Superacid-Catalyzed Reductive Friedel−Crafts Reaction of Arenes Using Arenecarbaldehyde Acetals

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Reaction of 2-aryl-1,3-dioxane with arenes in the presence of a catalytic amount of trifluoromethanesulfonic acid gave the corresponding diarylmethanes in good to excellent yields. The acid-catalyzed Friedel−Crafts benzylation of arenes could altenatively be carried out using arenecarbaldehyde and 1,3-propanediol. The reaction was assumed to proceed through a redox process involving hydride shift from the cyclic acetal moiety to the benzylic carbon. The hydride shift was confirmed by the reaction with 5-ethyl-2-phenyl-4,4,6,6-tetradeuterio-1,3-dioxane, wherein more than 90% deuterium was incorporated into the benzylic carbon of the diphenylmethane. Diphenylmethyl ether $Ph_2CHOCH_2CH_2CH_2OH$ also reacted with benzene to afford diphenylmethane under the same reaction conditions, suggesting that the ether should be the plausible intermediate that underwent the hydride shift.

Introduction

It has been reported that the Friedel−Crafts (FC) reaction of arenecarbaldehydes with arenes under highly acidic conditions gives a complex mixture of products like triarylmethane, triarylmethanol, diarylmethane, and anthracene derivatives.[1] The mechanism of this reaction has recently been studied independently by Shudo[2] and Olah,[3] and the product distribution was found to depend on the reaction conditions: triphenylmethane was exclusively produced when a large excess amount of trifluoromethanesulfonic acid (TFSA)[4] (100 equiv to benzaldehyde) was employed as the acid catalyst.[3] However, this type of FC reaction has eluded synthetic interest because of the need for a large excess amount of TFSA and the production of a complex mixture of products.

To the best of our knowledge, the synthetically useful FC reaction using an acetal as an electrophile has never been reported except for the gallium(II) dichloride-promoted reactions to give diarylmethane derivatives.[5] During the study of the activation of acetals by lanthanide(III) triflate,[6] we have coincidentally found that TFSA also effectively catalyzed the reductive FC reaction of arenecarbaldehyde cyclic acetals with arenes to produce diarylmethanes as the sole products. We report here the details of the acid-catalyzed reductive FC reaction using an acetal as the electrophile. We also discuss the mechanism of the reaction.

Results and Discussion

Reaction of Benzaldehyde Acetals with Benzene in the Presence of TFSA. When a solution of 2-phenyl-1,3-dioxane in benzene was heated to reflux for 10 h in the presence of a catalytic amount of TFSA (5 mol % to the acetal), diphenylmethane was isolated in good yields (Scheme 1, R = H, n = 1).[7] It is worth noting that the benzylation reaction took place with a redox process, and no triphenylmethane, triphenylmethanol, or anthracene was produced in sharp contrast to the FC reaction of benzaldehyde with benzene. Lewis acids like $AlCl_3$, $TiCl_4$, $ZnCl_2$, and $BF_3{\cdot}Et_2O$ were totally inactive except for $Sc(OTf)_3$[8] and $SnCl_4$. The use of such Brønsted acids as CF_3COOH and H_2SO_4 resulted in the production of a trace amount of diphenylmethane. We applied the above reaction conditions to 2-phenyl-1,3-dioxolane, 2-phenyl-1,3-dioxepane, and 2-phenyl-4,6-dimethyl-1,3-dioxane. The results are summarized in Table 1. 2-Phenyl-4,6-dimethyl-1,3-dioxane similarly reacted with benzene to give diphenylmethane in 51% yield (Table 1, run 2), but the reaction with 4,4,6,6-tetramethyl-1,3-dioxane (Table 1, run 3) did not produce diphenylmethane. Starting with 2-phenyl-1,3-dioxolane (Table 1, run 4), diphenylmethane was again obtained in 48% yield, but 2-phenyl-1,3-dioxepane (Table 1, run 5) afforded only a trace amount of the product. With dimethyl acetal, diisopropyl acetal, or dibutyl acetal of benzaldehyde, no or a small amount of the product formed, benzaldehyde being the main product (Table 1, runs 6−8).

Reaction of 2-Aryl-1,3-dioxanes with Arenes. As described above, 1,3-dioxane derivatives were found to be a suitable electrophile for the reductive FC reaction. Table 2 shows the results of the TFSA-catalyzed reductive FC reaction of various 2-aryl-1,3-dioxanes with representative arenes. The reaction was carried out in arene as a solvent when its boiling point was relatively

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(1) Roberts, R. M.; El-Khawaga, A. M.; Sweeney, K. M.; El-Zohry, M. F. *J. Org. Chem.* **1987**, *52*, 1591.
(2) Saito, S.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1995**, *117*, 11081.
(3) Olah, G. A.; Rasul, G.; York, C.; Prakash, G. K. *J. Am. Chem. Soc.* **1995**, *117*, 11211.
(4) TFSA is defined as the superacid by Olah et al. See: Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13.
(5) Hashimoto, Y.; Hirata, K.; Kagoshima, H.; Kihara, N.; Hasegwa, M, Saigo, K. *Tetrahedron* **1993**, *27*, 5969; *Tetrahedron Lett.* **1992**, *42*, 6351.
(6) Fukuzawa, S.; Tsuchimoto, T.; Hotaka, T.; Hiyama, T. *Synlett* **1995**, 1077.
(7) When the reaction was performed under Olah's conditions, i.e., adding 100 equiv of TFSA to the acetal, the reaction product was a complex mixture of compounds including diphenylmethane, triphenylmethanol, triphenylmethane, anthracene, etc.
(8) Tsuchimoto, T.; Hiyama, T.; Fukuzawa, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2345.

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Scheme 1

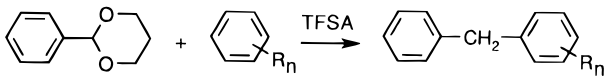
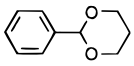
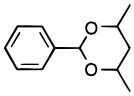
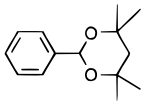
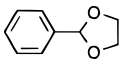
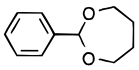
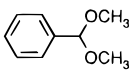
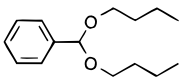
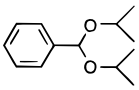


Table 1. TFSA-Catalyzed Reactions of Benzaldehyde Acetals with Benzene[a]

run	acetal	%, yield of Ph_2CH_2[b]
1		60
2		51
3		0
4		48
5		trace
6		0
7		trace
8		11

[a] A mixture of acetal (1.0 mmol), benzene (5.0 mL), and TFSA (0.05 mmol) was heated to reflux for 10 h. [b] GC yield.

low. With arenes of higher boiling point, 1,2-dichloroethane or nitromethane was used as the solvent. The reaction in dichloromethane, chloroform, or carbon disulfide resulted in no reaction. In every case, arene was employed in excess. The benzylation reaction proceeded smoothly with arenes substituted by electron-donating group(s) to give the corresponding diarylmethanes in good to excellent yields without contamination of byproducts. The reaction with anisole was an exception, giving a low yield of the desired benzylanisole albeit complete consumption of the starting acetal (Table 2, run 5). This is probably because the reactive benzylanisole might have undergone further benzylation to give complex polymeric products. The isomer ratio of *o*-:*m*-:*p*-products of the reaction with toluene or anisole was similar to that observed in the usual Lewis acid catalyzed FC reaction using benzyl chloride or benzyl alcohol.[9] Benzaldehyde acetals having an electron-donating or -withdrawing group at C(4) similarly reacted with arenes to give the corresponding diarylmethanes in good to excellent yields. The reaction was fast with such activated arenecarbaldehyde acetals as 4-methylphenyl and slow with such deactivated arenecarbaldehyde acetals as 4-chloro-, 4-fluoro-, or 4-nitrophenyl acetals.[10] Figure 1 illustrates time-dependent formation of diarylmethanes in the reaction of 2-(4-methylphenyl)-, 2-phenyl-, and 2-(4-chlorophenyl)-1,3-dioxane with benzene. The reactivity order is consistent with the mechanism involving a benzylic cationic intermediate. When 2-cyclohexyl-1,3-dioxane was employed instead of 2-aryl-1,3-dioxane for the reaction with *p*-xylene, the desired cyclohexyldimethylbenzene was not obtained and polymeric material formed. With 2-phenyl-2-methyl-1,3-dioxane, only trace amounts of alkylated products were detected along with several unidentified products.[11]

Reaction of Arenecarbaldehydes with Arenes in the Presence of 1,3-Propanediol. Since acetalization takes place under acidic conditions, we considered that the reductive FC benzylation reaction should be possible starting with arenecarbaldehyde and 1,3-propanediol. Actually, the acid-catalyzed benzylation of benzene using benzaldehyde and 1,3-propanediol cleanly proceeded to give diphenylmethane in accord with the reaction of 2-phenyl-1,3-dioxane. Thus, the reaction should involve the acid-catalyzed acetalization of benzaldehyde for the first step. The acetal formation was confirmed by the reaction of benzaldehyde with 1,3-propanediol in dichloromethane. In the absence of 1,3-propanediol, no reaction took place. Table 3 summarizes the reaction of various arenecarbaldehydes with some arenes in the presence of 1,3-propanediol. As readily seen, each reaction gave the corresponding diarylmethane(s) in good to excellent yields. The reaction has an advantage that preparation of acetals is not needed. The isomer ratios were virtually the same as those observed for the reaction with the acetals.

Reaction Mechanism. The reductive FC reaction with acetals should involve a redox process. Without a redox process, the expected products would be triphenylmethane and/or diphenylmethyl ether.[12] Thus, the question arises of where the hydride comes from. Since no triarylmethanol or triarylmethane could be isolated and a redox process should not occur between triarylmethane and diarylmethyl cation,[13] involvement of diarylmethyl cation is not likely. We attribute that to the hydride source to the cyclic acetal moiety and propose a reaction mechanism as presented in Scheme 2. The oxygen atom of the acetal ring is first protonated and then undergoes the acetal ring opening to form a benzyl cationic intermediate (**3**) stabilized by phenyl and the 3-hydroxypropoxy substituent. The cationic intermediate is electrophilically attacked by benzene to form diphenylmethyl ether **5**. The hydrogen atom on the alkoxy carbon then migrates to the benzylic carbon and eliminates 3-hydroxypropanal (**7**) or its equivalent.[14,15]

(9) (a) Olah, G. A.; Kobayashi, S.; Tashiro, M. *J. Am. Chem. Soc.* **1972**, *94*, 7448. (b) Olah, G. A.; Olah, J. A.; Ohyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 5284.

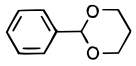
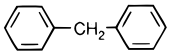
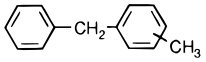
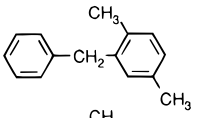
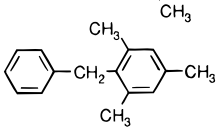
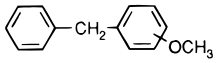
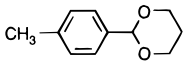
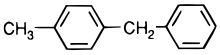
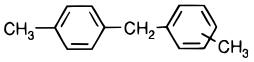
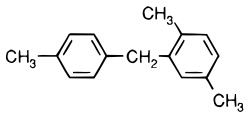
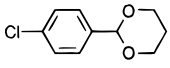
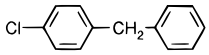
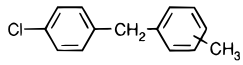
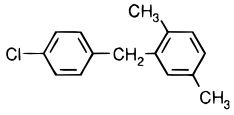
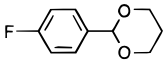
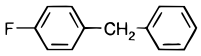
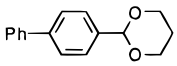
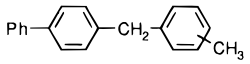
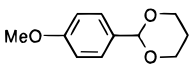
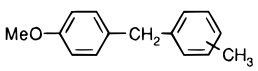
(10) (a) DeHaan, F. P.; Delker, G. L.; Covey, W. D.; Ahn, J.; Anksman, M. S.; Brehm, E. C.; Chang, J.; Chicz, R. M.; Cowan, R. L.; Ferrara, D. M.; Fong, C. H.; Harper, J. D.; Irani, C. D.; Kim, J. Y.; Meinhold, R. W.; Miller, K. D.; Roberts, M. P.; Stoler, E. M.; Suh, Y. J.; Tang, M.; Williams, E. L. *J. Am. Chem. Soc.* **1984**, *106*, 7038. (b) DeHaan, F. P.; Chan, W. H.; Chang, J.; Cheng, T. B.; Chiriboga, D. A.; Irving, M. M.; Kaufman, C. R.; Kim, G. Y.; Kumar, A.; Na, J.; Nguyen, T. T.; Nguyen, D. T.; Patel, B. R.; Sarin, N. P.; Tidwell, J. H. *J. Am. Chem. Soc.* **1990**, *112*, 356.

(11) Styrene dimer was one of the main products.

(12) For a review, see: Olah, G. A. *Friedel–Crafts and Related Reactions*; Wiley-Interscience: New York, 1964; Vol. 2, Part 1.

(13) In the acid-catalyzed Friedel–Crafts reaction with benzaldehyde, the methyne hydrogen of triphenylmethane transfers to the benzyl cation to give diphenylmethane and the trityl cation, which is attacked by water. See ref 2.

Table 2. TFSA-Catalyzed FC Benzylation of 2-Aryl-1,3-dioxane with Arenes[a]

run	acetal	arene	h, time	°C, temp.	product	%, yield[b]	*o* : *m* : *p*[c]
1		benzene	10	80		60	
2		toluene	7	110		94	42 : 8 : 50
3		*p*-xylene	10	125		88	
4[d]		mesitylene	11	125		72	
5[d]		anisole	12	100		38	45 : tr : 55
6		benzene	9	80		78	
7		toluene	7	110		100	38 : 4 : 58
8		*p*-xylene	8	125		89	
9		benzene	18	80		61	
10		toluene	17	110		81	27 : 7 : 56
11		*p*-xylene	17	110		75	
12		benzene	20	80		87	
13		toluene	18	110		100	35 : 6 : 59
14		toluene	7	110		17	37 : 3 : 60

[a] 2-Aryl-1,3-dioxane (1.0 mmol), arene (5.0 mL), TFSA (0.05 mmol). [b] GC yield. [c] Determined by GC. [d] The reaction was carried out in 1,2-dichloroethane.

The hydride shift was evidenced by the experiment using 2-phenyl-4,4,6,6-tetradeuterio-5-ethyl-1,3-dioxane (**10**); the reaction with benzene gave more than 90% deuteriated diphenylmethane (**11**) (Scheme 3). That no reaction took place with 2-phenyl-4,4,6,6-tetramethyl-1,3-dioxane is also consistent with the hydride shift mechanism (Table 1, run 3).

When the reaction was performed using benzene-d_6, no deuterium incorporation was observed into the benzylic carbon (Scheme 4). This fact strongly suggests that the hydrogen source is not benzene and the redox process should proceed *via* the hydride shift from the acetal moiety.

Diphenylmethyl ether (**5**) was separately prepared and

(14) Hydride ion transfer from the alkoxy carbon of tetrahydrofuran, 1,3-dioxolane, and 1,3-dioxepan to a trityl cation has been reported. Din, K-u.; Plesch, P. H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 937.

(15) The oxidation product of the alkyl group was not detected because it may undergo a condensation reaction to form polymeric products.

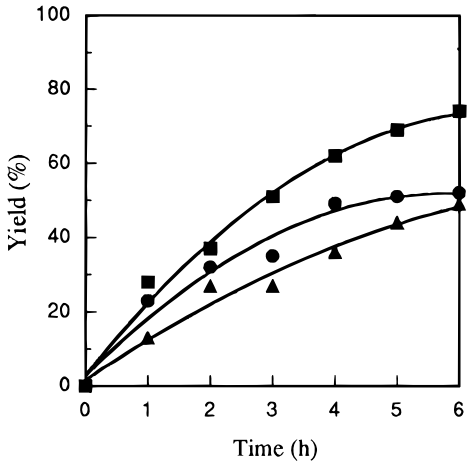
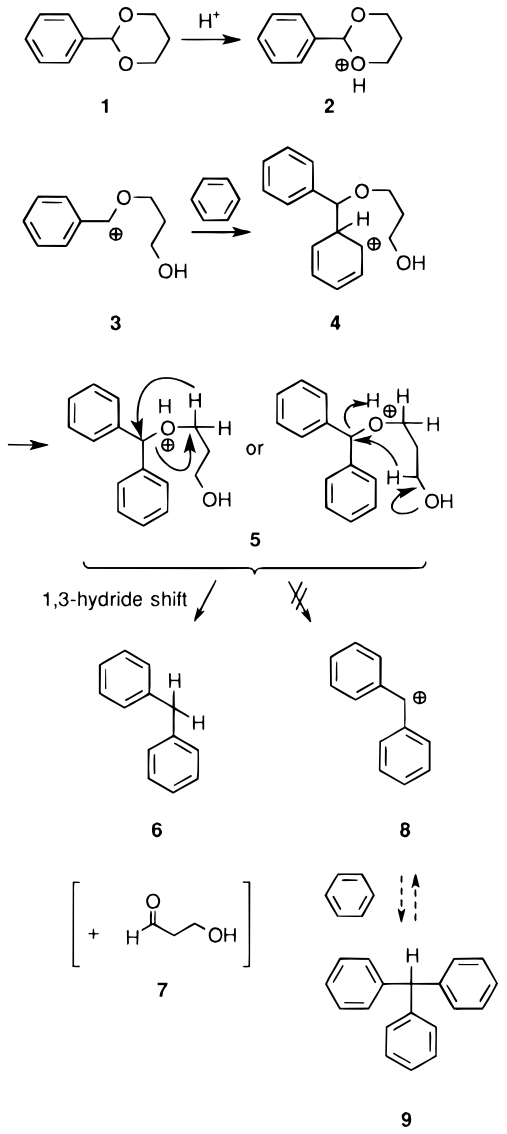


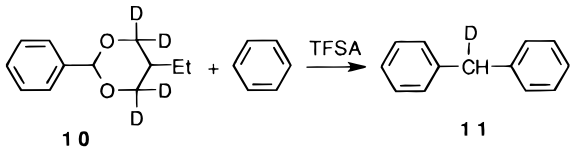
Figure 1. Reaction rate plot of the reaction of benzene with 2-(4-methylphenyl)- (■), 2-phenyl- (●), and 2-(4-chlorophenyl)-1,3-dioxane (▲).

Scheme 2

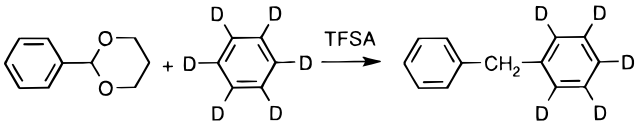


subjected to the reaction with benzene under the FC conditions. Here again, diphenylmethane was produced in 40−50% yield, suggesting that the diphenylmethyl ether was a likely intermediate for the hydride shift process (Scheme 5).[16] The driving force of the hydride shift must be protonation of the etheral oxygen because diphenylmethyl ether **5** was recovered in the absence of TFSA. Thus, it may safely be concluded that the hydride source is the alkoxy group of the acetal group and that diphenylmethyl ether **5** is the most likely intermediate. For the 1,3-hydride shift, two ways are possible as shown in Scheme 2. At present, no evidence is available to determine which is a probable pathway.

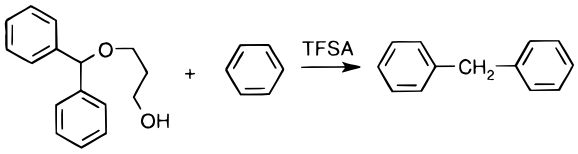
Scheme 3



Scheme 4



Scheme 5



Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions. The chemical shifts are reported in δ units downfield from the internal reference, Me_4Si. Infrared spectra were measured in $CHCl_3$ solutions or as KBr pellets. GC and GC/MS analyses were carried out on a capillary column (DB-5-30N-STD, J&W Scientific, 0.25 mm, 30 m) (helium as the carrier gas). High-resolution mass spectral analyses were carried out at Sagami Chemical Research Center, Kanagawa, Japan. Elemental analyses were carried out in the microanalytical laboratory of Chuo University. Column chromatography on SiO_2 was performed using Merck silica gel 60.

Materials. TFSA was kindly supplied from Central Glass Co., Ltd (Japan). Benzene, toluene, mesitylene, *p*-xylene, and anisole were distilled from CaH_2 and kept over molecular sieves 4A under nitrogen. All of the aldehydes are commercially available and were purified by distillation under reduced pressure before use. Authentic samples of substituted diarylmethanes for the GC/MS analyses were prepared by the Lewis acid-catalyzed Friedel−Crafts benzylation of the substituted benzyl chloride with arenes.[9]

Benzaldehyde diisopropyl acetal was prepared according to the literature procedure.[17] Benzaldehyde dibutyl acetal was prepared by acid-catalyzed transacetalization of benzaldehyde dimethyl acetal with 1-butanol.

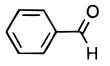
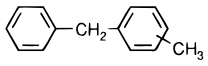
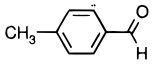
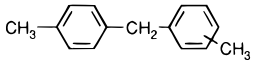
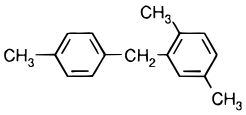
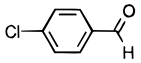
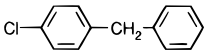
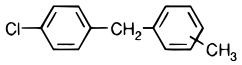
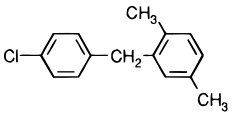
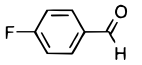
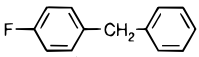
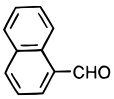
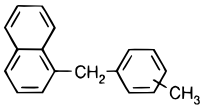
Preparation of Arenecarbaldehyde Acetals. Cyclic acetals of arenecarbaldehydes were prepared by the acid-catalyzed acetalization with the corresponding diol.[18] A typical experimental procedure for the acetalization reaction follows. A two-neck, round-bottom flask, equipped with a Dean−Stark trap, was charged with a mixture of *p*-tolualdehyde (2.4 g, 20

(16) Because treatment of diphenylmethyl ether $Ph_2CHOCH_2CH_2CH_3$ with a catalytic amount of TFSA similarly afforded diphenylmethane under the FC conditions, the terminal hydroxy group is not essential for the hydride shift process.

(17) Roelofsen, D. P.; van Bekkum, H. *Synthesis* **1972**, 419.

(18) Napolitano, E.; Fiaschi, R.; Mastrorilli, E. *Synthesis* **1986**, 122.

Table 3. TFSA-Catalyzed FC Benzylation of Aldehydes with Arenes in the Presence of 1,3-Propanediol[a]

run	aldehyde	arene	h, time	°C, temp.	product	%, yield[b]	*o* : *m* : *p*[b]
1		toluene	10	80		91	40 : 6 : 54
2		toluene	7	110		100	36 : 7 : 57
3		*p*-xylene	8	125		85	
4		benzene	17	110		66	
5		toluene	18	110		60	35 : 5 : 60
6		*p*-xylene	17	125		79	
7		benzene	20	110		85	
8		toluene	12	110		60	23 : 7 : 70

[a] Aldehyde (1.0 mmol), arene (5.0 mL), 1,3-propanediol (1.1 mmol), TFSA (0.05 mmol). [b] GC yield. [c] Determined by GC.

mmol), 1,3-propanediol (1.9 g, 25 mmol), *p*-toluenesulfonic acid (40 mg), and benzene (100 mL). The solution was heated at reflux with stirring until no further water separated. The solution was then cooled to room temperature. Triethylamine (1.0 mL) was added to the reaction mixture, which was then partitioned between diethyl ether and water. The organic phase was washed with 10% sodium hydroxide (20 mL) and then with brine and dried over K_2CO_3. Evaporation of the solvent gave almost pure 2-(4-methylphenyl)-1,3-dioxane, which was purified by recrystallization from pentane (3.5 g, 19.7 mmol, 98% yield). Spectral and analytical data of the arenecarbaldehyde acetals of the substituted benzaldehydes are as follows.

2-(4-Methylphenyl)-1,3-dioxane (5563-40-1): mp 30−33 °C; IR ($CHCl_3$) 813, 988, 1103, 1152, 1237, 1379, 2858, 3014 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.4 (m, 1H), 2.0−2.1 (m, 1H), 2.19 (s, 3H), 3.98 (dt, 2H, J = 11.9, 2.2 Hz), 4.25 (dd, 2H, J = 10.7, 4.9 Hz), 5.47 (s, 1H), 7.16 (d, 2H, J = 8.1 Hz), 7.36 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1, 25.7, 67.3, 101.6, 125.8, 128.8, 135.9, 138.4. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.10; H, 7.82.

2-(4-Chlorophenyl)-1,3-dioxane (6413-52-1): mp 59−60 °C; IR ($CHCl_3$) 821, 1017, 1107, 1149, 1222, 1237, 1378, 2859 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.2 (m, 1H), 2.0−2.1 (m, 1H), 3.80 (dt, 2H, J = 11.9, 2.2 Hz), 4.10 (dd, 2H, J = 10.7, 4.9 Hz), 5.31 (s, 1H), 7.20 (d, 2H, J = 8.8 Hz), 7.30 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 25.4, 67.1, 100.3, 127.3, 128.4, 134.1, 137.1. Anal. Calcd for $C_{10}H_{11}ClO_2$: C, 60.46; H, 5.58. Found: C, 60,47; H, 5.52.

2-(4-Fluorophenyl)-1,3-dioxane: bp 90 °C/0.6 mmHg (Kugelrohr distillation); IR (neat) 833, 992, 1017, 1105, 1154, 1225, 1280, 1381, 1514, 1605, 1612, 2857, 2969 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.3−1.5 (m, 1H), 2.05−2.33 (m, 1H), 3.96 (dt, 2H, J = 17.4, 2.4 Hz), 4.21 (dd, 2H, J = 5.1, 1.2 Hz), 5.46 (s, 1H), 7.03 (m, 2H), 7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.6, 67.3, 100.8, 115.0 (d, $^2J_{CF}$ = 44 Hz), 127.8 (d, $^3J_{CF}$ = 18 Hz), 134.7 (d, $^4J_{CF}$ = 6 Hz), 162.9 (d, $^1J_{CF}$ = 490 Hz). Anal. Calcd for $C_{10}H_{11}FO_2$: C, 65.92; H, 6.09. Found: C, 65.86; H, 6.20.

2-(4-Nitrophenyl)-1,3-dioxane (833-64-7): mp 108−109 °C; IR ($CHCl_3$) 1105, 1349, 1525, 2860 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.5 (m, 1H), 2.1−2.3 (m, 1H), 4.03 (m, 2H), 4.29 (m, 2H), 5.57 (s, 1H), 7.66 (d, 2H, J = 8.8 Hz), 8.21 (d, 2H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 25.5, 67.2, 99.7, 123.2, 127.0, 145.1, 147.9. Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.57; H, 5.40; N, 6.69.

2-(Biphenyl-4-yl)-1,3-dioxane: mp 56−59 °C; IR (KBr) 700, 768, 826, 849, 970, 992, 1015, 1103, 1148, 1235, 1379, 1389, 1487, 2872 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.4 (m, 1H), 2.1−2.2 (m, 1H), 3.99 (dt, 2H, J = 11.9, 2.2 Hz), 4.26 (dd, 2H, J = 10.7, 5.0 Hz), 5.50 (s, 1H), 7.2−7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.7, 67.3, 101.3, 126.3, 126.9, 127.1, 127.3, 128.6, 137.7, 140.8, 141.5. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.08; H, 6.74.

2-(1-Naphthyl)-1,3-dioxane (66671-26-9): mp 64−66 °C; IR ($CHCl_3$) 998, 1081, 1113, 1151, 1209, 1238, 2856, 3013 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.40 (m, 1H), 2.2−2.4 (m, 1H), 4.0 (m, 2H), 4.3 (m, 2H), 6.01 (s, 1H), 7.4−8.2 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 25.7, 67.5, 100.8, 124.1, 124.2, 125.0, 125.5, 126.0, 128.4, 129.3, 130.4, 133.7, 133.8. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.09; H, 6.62.

2-(4-Methoxyphenyl)-1,3-dioxane (5689-71-4): mp 42−45 °C; IR ($CHCl_3$) 829, 988, 1036, 1103, 1149, 1173, 1210, 1251, 1379, 1519, 1615, 2857, 2960, 3014 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.33−1.47 (m, 1H), 2.05−2.34 (m, 1H), 3.95 (dt, 2H, J = 12.1, 2.4 Hz), 4.23 (dd, 2H, 10.6, 5.1 Hz), 5.44 (s, 1H), 6.87 (m, 2H), 7.40 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.7, 55.2, 67.2, 101.5, 113.5, 127.2, 131.3, 159.8. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.68; H, 7.20.

2-Phenyl-4,4,6,6-tetradeuterio-5-ethyl-1,3-dioxane (10). This compound was obtained as a ca. 7:3 diastereomeric

mixture by the reaction of benzaldehyde with 1,1,3,3-tetradeuterio-2-ethyl-1,3-propanediol (*vide infra*), which was obtained by the reduction of diethyl ethylmalonate with $LiAlD_4$: IR (neat) 698, 744, 1032, 1069, 1103, 1167, 1385, 1456, 2087, 2213 2963 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (major diastereomer) δ 0.91 (t, 3H, J = 7.9 Hz), 1.13 (quint, 2H, J = 7.2Hz), 2.02 (br t, 1H, J = 6.6Hz), 5.40 (s, 1H), 7.25−7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.9, 21.1, 35.4, 71.6 (quint, J = 84 Hz), 101.4, 126.0, 128.2, 128.7, 138.5; ^1H NMR (400 MHz, $CDCl_3$) (minor diastereomer) δ 1.00 (t, 3H, J = 7.5 Hz), 1.27 (t, 1H, J = 7.3Hz), 1.84 (quint, 2H, J = 7.3 Hz), 5.49 (s, 1H), 7.25−7.54 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.0, 22.2, 35.7, 69.5 (quint, J = 84 Hz), 101.7, 126.0, 128.2, 128.7, 138.8; HRMS calcd for $C_{12}H_{12}D_4O_2$ m/z 196.1397, found 196.1376.

1,1,3,3-Tetradeuterio-2-ethyl-1,3-propanediol. This compound was prepared by the following procedure. A 50-mL two-neck round-bottom flask, fitted with a dropping funnel and a reflux condenser connected with a argon line, was charged with lithium aluminum deuteride (949 mg, 25 mmol) and diethyl ether (20 mL). The mixture was heated to reflux for 30 min and then cooled to room temperature. A solution of diethyl ethylmalonate (3.8 g, 20 mmol) dissolved in diethyl ether (20 mL) was added slowly with stirring at such a rate that the solvent continued to reflux gently. After the addtion was completed, the mixture was stirred at the reflux temperature for an additional 3 h. The mixture was cooled to room temperature, and the excess deuteride was decomposed by the addition of saturated sodium sulfate solution. The insoluble material was filtered and washed fully with chloroform. The combined filtrate was dried over $MgSO_4$ and concentrated to give a crude product. Purification by flash chromatography, using hexane/ether (1/1), afforded the diol (984 mg, 46%) as an oil. IR (neat) 943, 1071, 1092, 1105, 1156, 1171, 1381, 1464, 2093, 2207, 2878, 2936, 2964, 3345 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.8 Hz), 1.29 (quint, 2H, J = 7.5 Hz), 1.60 (br t, 1H, J = 6.3 Hz), 4.00 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 11.5, 11.5, 20.4, 43.3, 63.9 (quint, J = 83 Hz).

Acid-Catalyzed Reaction of Arenecarbaldehyde Acetals with Arenes. A Typical Experimental Procedure. TFSA (8 mg, 0.05 mmol) was added to a solution of 2-(4-chlorophenyl)-1,3-dioxane (199 mg, 1.0 mmol) in toluene (5.0 mL) at room temperature with stirring. The mixture was stirred at reflux temperature for 17 h, cooled, and poured into aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with brine and dried over $MgSO_4$. GC/MS analysis revealed that the crude product contained (4-chlorophenyl)-*p*-tolylmethane, (4-chlorophenyl)-*o*-tolylmethane, and (4-chlorophenyl)-*m*-tolylmethane; each amount and the isomer ratio were determined using naphthalene as the standard and compared with each authentic sample.[9] Most of the products are known compounds and were characterized by a comparison of their spectral data with those of authentic samples unless otherwise noted.[9]

Spectral and analytical data of new compounds prepared follow.

(Biphenyl-4-yl)tolylmethane. This compound was obtained by the reaction of toluene with (2-biphenyl-4-yl)-1,3-dioxane: mp 55−60 °C; IR (KBr) 689, 696, 727, 745, 756, 772, 797, 816, 1406, 1487, 1512 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) (*o*-isomer) δ 2.26 (s, 3H), 4.00 (s, 2H), 7.00−7.60 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 19.7, 39.1, 124−141 (additional several peaks); ^1H NMR (200 MHz, $CDCl_3$) (*p*-isomer) δ 2.30 (s, 3H), 3.96 (s, 2H), 7.00−7.60 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 21.0, 41.5, 124−141 (additional several peaks). Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.92; H, 7.15.

(1-Naphthyl)tolylmethane. This compound was obtained by the reaction of toluene with 2-(1-naphthyl)-1,3-dioxane: bp 165 °C/0.6 mmHg (Kugelrohr distillation); IR (neat) 779, 791, 1397, 1512 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) (*o*-isomer) δ 2.30 (s, 3H), 4.39 (s, 2H), 6.85−7.53 (m, 8H), 7.67−8.05 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 19.6, 36.2, 124−139 (additional several peaks); ^1H NMR (200 MHz, $CDCl_3$) (*m*-isomer) δ 2.27 (s, 3H), 4.39 (s, 2H), 6.85−7.53 (m, 8H), 7.67−8.05 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 21.0, 41.5, 124−139 (additional several peaks); ^1H NMR (200 MHz, $CDCl_3$) (*p*-isomer) δ 2.28 (s, 3H), 4.39 (s, 2H), 6.85−7.53 (m, 8H), 7.67−8.05 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 21.0, 38.6, 124−139 (additional several peaks). Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.29; H, 6.93.

Acid-Catalyzed Reaction of Arenecarbaldehydes with Arenes in the Presence of 1,3-Propanediol. A Typical Experimental Procedure. TFSA (8.0 mg, 0.05 mmol) was added to a solution of 4-chlorobenzaldehyde (141 mg, 1.0 mmol) and 1,3-propanediol (84 mg, 1.1 mmol) in toluene (5.0 mL) at room temperature with stirring. The mixture was stirred at reflux temperature for 18 h. The reaction mixture was cooled and poured into aqueous $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with brine and dried over $MgSO_4$. GC/MS analysis revealed the presence of an isomeric mixture of ditolylmethanes, each amount being determined with naphthalene as the internal standard. The isomer ratio of the *o*-, *m*-, and *p*-substituted diarylmethane was determined by GC, and retention times were compared with those of the authentic samples.[9]

3-Hydroxypropyl Diphenylmethyl Ether (5). This ether was prepared by the reduction of 2,2-diphenyl-1,3-dioxane with $LiAlH_4$−$AlCl_3$:[19] mp 41−42 °C; IR (KBr) 698, 739, 1022, 1082, 1100, 3359, 3432 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.89 (quint, 2H, J = 5.7 Hz), 2.23 (br s 1H), 3.64 (t, 2H, J = 5.7 Hz), 3.80 (t, 2H, J = 5.7 Hz), 5.35 (s, 1H), 7.18−7.38 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 32.2, 61.8, 68.0, 84.2, 126.8, 127.5, 128.4, 142. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 78.98; H, 7.56.

Registry nos. provided by the author: benzaldehyde dimethyl acetal, 1125-88-8; benzaldehyde dibutyl acetal, 5395-08-4; benzaldehyde diisopropyl acetal, 38115-81-0; 2-phenyl-1,3-dioxolane, 936-51-5; 2-phenyl-1,3-dioxane, 772-01-0; 2-phenyl-4,6-dimethyl-1,3-dioxane, 4233-09-4; 2-phenyl-4,4,6,6,-tetramethyl-1,3-dioxane, 62977-15-5; 2-phenyl-1,3-dioxepane, 2749-68-0; 2-(4-methylphenyl)-1,3-dioxane, 5663-40-1; 2-(4-chlorophenyl)-1,3-dioxane, 6413-52-1; 2-(4-methoxyphenyl)-1,3-dioxane, 5689-71-4; 2-(4-nitrophenyl)-1,3-dioxane, 833-64-7; 2-(1-naphthalenyl)-1,3-dioxane, 66671-26-9; 1,1′-methylenebisbenzene, 101-81-5; 1,1′-(methylene-*d*)bisbenzene, 20389-18-8; phenylmethylbenzene-d_5, 103730-93-4; 1-methyl-2-(phenylmethyl)benzene, 713-36-0; 1-methyl-3-(phenylmethyl)benzene, 620-47-3; 1-methyl-4-(phenylmethyl)benzene, 620-83-7; 1,4-dimethyl-2-(phenylmethyl)benzene, 13540-50-6; 1,3,5-trimethyl-2-(phenylmethyl)benzene, 4453-79-6; 1-methoxy-2-(phenylmethyl)benzene, 883-90-9; 1-methoxy-3-(phenylmethyl)benzene, 23450-27-3; 1-methoxy-4-(phenylmethyl)benzene, 834-14-0; 1-methyl-2-(4-methylphenyl)methylbenzene, 21895-17-0; 1-methyl-3-(4-methylphenyl)methylbenzene, 21895-16-9; 1,1′-ethylenebis(4-methylbenzene), 4957-14-6; 1,4-dimethyl-2-(4-methylphenyl)methylbenzene, 721-45-9; 1-chloro-4-(phenylmethyl)benzene, 831-81-2; 1-fluoro-4-(phenylmethyl)benzene, 587-79-1; 1-[(4-chlorophenyl)methyl]-2-methylbenzene, 55676-88-5; 1-chloro-4-[(3-methylphenyl)methyl]benzene, 91410-28-5; 1-chloro-4-[(4-methylphenyl)methyl]benzene, 30203-87-3; 2-[(4-chlorophenyl)methyl]-1,4-dimethylbenzene, 85716-72-9; 1-[(4-methoxyphenyl) methyl]-2-methylbenzene, 53039-52-4; 1-[(4-methoxyphenyl)methyl]-3-methylbenzene, 53039-51-3; 1-methoxy-4-[(4-methylphenyl)methyl]benzene, 22865-60-7; 4-(*p*-methylbenzyl)biphenyl, 30203-93-1; 1-[(2-methylphenyl)methyl]naphthalene, 20204-73-3; 1-[(4-methylphenyl)methyl]naphthalene, 20204-71-1; 1,1′-(propoxymethylene)bisbenzene, 13594-71-3.

Supporting Information Available: ^1H and ^{13}C NMR spectra of all benzaldehyde and 4-substituted benzaldehyde acetals and diarylmethanes prepared in the present study (33 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(19) The general experimental protocols followed in this study parallel those described in the literature: Eliel, E. L.; Badding, V. D.; Rerick, M. N. *J. Am. Chem. Soc.* **1962**, *84*, 2371.