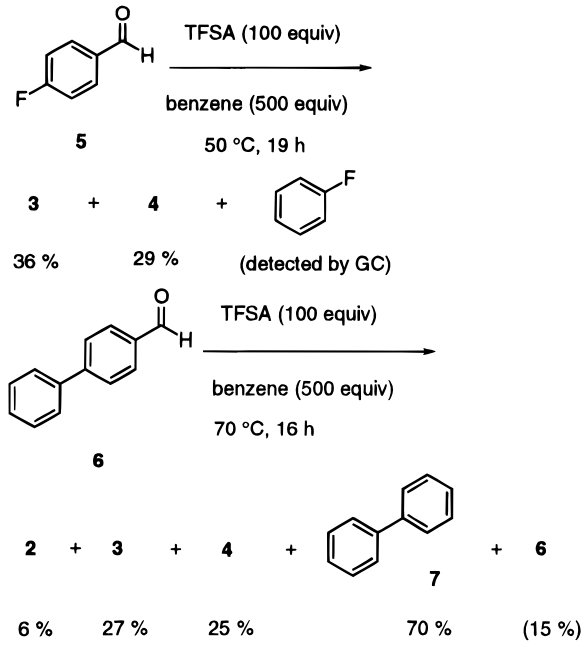
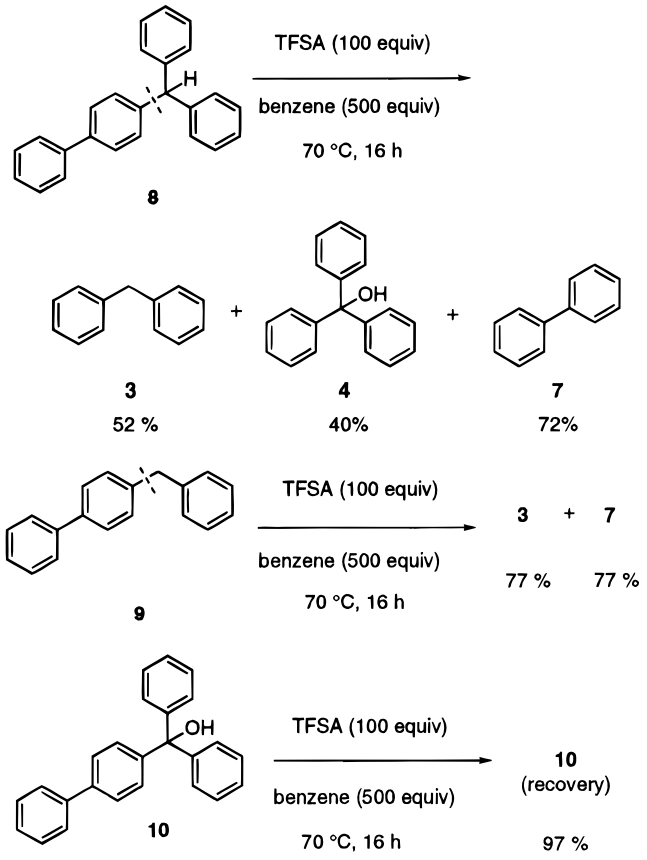
Scheme 3



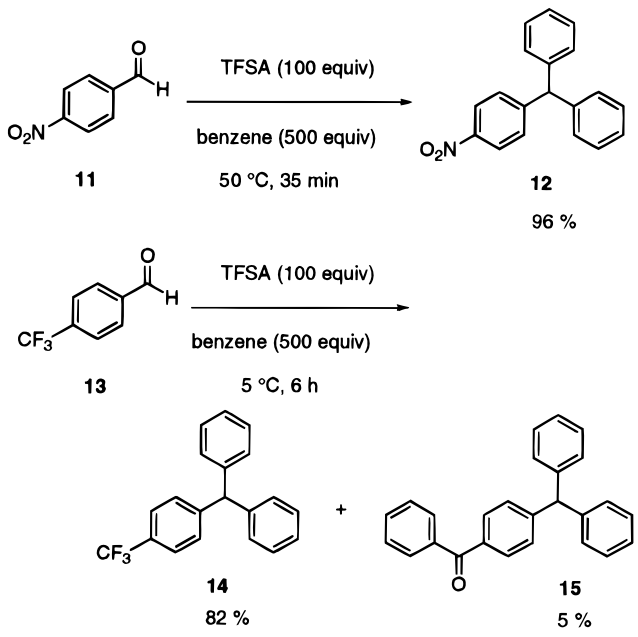
Scheme 4



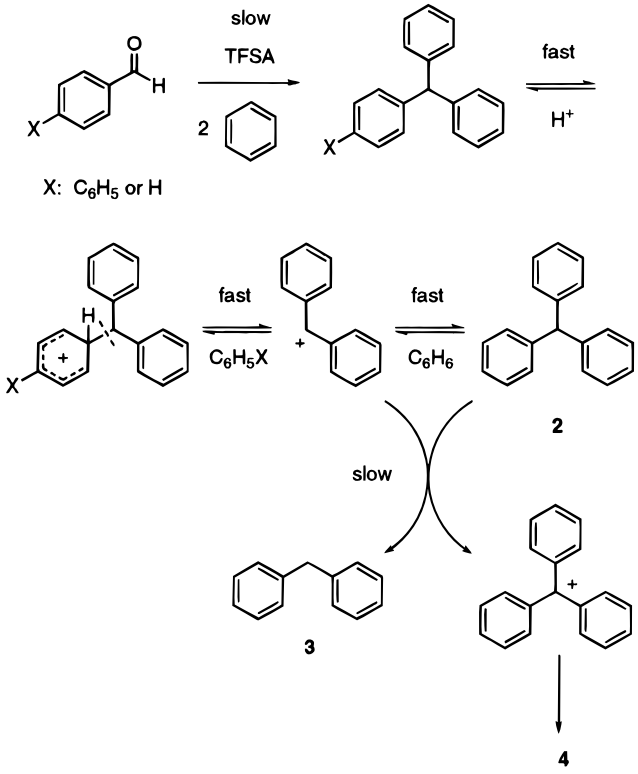
products, together with a small amount of **2**. Biphenyl (**7**) was formed in high yield (Scheme 3).[10]

It is noteworthy that the reaction of 4-(diphenylmethyl)biphenyl (**8**), which would be the expected primary product according to Scheme 2, gave a high yield of biphenyl **7**, together with diphenylmethane (**3**) and triphenylmethanol (**4**). Triphenylmethane (**2**) was detected as an intermediate in the reaction. 4-Benzylbiphenyl (**9**) also reacted to give diphenylmethane **3** and biphenyl **7** in high yield. Biphenyldiphenylmethanol (**10**) did not react with benzene (Scheme 4).

Scheme 5



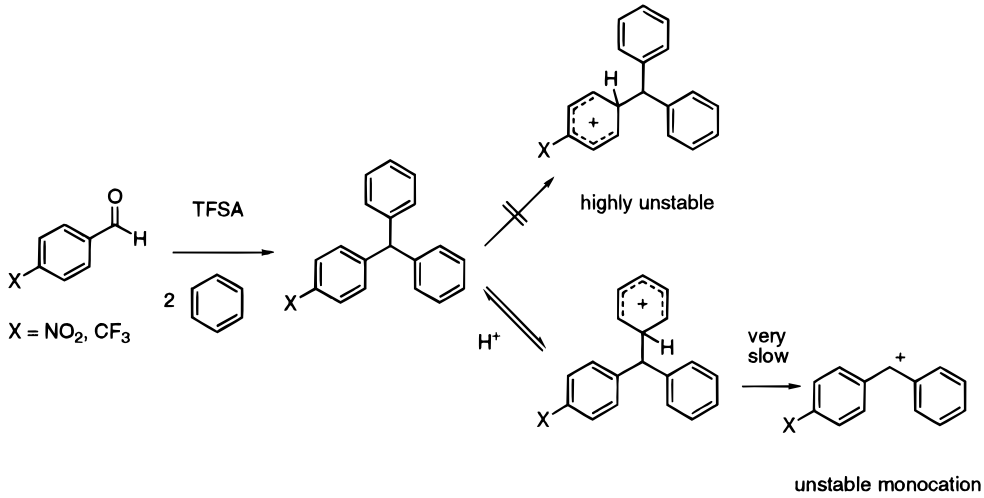
Scheme 6



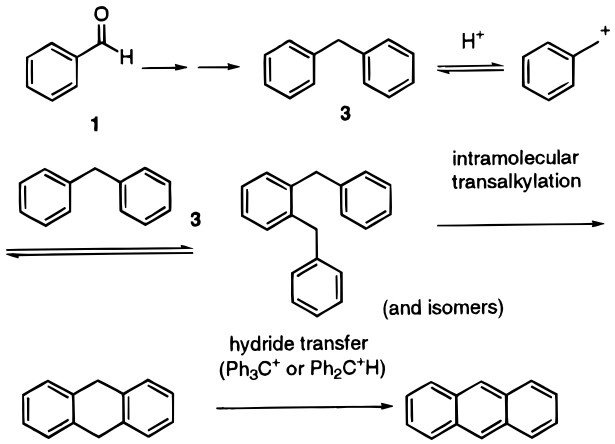
The reaction of benzaldehydes with an electron-withdrawing group was much simpler than the reaction of other benzaldehydes. 4-Nitrobenzaldehyde (**11**) reacted quickly to give 4-nitrotriphenylmethane (**12**) in high yield, while triphenylmethane (**2**), diphenylmethane (**3**), and triphenylmethanol (**4**) were not detected. 4-(Trifluoromethyl)benzaldehyde (**13**) also reacted to give 4-(trifluoromethyl)triphenylmethane (**14**), together with

(10) Since 1 mol of **6** reacted with benzene to give 1 mol of **7** and a total of 1 mol of **3** plus **4** (0.5 mol each), the total yield would theoretically be 200%. The yields of the following reactions were also calculated similarly.

Scheme 7



Scheme 8



a small amount of 4-benzoyltriphenylmethane (**15**) (Scheme 5).

Discussion

The formation of fluorobenzene and biphenyl (**7**) in the reaction of 4-fluorobenzaldehyde (**5**) and biphenyl-4-carboxyaldehyde (**6**), respectively, means that the [aromatic-C]−[formyl-C] bond is broken during the reaction of the benzaldehyde substituted with an electron-donating or a neutral group. We may account for these results in terms of two possible mechanisms: transformylation of the starting aldehyde, or transalkylation (or transdiphenylmethylation) of substituted triphenylmethane, diphenylmethane, and/or triphenylmethanol. Hey proposed that transformylation took place, with carbon monoxide as the intermediate.[3] The elimination of the formyl group as a formyl cation may also take place.[11,12] In the reaction of fluorobenzaldehyde **5**, however, we could not detect benzaldehyde (**1**), the product which would be formed by transformylation of **5** in TFSA−benzene solution: if formed, **1** should have been detected, because the reaction of **1** is as slow as that of **5**. Furthermore, we have already demonstrated[8] that no deformylated or isomerized compound was detected when 2-fluoro- or 4-fluorobenzaldehyde (**5**) was heated in TFSA. There is no evidence that the transformylation of benzaldehydes occurred in this system.

On the other hand, transalkylation of the intermediates (Scheme 4) proceeded smoothly under these reaction conditions. 4-(Diphenylmethyl)biphenyl (**8**) and 4-benzylbiphenyl (**9**) underwent transalkylation (transdiphenylmethylation or transbenzylation, respectively) in TFSA−benzene solution, while biphenyldiphenylmethanol (**10**) was not converted to triphenylmethanol (**4**). Transalkylation is likely to occur under highly acidic conditions.[13] Therefore, the formation of diphenylmethane (**3**) and triphenylmethanol (**4**) in the reaction of substituted benzaldehydes can be explained in terms of transalkylation of the substituted triphenylmethanes (Scheme 6). The protonation of the substituted triphenylmethane took place at the *ipso* position of the substituted benzene, followed by the removal of the substituted benzene to give a diphenylmethyl cation. This would recombine with benzene to give unsubstituted triphenylmethane (**2**).

Transalkylation should be much faster than hydride transfer of substituted triphenylmethanes, since no substituted triphenylmethanol was obtained from the substituted triphenylmethane. The formation of diphenylmethane (**3**) and biphenyl (**7**) in the reaction of 4-benzylbiphenyl (**9**) could be explained similarly; a benzyl cation is formed by the protonation of 4-benzylbiphenyl (**9**) at the *ipso* position, followed by recombination with benzene to give unsubstituted diphenylmethane (**3**) and substituted benzene **7**.

The benzaldehydes with an electron-withdrawing group reacted more quickly with benzene to give the substituted triphenylmethanes; diphenylmethane (**3**) or biphenyl (**4**) was not detected.[14] No redox reaction or transalkylation was observed, probably because an electron-withdrawing group retarded the protonation of the triphenylmethane derivatives. The elimination of benzene from 4-nitro- or

(11) Transacetylation of acetylmesitylene has been reported. See, Keumi, T.; Morita, T.; Shimada, T.; Teshima, N.; Kitajima, H.; Prakash, G. K. S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 847−852.

(12) The reversibility of Friedel−Crafts acylation has been reported by Agranat *et al*. See, Agranat, I.; Bentor, Y.; Shih, Y.-S. *J. Am. Chem. Soc.* **1977**, *99*, 7068−7070. Agranat, I.; Shih, Y.-S.; Bentor, Y. *J. Am. Chem. Soc.* **1974**, *96*, 1259−1260. Agranat, I.; Avnir, D. *J. Chem. Soc., Chem. Commun.* **1973**, 362−363.

(13) For recent examples, see Kim, E. K.; Lee, K. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1756−1770. Xiong, Y.; Rodewald, P. G.; Chang, C. D. *J. Am. Chem. Soc.* **1994**, *116*, 9427−9431.

(14) The importance of the use of the superacid catalyst TFSA was also demonstrated in the reactions of substituted benzaldehydes with benzene. The rate of the reaction decreased in the presence of less acidic catalysts such as 5−10% (w/w) TFSA-90−95% trifluoroacetic acid, which is acidic enough to monoprotonate the aldehydes. Though monoprotonated aldehydes may react slowly with benzene, the reactivity is greatly enhanced in the presence of TFSA. See also refs 7 and 8.

4-(trifluoromethyl)triphenylmethane may be slower (Scheme 7).[15] The facile formation of these triphenylmethanes from nitro- and (trifluoromethyl)benzaldehyde can be reasonably interpreted in terms of the participation of protonated benzaldehyde, which is highly reactive.

Though we could not directly study the mechanism of the formation of anthracene (Scheme 1) at high concentration of benzaldehyde in benzene,[8] our results provide some basis for speculation. The formation of diphenylmethane (**3**) and biphenyl (**7**) in the reaction of 4-benzylbiphenyl (**9**) could be reasonably interpreted in terms of the formation of benzyl cation and its reaction with benzene. When the concentration of substrate is relatively high, the benzyl cation may react with the diphenylmethane formed to give 1,2-dibenzylbenzene, which again eliminates benzene and undergoes intramolecular Friedel−Crafts reaction to give dihydroanthracene. Hydride transfer would afford the final product, anthracene (Scheme 8).

Conclusion

We propose a mechanism for the reaction of substituted benzaldehyde with benzene, which can explain the puzzling results in previously reported reactions. Transformylation or formation of carbon monoxide is not a likely process. The key step is transalkylation after the formation of a substituted triphenylmethane as the intermediate.

Experimental Section

General Methods. The instrumentation used for this study was described previously.[8]

Materials. Trifluoromethanesulfonic acid (TFSA) was purchased from Central Glass Co. (Japan) and was purified as reported.[16] Trifluoroacetic acid (TFA) was also purified as reported.[16] 4-Fluorobenzaldehyde (**5**) (bp 75 °C/18 mmHg) and 4-(trifluoromethyl)benzaldehyde (**13**) (bp 75−76 °C/16 mmHg) were purified by distillation and stored in glass ampules under Ar. 4-(Phenylmethyl)-1,1′-biphenyl (**9**) (mp 84−85 °C) was purified by recrystallization from ethanol. 4-Nitrobenzaldehyde (**11**) (mp 105−106 °C) was purified by recrystallization from water.

Reaction of 4-Fluorobenzaldehyde (5) with Benzene in the Presence of TFSA. (a) Longer Reaction Time (50 °C, 19 h). TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **5** (124 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous yellow solution was heated to 50 °C and stirred vigorously for 19 h under Ar. The solution was added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a red oily solid. The residue was purified by column chromatography (hexane → hexane:AcOEt = 10:1) to give 64 mg (0.36 mmol, 36%) of **3** as a colorless oil and 75 mg (0.29 mmol, 29%) of **4** as a pale yellow powder.

In another run, fluorobenzene was detected in the reaction mixture by gas chromatography (column, Shimadzu PEG 20 M 25%, 4 m; column temp 60 °C).

(b) Shorter Reaction Time (50 °C, 5 h). TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **5** (124 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous yellow solution was heated to 50 °C and stirred vigorously for 5 h under Ar. The solution was added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a brown oily solid. The residue was purified by repeated column chromatography (hexane and/or hexane:AcOEt = 10:1) to give 6 mg (0.02 mmol, 2%) of **2** as a colorless solid, 13 mg (0.08 mmol, 8%) of **3** as a colorless oil, and 26 mg (0.11 mmol, 11%) of **4** as a colorless solid. The fluorobenzaldehyde fraction (69 mg) was also obtained as a pale brown oil which contained only **5** (0.55 mmol, 55%), but no benzaldehyde (examined by NMR).

Reaction of 1,1′-Biphenyl-4-carboxyaldehyde (6) with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **6** (182 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous yellow solution was heated to 70 °C and stirred vigorously for 16 h under Ar. The solution was added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a brown semisolid. The residue was purified by repeated column chromatography (hexane and/or hexane:AcOEt = 10:1) to give 14 mg (0.06 mmol, 6%) of **2** as a colorless solid, 45 mg (0.27 mmol, 27%) of **3** as a colorless oil, 65 mg (0.25 mmol, 25%) of **4** as a pale brown powder, 27 mg (0.15 mmol, 15%) of **6** as a brown solid, and 107 mg (0.70 mmol, 70%) of **7** as a colorless solid. The NMR spectra and TLC behavior of **2**−**4**, **6**, and **7** were identical with those of authentic samples.

Synthesis of α,α-Diphenyl-1,1′-biphenyl-4-methanol (10). To a suspension of Mg (0.75 g, 31 mmol) in dry ether (10 mL) was added a solution of 4-bromo-1,1′-biphenyl (6.20 g, 27 mmol) in dry ether (40 mL) under Ar, followed by the addition of a small amount of I_2. The solution was heated to reflux for 3 h (red-brown suspension). To the suspension was added a solution of benzophenone (3.64 g, 20 mmol) in dry ether (40 mL) over 5 min at room temperature. After 15 min, the solution was added slowly to ice−water (100 mL), followed by the addition of 100 mL of 2 N aqueous HCl. The solution was extracted with 500 mL of ethyl acetate. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a yellow oil. The oil was purified by column chromatography (hexane:AcOEt = 10:1) to give 4.71 g (14 mmol, 52%) of **10** as a pale yellow amorphous solid. The product was recrystallized from MeOH.

Data for 10: mp 134−135 °C, pale yellow cubes (recrystallized from MeOH) (lit.[17] 136−137 °C); ^{1}H NMR ($CDCl_3$) δ 7.59 (d, 2 H, 7.3 Hz), 7.54 (d, 2 H, 8.4 Hz), 7.43 (t, 2 H, 7.7 Hz), 7.3−7.4 (m, 13 H), 2.83 (s, 1 H). Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.50; H, 6.04.

Synthesis of 4-(Diphenylmethyl)-1,1′-biphenyl (8).[18] A mixture of **10** (1.34 g, 4 mmol) and $NaBH_4$ (powder, 1.52 g, 40 mmol) was added in portions over 5 min to TFA (50 mL) at 0 °C under a stream of Ar (red solution). The solution was stirred vigorously. An additional 6 mL of TFA was added to complete the addition, and 40 min later, the solution was evaporated. To the residue was added 100 mL of water, and the solution was extracted with 300 mL of hexane. The organic layer was separated, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated to give **8** (1.25 g, 98%) as a pale yellow solid.

Data for 8: mp 112−113 °C ("melted" once at 102−103 °C), pale yellow needles (recrystallized from hexane) (lit.[19] 112−113 °C); ^{1}H NMR ($CDCl_3$) δ 7.58 (d, 2 H, 8.4 Hz), 7.51 (d, 2 H, 8.4 Hz), 7.43 (t, 2 H, 7.7 Hz), 7.3−7.4 (m, 5 H), 7.1−7.3 (m, 7 H), 5.59 (s, 1 H). Anal. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29. Found: C, 93.76; H, 6.21.

(15) The formation of a small amount of **15** in the reaction of 4-(trifluoromethyl)benzaldehyde (**13**) with benzene could be explained by the solvolytic transformation of **14** to 4-(diphenylmethyl)benzenecarboxylic acid or its equivalent, followed by reaction with benzene. See also, Saito, S.; Sato, Y.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1994**, *116*, 2312−2317.

(16) Saito, S.; Saito, S.; Ohwada, T.; Shudo, K. *Chem. Pharm. Bull.* **1991**, *39(10)*, 2718−2720.

(17) Lichtin, N. N.; Glazer, H. *J. Am. Chem. Soc.* **1951**, *73*, 5537−5541.

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(19) Schlenk, W.; Weickel, T.; Herzenstein, A. *Justus Liebig Ann. Chem.* **1910**, *372*, 1−20.

Reaction of 8 with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **8** (320 mg, 1 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous red solution was stirred vigorously at 50 °C for 19 h under Ar and then added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography (hexane → hexane: AcOEt = 10:1) to give 88 mg (0.52 mmol, 52%) of **3** as a colorless oil, 104 mg (0.40 mmol, 40%) of **4** as a colorless powder, and 111 mg (0.72 mmol, 72%) of **7** as a colorless powder. The formation of **2** as an intermediate was confirmed by GC analysis (column, Shimadzu OV-17 3%, 2 m, 250 °C) of the reaction mixture at a shorter reaction time (0.5 h).

Reaction of 4-(phenylmethyl)-1,1′-biphenyl (9) with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **9** (244 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous brown solution was heated to 70 °C and stirred vigorously for 16 h under Ar and then added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a yellow semisolid. The residue was purified by column chromatography (hexane) to give 119 mg (0.77 mmol, 77%) of **7** as a colorless powder and 129 mg (0.77 mmol, 77%) of **3** as a colorless oil.

Reaction of 10 with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **10** (336 mg, 1 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous red solution was stirred vigorously at 70 °C for 16 h under Ar, and then the deep red solution was added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography (hexane: AcOEt = 10:1) to give 327 mg (0.97 mmol, 97%) of **10** as a yellow amorphous solid.

Reaction of 4-Nitrobenzaldehyde (11) with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **11** (150 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at room temperature. The heterogeneous red solution was heated to 50 °C and stirred vigorously for 35 min under Ar and then added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a pale yellow solid. The residue was purified by column chromatography (hexane: AcOEt = 10:1) to give 279 mg (0.96 mmol, 96%) of 1-(diphenylmethyl)-4-nitrobenzene (**12**) as a pale yellow solid. This was further purified by recrystallization from ethanol.

Data for 12: mp 95−96 °C (lit.[5] mp 90−91 °C), pale yellow plates (recrystallized from EtOH); ^{1}H NMR δ 8.14 (d, 2 H, 8.8 Hz), 7.2−7.4 (m, 8 H), 7.09 (d, 4 H, 7.3 Hz), 5.64 (s, 1 H). Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.60; H, 5.17; N, 5.01.

Reaction of 4-(Trifluoromethyl)benzaldehyde (13) with Benzene in the Presence of TFSA. TFSA (8.8 mL, 100 mmol) was added slowly to a solution of **13** (174 mg, 1.0 mmol) in dry benzene (39 g, 500 mmol) at 5 °C. The heterogeneous yellow solution was stirred vigorously under Ar at 5 °C for 6 h, and then added slowly to 200 mL of ice−water and extracted with 200 mL of CH_2Cl_2. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to give a colorless oil. The residue was purified by column chromatography (hexane → hexane: AcOEt = 10:1) to give 257 mg (0.82 mmol, 82%) of 1-(diphenylmethyl)-4-(trifluoromethyl)-benzene (**14**) as a colorless oil and 18 mg (0.05 mmol, 5%) of [4-(diphenylmethyl)phenyl]phenylmethanone (**15**) as a colorless powder.

Data for 14: colorless oil (molecular distillation, 60 °C/4 mmHg); ^{1}H NMR δ 8.14 (d, 2 H, 8.8 Hz), 7.2−7.4 (m, 8 H), 7.09 (d, 4 H, 7.3 Hz), 5.64 (s, 1 H). MS (EI) *m/e* 312 (M^+). Anal. Calcd for $C_{20}H_{15}F_3$: C, 76.91; H, 4.84. Found: C, 76.74; H, 4.86.

Data for 15:[20] colorless powder; ^{1}H NMR δ 7.80 (d, 2H, 7.0 Hz), 7.74 (d, 2 H, 8.4 Hz), 7.57 (t, 1 H, 7.5 Hz), 7.46 (t, 2 H, 8.2 Hz), 7.31 (t, 4 H, 7.3 Hz). 7.2−7.3 (m, 4 H), 7.13 (d, 4 H, 7.0 Hz), 5.63 (s, 1 H).

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