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Formation of 3-Methylene-1,4-cyclohexadienes from $\alpha,\alpha,\alpha',\alpha'$-Tetraaryl-1,4-benzenedimethanols by the Intramolecular Migration of an Aryl Group

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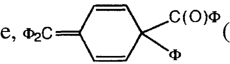
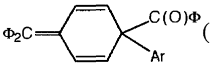
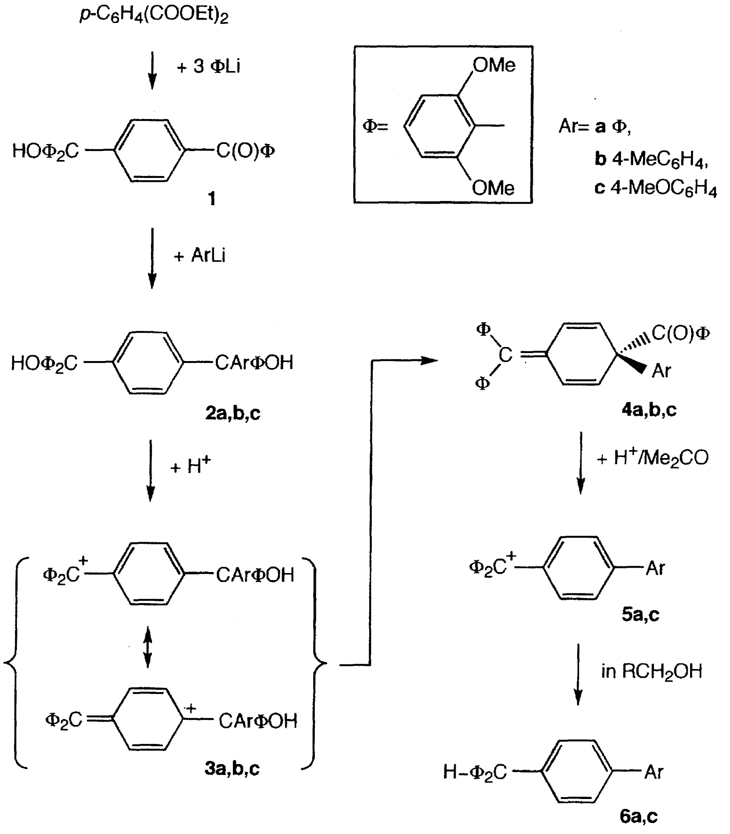
By reactions of diethyl *p*-phthalate with 2,6-dimethoxyphenyllithium, ΦLi, a tri-substituted compound, *p*-HOCΦ_2C$_6$H$_4$C(O)Φ (**1**), or tetra-substituted 1,4-benzenedimethanol, *p*-HOCΦ_2C$_6$H$_4$CΦ_2OH (**2a**), were obtained. Compound **1** further reacted with aryllithium, ArLi, to give the 1,4-benzenedimethanols, *p*-HOCΦ_2C$_6$H$_4$CArΦOH (Ar = 4-MeC$_6$H$_4$ **2b**, 4-MeOC$_6$H$_4$ **2c**). When **2a** was treated with acid in dimethyl sulfoxide, 3-(2,6-dimethoxybenzoyl)-3-(2,6-dimethoxyphenyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene,  (**4a**) was obtained in quantitative yield under a variety of conditions. The reaction is understood to involve an initial formation of carbenium ion, [*p*-Φ_2C$^+$–C$_6$H$_4$CΦ_2OH] (**3a**), of which the positive charge must be partly shared with the other end of the *p*-phenylene ring, where one of the neighboring Φ-groups migrates. Reactions in acetone resulted to give **4a** or dark-violet crystals of (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)carbenium perchlorate, [(4-ΦC$_6$H$_4$)CΦ_2]ClO$_4$, depending on the reaction conditions. Reactions in methanol, ethanol, or in hot 2-propanol resulted to give the reduced compound, (4-ΦC$_6$H$_4$)Φ_2CH. The 1,4-benzenedimethanols, **2b** and **2c**, also reacted with perchloric acid in dimethyl sulfoxide to form the 3-methylene-1,4-cyclohexadiene derivatives,  (Ar = 4-MeC$_6$H$_4$ **4b**, 4-MeOC$_6$H$_4$ **4c**), respectively. Evidence is given by the ^{1}H NMR spectrum, which shows the formation of intermediate carbenium ions **3a**—**c**.

Due to electronic and steric effects, 2,6-dimethoxyphenyl derivatives often exhibit unusual properties. For example, triarylmethanols bearing two 2,6-dimethoxyphenyl groups, ArΦ_2COH [Φ = 2,6-(MeO)$_2$C$_6$H$_3$], are highly basic to react with a slight excess of acid to form the triaryl carbenium salts, [ArΦ_2C]X, which are easily isolable, even from 2-propanol, and are generally highly colored.[1,2] These carbenium ions further react in a variety of fashions, depending on the conditions.[1,2] With a hope to investigate the possibility to obtain a dication, a cation radical, or *p*-quinodimethane derivatives, we have prepared $\alpha,\alpha,\alpha',\alpha'$-tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol, *p*-HOCΦ_2C$_6$H$_4$CΦOH (**2a**). We report here on an unexpected aryl group migration observed for **2a** catalyzed by an acid, as well as for some α-aryl-α,α',α'-tris(2,6-dimethoxyphenyl)-1,4-benzenedimethanols, *p*-HOCΦ_2C$_6$H$_4$CArΦOH (Ar = 4-MeC$_6$H$_4$ **2b**, 4-MeOC$_6$H$_4$ **2c**). The products are unusual 3-methylene-1,4-cyclohexadiene derivatives bearing aryl and aroyl groups, or their decomposition products derived by a cleavage of the aroyl group. The facile formation of a 3-methylene-1,4-cyclohexadiene skeleton is unexpected, although 3-diphenylmethylene-6-triphenylmethyl-1,4-cyclohexadiene is a well-known compound, since it is formed by dimerization of the trityl radical.[3—7] We believe that the present results add new information concerning the properties of the 3-methylene-1,4-cyclohexadiene derivatives, as well as of the 2,6-dimethoxyphenyl derivatives. The reactions reported here are summarized in Scheme 1.

Experimental

Physical Measurements. The NMR spectra were recorded for solutions in CDCl$_3$ using a JEOL JNM-GX-270 spectrometer. IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-4200 spectrophotometer. GC-MS spectra were recorded using a Shimadzu QP-5000 mass spectrometer (gasified at 250 °C). The ^{1}H and ^{13}C NMR spectral data are given in Tables 1 and 2, respectively. UV spectra were recorded using a Shimadzu UV-160 spectrophotometer.

Preparation of 2,6-Dimethoxyphenyl 4-[Bis(2,6-dimethoxyphenyl)hydroxymethyl]phenyl Ketone, *p*-HOCΦ_2C$_6$H$_4$C(O)Φ (1). To a 15% hexane solution of butyllithium (7.5 ml, 12 mmol) were added 1,3-dimethoxybenzene (1.7 ml, 13 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (0.03 ml) at 0 °C under argon. The mixture was stirred at room temperature for 3 h to give a white suspension of 2,6-dimethoxyphenyllithium, ΦLi, which was diluted with diethyl ether (10 ml). To the suspension was added diethyl *p*-phthalate (0.822 g, 3.7 mmol) dissolved in toluene (20 ml); the mixture was stirred at room temperature for 2 d to give a yellow suspension. Methanol (1 ml) was added, and yellow precipitates were recrystallized from 2-propanol to give colorless crystals of **1** in a 78—66% yield based on butyllithium; mp 191—193 °C; IR 3480 (OH) and 1665 cm^{-1} (C=O). Found: C, 70.57; H, 5.88%. Calcd for C$_{32}$H$_{32}$O$_8$: C, 70.58; H, 5.92%. This compound was very soluble in chloroform, acetone, and acetonitrile, soluble in methanol, 2-propanol, and hot toluene, but was insoluble in diethyl ether and hexane.



Scheme 1.

Preparation of α,α,α′,α′-Tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol (2a). From Diethyl *p*-Phthalate. To a suspension of *Φ*Li prepared in diethyl ether (5 ml), as mentioned above from 1,3-dimethoxybenzene (1.7 ml, 13 mmol), was added diethyl *p*-phthalate (0.556 g, 2.5 mmol) dissolved in benzene (10 ml). The mixture was stirred at room temperature for 4 d; methanol (1 ml) was then added to give colorless crystals, which were washed with acetonitrile to give **2a** in a 79% yield based on butyllithium; mp 230—232 °C; IR 3480 $\mathrm{cm^{-1}}$ (OH). Found: C, 70.59; H, 6.22%. Calcd for $C_{40}H_{42}O_{10}$: C, 70.37; H, 6.20%.

Compound **2a** was soluble in chloroform, hot toluene, and hot acetonitrile, but was insoluble in acetone, methanol, 2-propanol, diethyl ether, and hexane.

From 1. A suspension of *Φ*Li, prepared in diethyl ether (5 ml) as mentioned above from 1,3-dimethoxybenzene (0.39 ml, 3 mmol), was added to a suspension of **1** (0.544 g, 1.0 mmol) in toluene (10 ml). The mixture was stirred at room temperature for 4 d to give a light-yellow suspension. Methanol (1 ml) was added to give colorless crystals, which were washed with acetonitrile to give **2a** in a 78—67% yield based on **1**; mp 230—232 °C.

Preparation of α,α,α′-Tris(2,6-dimethoxyphenyl)-α′-*p*-tolyl-1,4-benzenedimethanol (2b). To a solution of 4-bromotoluene (0.40 ml, 3.2 mmol) in diethyl ether (5 ml) was added a 15% hexane solution of butyllithium (1.9 ml, 3.0 mmol) with stirring at room temperature under argon. After it was stirred for 3 h, a suspension of **1** (0.544 g, 1 mmol) in toluene was added. The mixture was stirred at room temperature for 3 d to give a yellow solution. It was washed with three 10 ml portions of water and dried under reduced pressure as much as possible. To the residue was added diethyl ether (10 ml) to give colorless crystals, which were recrystallized from 2-propanol to give **2b** in an 80—63% yield based on **1**; mp 168—170 °C; IR 3400 $\mathrm{cm^{-1}}$ (OH). Found: C, 73.29; H, 6.38%. Calcd for $C_{39}H_{40}O_{8}$: C, 73.57; H, 6.33%.

Compound **2b** was soluble in chloroform, acetone, hot methanol, hot 2-propanol, hot toluene, and hot acetonitrile, but was insoluble in diethyl ether and hexane.

Preparation of α,α,α′-Tris(2,6-dimethoxyphenyl)-α′-(4-methoxyphenyl)-1,4-benzenedimethanol (2c). A solution of 4-methoxyphenyllithium in diethyl ether (5 ml) was prepared from 4-bromoanisole (0.40 ml, 3.2 mmol) and butyllithium, as mentioned above. It was treated with a suspension of **1** (0.544 g, 1 mmol) in toluene in an analogous manner, as mentioned above, to give colorless crystals of **2c** in an 86—61% yield after recrystallization from 2-propanol; mp 164—166 °C; IR 3480 $\mathrm{cm^{-1}}$ (OH). Found: C, 71.56; H, 6.32%. Calcd for $C_{40}H_{39}O_{9}$: C, 71.76; H, 6.18%.

Compound **2c** was soluble in chloroform, hot acetone, hot methanol, hot 2-propanol, hot toluene, and hot acetonitrile, but was insoluble in diethyl ether and hexane.

Reactions of α,α,α′,α′-Tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol (2a) with Acids. In Dimethyl Sulfoxide. 1) To a suspension of **2a** (0.682 g, 1 mmol) in dimethyl sulfoxide (DMSO) (20 ml) was added 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) at room temperature to immediately give a violet suspension. The mixture was stirred at room temperature for 2 h, during which time the violet color degraded to give a brown solution. Water (40 ml) was added, resulting in a light-yellow precipitation of 3-(2,6-dimethoxybenzoyl)-3-(2,6-dimethoxyphenyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene (**4a**) in a 93% yield. An analytical sample was obtained by recrystallization from 2-propanol; mp 162—164 °C decomposition; IR 1685 $\mathrm{cm^{-1}}$ (C=O). Found: C, 71.88; H, 6.21%. Calcd for $C_{40}H_{40}O_{9}$: C, 72.27; H, 6.06%. The GC spectrum of **4a** showed the decomposition to

Table 1. ^{1}H NMR Spectral Data[a] for 2,6-Dimethoxyphenyl Derivatives

Compounds	4-H (Φ)[b]	3,5-H (Φ)[c]	2,6-MeO[d]	Others[e]
1	7.28 (1H), 7.10 (2H)	6.58 (2H), 6.52 (4H)	3.68 (6H), 3.39 (12H)	7.70d and 7.50d [8] (4H, C_6H_4), 6.56s (1H, OH).
2a	7.08 (4H)	6.50 (8H)	3.34 (24H)	7.32s (4H, C_6H_4), 6.20s (2H, OH).
2a[f]	7.12 (4H)	6.54 (8H)	3.37 (24H)	7.22s (4H, C_6H_4), 6.22s (2H, OH).
2b	7.21—7.08[g]	6.56 (2H), 6.53 (4H)	3.38 (12H), 3.36 (6H)	7.35d [9] (2H), 7.21—7.08m,[g] 7.00d [9] (2H), 6.31s (1H), and 6.16s (1H) (OH), 2.30s (3H, *p*-Me).
2b[f]	7.22 (1H), 7.12 (2H)	6.79 (2H), 6.69 (4H)	3.42 (6H) 3.41 (12H)	7.30d and 7.12d [9] (4H, C_6H_4), 7.19d and 7.17d [9] (4H, C_6H_4), 6.36s (1H) and 6.23s (1H) (OH), 2.38s (3H, *p*-Me).
2b[h]	7.35 (1H), 7.23 (2H)	6.79 (2H), 6.69 (4H)	3.44 (18H)	7.30d and 7.09d [9] (4H, C_6H_4), 7.11d and 7.06d [9] (4H, C_6H_4), 6.36s (1H) and 6.24s (1H) (OH), 2.38s (3H, *p*-Me).
2c	7.2—7.1[g]	6.55 (2H), 6.52 (4H)	3.39 (12H), 3.38 (6H)	7.36d [9] (2H), 7.2—7.1m,[g] 6.73d [9] (2H), 6.32 s (1H) and 6.17s (1H) (OH), 3.77s (3H, *p*-MeO).
2c[f]	7.24 (1H), 7.13 (2H)	6.61 (2H), 6.56 (4H)	3.43 (6H), 3.42 (12H)	7.32d and 7.08d [9] (4H, C_6H_4), 7.12d and 6.74d [9] (4H, C_6H_4), 6.32s (1H) and 6.14s (1H) (OH), 3.78s (3H, *p*-MeO).
2c[h]	7.35 (1H), 7.23 (2H)	6.79 (2H), 6.69 (4H)	3.47 (6H), 3.42 (12H)	7.31d and 7.08d [9] (4H, C_6H_4), 7.10d and 6.88d [9] (4H, C_6H_4), 6.36s (1H) and 6.24s (1H) (OH), 3.83s (3H, *p*-MeO).
3a[f]	7.67 (2H), 7.33 (2H)	6.63 (4H) 6.58 (4H)	3.50 (12H), 3.49 (12H)	7.76d and 7.61d [9] (4H, C_6H_4).
3a[i]	7.62 (2H), 7.36 (2H)	6.61 (4H), 6.56 (4H)	3.60 (12H), 3.57 (12H)	7.70d and 7.57d [9] (4H, C_6H_4).
3b[h]	7.64 (2H), 7.39 (1H)	6.92 (4H), 6.85 (2H),	3.60 (12H), 3.50 (6H)	7.92d and 7.47d [9] (4H, C_6H_4), 7.19d and 7.08d [9] (4H, C_6H_4), 2.38s (*p*-Me).
3c[h]	7.66 (2H), 7.4—7.3[f]	6.93 (4H), 6.85 (2H),	3.61 (12H), 3.51 (6H)	7.93d and 7.47d [9] (4H, C_6H_4), 7.2—6.7m,[g] 3.84s (3H, *p*-MeO).
4a	7.17 (1H), 7.13 (1H), 7.09 (2H)	6.56 (2H), 6.46 (4H), 6.45 (2H)	3.68 (6H), 3.66 (6H), 3.56 (6H), 3.49 (6H)	6.24d and 6.10d [11] (4H, C_6H_4).
4a[h]	7.35 (1H), 7.26 (1H), 7.22 (2H)	6.71 (2H), 6.69 (2H), 6.63 (2H), 6.62 (2H)	3.75 (6H), 3.70 (6H), 3.62 (6H), 3.56 (6H)	6.23d and 5.99d [11] (4H, C_6H_4).
4b	7.20 (1H), 7.12 (2H)	6.48 (4H) 6.47 (2H)	3.66 (6H), 3.60 (6H), 3.53 (6H)	7.37d and 7.09d [9] (4H, C_6H_4), 6.20d and 5.97d [10] (4H, C_6H_4), 2.30s (3H, *p*-Me).
4c	7.20 (1H), 7.12 (2H)	6.48 (4H), 6.47 (2H)	3.66 (6H), 3.60 (6H), 3.53 (6H)	7.40d and 6.82d [9] (4H, C_6H_4), 6.20d and 5.97d [10] (4H, C_6H_4), 3.78s (3H, *p*-MeO).
4f	7.14 (3H)	6.59 (2H), 6.51 (2H), 6.50 (2H)	3.77 (6H), 3.66 (6H), 3.61 (6H)	6.21d and 6.09d [10] (4H, C_6H_4), 5.56s (1H, OH).
5a	7.77 (2H), 7.36 (1H)	6.67 (6H)	3.76 (6H), 3.60 (12H)	7.56s (4H, C_6H_4).
5c	7.74 (2H)	6.65 (4H)	3.59 (12H)	7.86d [9] (2H), 7.3—7.1m,[g] 7.08d [9] (2H), 3.91s (3H, *p*-MeO).
5′a	7.22 (1H), 7.12 (2H)	6.55 (4H) 6.52 (2H)	3.68 (6H), 3.42 (12H)	7.47d and 7.15d [9] (4H, C_6H_4), 6.30s (1H, OH).
6a	7.22 (1H), 7.12 (2H)	6.61 (2H), 6.53 (4H)	3.68 (6H), 3.52 (12H)	7.09s (4H, C_6H_4), 6.41s (1H, *t*-C–H).
6c	7.14 (2H)	6.54 (4H)	3.51 (12H)	7.52d and 6.94d [9] (4H, C_6H_4), 7.37d and 7.11d [8] (4H, C_6H_4), 6.40s (1H, *t*-C–H), 3.83s (3H, *p*-MeO).

a) In $CDCl_3$ otherwise noted (δ/ppm; s = singlet, d = doublet, t = triplet, m = multiplet). b) Triplet with $J_H = 8$—9 Hz otherwise noted. c) Doublet with $J_H = 8$—9 Hz. d) Singlet. e) The coupling constants J_H greater than 2 Hz are given in square brackets in Hz, while those less than 2 Hz are omitted for clarity. f) In CD_2Cl_2. g) Overlapped. h) In DMSO-d_6. i) In CD_3OD.

Table 2. ^{13}C NMR Spectral Data[a)] for 2,6-Dimethoxyphenyl Derivatives

Compounds	δ/ppm; in CDCl$_3$
1	158.1, 157.6, 155.3, 135.3, 130.3, 128.6, 127.6, 126.5, 106.7, 104.1, 79.5 (C–OH), 56.2 and 55.8 (MeO).
2a	158.0, 146.4, 126.9, 125.0, 106.8, 79.3 (C–OH), 56.2 (MeO).
2b	158.6, 147.8, 146.4, 135.6, 128.3, 127.8, 127.5, 127.0, 125.9, 107.0, 81.9 and 79.6 (C–OH), 56.5 and 56.2 (MeO), 21.1 (*p*-Me).
2c	158.3, 147.7, 144.4, 141.7, 128.5, 127.2, 125.8, 112.4, 106.9, 81.3 and 79.5 (C–OH), 56.4 (2,6-MeO, overlapped), and 55.3 (*p*-MeO).
4a	199.5 (C=O), 159.2, 159.1, 157.9, 131.2, 129.8, 129.5, 128.0, 127.7, 125.4, 120.5, 107.5, 105.9, 104.5, 104.1, 63.2 (3-C); 56.9, 56.4, 55.9, and 55.5 (MeO).
4c	206.2 (C=O), 158.9, 158.5, 158.0, 156.6, 136.2, 130.1, 129.6, 129.1, 127.9, 126.5, 123.5, 113.4, 104.6, 104.5, 104.2, 61.6 (3-C); 56.1, 55.8, 55.7, and 55.3 (MeO).
5a	191.1 (C$^+$), 163.2, 143.9, 135.7, 132.6, 131.2, 105.4, 104.5; 56.9 and 56.4 (MeO).
6a	159.5, 158.0, 143.2, 129.5, 128.0, 127.3, 126.8, 122.2, 120.8, 105.6, 104.4; 56.2 and 55.8 (MeO), 38.1 (*t*-C).

a) In the order of chemical shift.

give two species, p-ΦC(O)C$_6$H$_4$$\Phi$ (M1) and p-Φ_2CH–C$_6$H$_4$$\Phi$ (**6a**) (M2); MS: (M1) *m*/*z* (%) 378 (M1$^+$; 55), 241 (M1$^+ - \Phi$; 30), 183 (M1$^+ - \Phi$CO; 14), 165 (ΦCO; 100); (M2) *m*/*z* (%) 500 (M2$^+$; 100), 469 (M2$^+$ – OMe; 35), 362 (M2$^+ - \Phi$H; 40), 331 (M2$^+ - \Phi$OMe; 33), 138 (ΦH$^+$; 17).

The results of analogous reactions are summarized as follows, where the change in the condition is given first, followed by the yield of **4a**: 2) with 42% aqueous tetrafluoroboric acid (0.35 ml, 2.2 mmol) in place of perchloric acid, 90% yield; 3) with trifluoroacetic acid (0.16 ml, 2.2 mmol), 93% yield; 4) with 12 M (1 M = 1 mol dm^{-3}) hydrochloric acid (2.2 mmol), 92% yield; 5) with 1 M perchloric acid (2.2 mmol), 89% yield; 6) with 0.27 mmol of 60% perchloric acid, 93% yield; 7) at 80 °C, 0.5 h, 92% yield; 8) at room temperature, 24 h, 90% yield; 9) in 40 ml of DMSO, 91% yield; 10) in 10 ml of DMSO, 92% yield; 11) without acid, **2a** recovered in 96% yield; 12) with acetic acid (2.2 mmol), **2a** recovered in a 95% yield.

Compound **4a** was soluble in chloroform, acetone, hot methanol, hot 2-propanol, hot toluene, and hot acetonitrile, but was insoluble in diethyl ether and hexane.

In Acetone. A suspension of **2a** (1 mmol) in acetone (20 ml) was treated with 60% aqueous perchloric acid as above to immediately give a violet suspension. After the mixture was stirred at room temperature for 1 h, it was diluted with acetone (40 ml), and a small amount of insoluble materials was removed by filtration. The violet filtrate was dried under reduced pressure, and the residue was well washed with a 1 : 9 mixture of 2-propanol and toluene to give violet crystals of (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)carbenium perchlorate (**5a**) in a 67% yield; mp 152—155 °C; IR 1100 cm^{-1} (broad) (ClO$_4$); UV (acetone) 532 (log ε = 4.15) and ca. 620 nm (shoulder). Found: C, 61.89; H, 5.35; Cl, 5.92%. Calcd for C$_{31}$H$_{31}$O$_{10}$Cl: C, 62.16; H, 5.22; Cl, 5.91%.

When trifluoroacetic acid was used in place of 60% aqueous perchloric acid, **4a** was obtained in quantitative yield. When a small amount of dimethyl sulfoxide (2 ml) was added to the starting acetone suspension, **4a** was obtained in quantitative yield.

Compound **5a** was soluble in hot chloroform and hot acetone, and was insoluble in toluene, diethyl ether, and hexane. It is reduced in hot alcohols, as described below.

In 2-Propanol and 1-Butanol. A suspension of **2a** (1 mmol) in 2-propanol (20 ml) was treated with 60% aqueous perchloric acid, as mentioned above, for 2 d to give a violet suspension, which was extracted with acetone to remove a small amount of insoluble materials. From the filtrate, **5a** was isolated in a 64% yield.

An analogous treatment of **2a** in 1-butanol also resulted to give **5a** in a 62% yield.

In Methanol and Ethanol. A suspension of **2a** (1 mmol) in methanol (20 ml) was treated with 60% aqueous perchloric acid, as mentioned above, for 2 d to give gray suspension. The precipitates were extracted with toluene (10 ml) to leave an uncharacterized light-yellow solid. The filtrate was dried under reduced pressure, and the residue was recrystallized from 2-propanol to give light-yellow crystals of (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)methane (**6a**) in a 43—31% yield; mp 189—191 °C; MS *m*/*z* (%) 500 (M$^+$; 100), 469 (M$^+$ – OMe; 35), 362 (M$^+ - \Phi$H; 45), 331 (M$^+ - \Phi$OMe; 34), 138 (ΦH$^+$; 10). Found: C, 74.30; H, 6.40%. Calcd for C$_{31}$H$_{32}$O$_6$: C, 74.38; H, 6.44%.

An analogous treatment of **2a** in ethanol also resulted to give **6a** in 47% yield.

Compound **6a** was soluble in chloroform, acetone, toluene, hot methanol, and hot 2-propanol, but was insoluble in diethyl ether and hexane.

Reaction of α,α,α'-Tris(2,6-dimethoxyphenyl)-α'-*p*-tolyl-1,4-benzenedimethanol (2b) with Perchloric Acid. To a colorless solution of **2b** (0.636 g, 1 mmol) in DMSO (20 ml) was added 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) to give immediately a violet solution. It was stirred at room temperature for 2 d to give a brown solution. Water (40 ml) was added to give yellow precipitates, of which the ^{1}H NMR spectrum showed the formation of two compounds with 3-(2,6-dimethoxybenzoyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-3-*p*-tolyl-1,4-cyclohexadiene (**4b**) as the main product in less than 87% yield; IR 1690 cm^{-1} (C=O). The separation of a small amount of impurity did not succeed.

Reaction of α,α,α'-Tris(2,6-dimethoxyphenyl)-α'-(4-methoxyphenyl)-1,4-benzenedimethanol (2c) with Perchloric Acid. To a colorless solution of **2c** (0.651 g, 1 mmol) in DMSO (20 ml) was added 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) to immediately give a violet solution. It was stirred for 6 h to give a green solution. Water (40 ml) was added to give light-yellow precipitates, which were recrystallized from 2-propanol to give light-yellow crystals of 3-(2,6-dimethoxybenzoyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-3-(4-methoxyphenyl)-1,4-cyclohexadiene (**4c**) in a 93—67% yield; mp 184—185 °C; IR 1680 cm^{-1} (C=O). Found: C, 73.55; H, 6.12%. Calcd for C$_{39}$H$_{38}$O$_8$: C, 73.80; H, 6.03%.

Compound **4c** was soluble in chloroform, hot acetone, hot methanol, hot 2-propanol, hot toluene, and hot acetonitrile, but was insoluble in diethyl ether and hexane.

Reactions of 3-(2,6-Dimethoxybenzoyl)-3-(2,6-dimeth-

oxyphenyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene (4a) with Perchloric Acid. **In Acetone.** To a yellow solution of **4a** (0.664 g, 1 mmol) in acetone (20 ml) was added 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) at room temperature to immediately give a violet solution. The mixture was stirred for 1 h to give a violet suspension; acetone (40 ml) was then added to dissolve most of the precipitates. It was filtered to leave a small amount of gray solid, which was poorly soluble in common organic solvents. The filtrate was dried under reduced pressure, and the residue was washed with 1 : 9 mixture of 2-propanol and toluene to give violet crystals of **5a** in an 83% yield.

When a catalytic amount of acid (0.1—0.2 mmol) was used, most of **4a** was recovered.

In Ethanol. To a light-yellow solution of **4a** (1 mmol) in ethanol (20 ml) was added 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) to immediately give a violet solution. It was stirred at room temperature for 20 h to give a gray suspension. The precipitates were separated and then extracted with toluene (10 ml) to leave an uncharacterized light-yellow solid. The toluene filtrate was dried under reduced pressure, and the residue was recrystallized from 2-propanol to give light-yellow crystals of **6a** in a 47—34% yield.

Reaction of 3-(2,6-Dimethoxybenzoyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-3-(4-methoxyphenyl)-1,4-cyclohexadiene (4c) with Perchloric Acid. A solution of **4c** (0.634 g, 1 mmol) in acetone (20 ml) containing 60% aqueous perchloric acid (0.24 ml) was treated in an analogous manner as mentioned above to give dark-violet crystals of [bis(2,6-dimethoxyphenyl)](4′-methoxy-4-biphenylyl)carbenium perchlorate (**5c**) in a 59% yield; mp 94—99 °C; IR 1090 cm^{-1} (broad)(ClO$_4$); UV (acetone) 530 (log $\varepsilon = 4.09$) and 631 nm (log $\varepsilon = 4.16$).

Compound **5c** was soluble in chloroform and acetone, but was insoluble in toluene, diethyl ether, and hexane. It was reduced in hot alcohols to give colorless crystals of **6c**; mp 196—200 °C.

Reaction of (2′,6′-Dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)carbenium Perchlorate (5a) in 2-Propanol. A violet suspension of **5a** (0.599 g, 1 mmol) in 2-propanol (20 ml) was heated at 80 °C for 2 h to give a gray suspension. The precipitates were separated and extracted with toluene (10 ml) to leave an uncharacterized light-yellow solid. The toluene filtrate was dried under reduced pressure, and the residue was recrystallized from 2-propanol to give **6a** in a 46—33% yield.

Preparation of 1-(2,6-Dimethoxyphenyl)-4-[bis(2,6-dimethoxyphenyl)methylene]-2,5-cyclohexadien-1-ol (4f). 4-[Bis(2,6-dimethoxyphenyl)methylene]-2,5-cyclohexadien-1-one was obtained as described.[2] To a suspension of ΦLi, prepared as mentioned above from 1,3-dimethoxybenzene (0.88 ml, 6.8 mmol), was added toluene (40 ml) at 0 °C, followed by the crystals of 4-[bis(2,6-dimethoxyphenyl)methylene]-2,5-cyclohexadien-1-one (1.890 g, 5 mmol) to give an orange suspension. The mixture was stirred at room temperature for 24 h under argon and treated with methanol (2 ml) in air to give light-yellow crystals of 1-(2,6-dimethoxyphenyl)-4-[bis(2,6-dimethoxyphenyl)methylene]-2,5-cyclohexadien-1-ol (**4f**) in an 87% yield; mp 163—166 °C; IR 3500 cm^{-1} (OH). To the filtrate was added hexane (40 ml) at −30 °C to give additional crystals of **4f** in a 9% yield. The recrystallization of **4f** (2.07 g, 4 mmol) from acetone (200 ml) by heating at 50 °C for a short period resulted to selectively give the isomer, (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)methanol (**5′a**), in a 96% yield; mp 188—190 °C; IR 3500 cm^{-1} (OH). Recrystallization of **4f** from ethanol resulted to give light-yellow crystals, of which the IR, ^{1}H NMR, and GC-MS spectra were identical to those of the reduced compound, **6a** (41% yield).

Results and Discussion

Preparation of $\alpha,\alpha,\alpha',\alpha'$-Tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol (2a) and the Related Compounds. When diethyl p-phthalate was treated with 2,6-dimethoxyphenyllithium, ΦLi (3.0—3.6 molar amounts), in diethyl ether–toluene (or benzene), colorless crystals of a diaryl ketone, p-HOCΦ_2C$_6$H$_4$C(O)Φ (**1**), were obtained. The best yield of **1** was attained when diethyl p-phthalate was treated with 3.2 molar amounts of ΦLi in diethyl ether–toluene at room temperature. Compound **1** further reacted with ΦLi at room temperature or at 60 °C to give the $\alpha,\alpha,\alpha',\alpha'$-tetraaryl-1,4-benzenedimethanol, p-HOCΦ_2C$_6$H$_4$CΦ_2OH (**2a**), also as colorless crystals. It could be prepared more conveniently by the reaction of diethyl p-phthalate and a slight excess of ΦLi (4.6 molar amounts) in diethyl ether–toluene.

The IR spectrum of **1** showed bands at 3480 and 1665 cm^{-1} due to OH and C=O stretching vibrations, respectively. ^{1}H NMR spectra of 2,6-dimethoxyphenyl derivatives (Φ-derivatives) generally showed a triplet due to 4-H, a doublet due to 3,5-H, and a sharp singlet due 2,6-MeO protons.[1,2] The spectrum of **1** (Table 1) showed the presence of two kinds of Φ-groups in 2 : 1 ratio, two doublets assignable to phenylene protons, and a singlet at $\delta = 6.56$ ppm assignable to OH proton. The IR spectrum of **2a** showed a band at 3480 cm^{-1} due to OH stretching vibration. The ^{1}H NMR spectrum showed the presence of only one kind of Φ-group, a singlet at $\delta = 7.32$ ppm assignable to the phenylene protons, and a singlet at $\delta = 6.21$ ppm assignable to OH proton.

The two other tetraaryl-1,4-benzenedimethanols, p-HOCΦ_2C$_6$H$_4$CArΦOH (Ar = 4-MeC$_6$H$_4$ **2b**, 4-MeOC$_6$H$_4$ **2c**), were prepared by reactions of **1** with the corresponding aryllithium reagent. The ^{1}H NMR spectra of **2b** and **2c** were measured for CDCl$_3$, CD$_2$Cl$_2$, and DMSO-d_6 solutions, since some resonances often overlapped. They showed the presence of two kinds of Φ-groups in a 2 : 1 ratio, two kinds of A$_2$B$_2$ phenylene protons, the methyl protons of p-tolyl or p-methoxyphenyl group, and two hydroxy protons.

The ^{13}C NMR spectra of Φ-derivatives generally showed five resonances due to Φ-group carbon atoms.[1,2] The *ipso*-carbon (C-1) resonance (δ = 130—120 ppm) is often too weak to be observed. The *ortho*-carbon (C-2,6) resonance is observed at such a low magnetic field as δ = 164—157 ppm owing to the presence of the methoxy substituent. The *meta*-carbon (C-3,5) resonance was observed in a very narrow region of δ = 108—105 ppm. The *para*-carbon (C-4) resonance was sensitive to the type of compound, which was observed in a region of δ = 130—125 ppm for neutral compounds or in a region of δ = 146—130 ppm for cationic compounds.[1,2] The methoxy proton resonance was observed in a region of δ = 57—55 ppm. Thus, the three extra resonances observed for **2a** at δ = 146.4, 126.9 (or 125.0), 79.3 ppm (Table 2) could be assigned to the phenylene (C$_6$H$_4$) carbons and the *tert*-carbon (C–OH). The ^{13}C NMR spectra of **2b** and **2c** showed a greater number of aromatic carbon resonances, reflecting the asymmetric structures. The resonances at $\delta = 81.9$ and

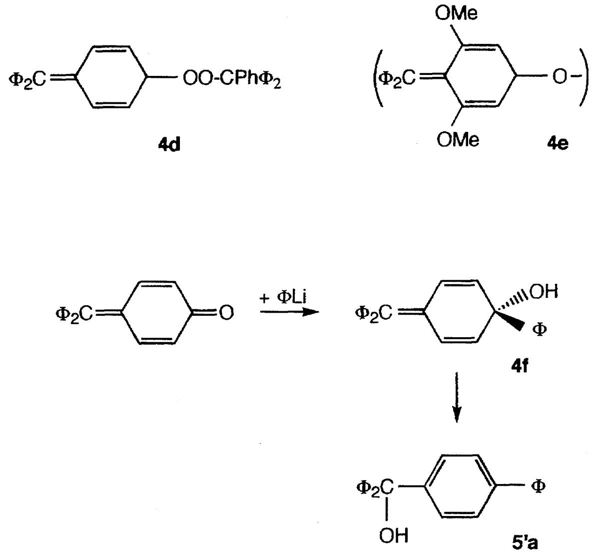
79.6 ppm for **2b** and at $\delta = 81.3$ and 79.5 ppm for **2c** could be assigned to the *tert*-carbons (C–OH). The spectrum of **1** was also consistent with the structure bearing two kinds of Φ-groups, except that the resonance of carbonyl carbon could not be detected, probably due to the weakness.

Reactions of α,α,α′,α′-Tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol (2a) and the Related Compounds, 2b and 2c, with Acid. When a slight excess (2.2 molar amounts) of perchloric acid was added to a suspension of **2a** in dimethyl sulfoxide, a deep violet coloration took place, which must have been an indication of carbenium ion **3a** formation. The color degraded in 2 h at room temperature to give a brown solution, and the addition of water resulted to give light-yellow crystals of **4a** in quantitative yield. The IR spectrum of **4a** showed a strong band at 1685 cm^{-1} attributable to the C=O stretching vibration. The ^{1}H NMR spectrum ($CDCl_3$) of **4a** showed, in addition to Φ-group proton resonances, an A_2B_2 quartet ($\delta = 6.24$ and 6.10) attributable to alkenyl protons (C_6H_4), indicative of the presence of different substituents at the 1,4-positions of the C_6H_4 ring. The most characteristic observation was that the methoxy proton resonances were composed of four peaks with a 1 : 1 : 1 : 1 ratio of the intensity. No essential change in the ^{1}H NMR spectrum was observed at elevated temperatures, such as 50 and 80 °C, in DMSO-d_6. While the spectrum for $CDCl_3$ solution showed three triplets due to 4-H and three doublets due to 3,5-H of the Φ-groups with a 1 : 1 : 2 ratio of intensity, the spectrum for DMSO-d_6 showed four doublets due to 3,5-H with a 1 : 1 : 1 : 1 ratio. The ^{13}C NMR spectrum showed a resonance at $\delta = 199.5$ ppm (C=O), four kinds of methoxy carbon resonances, and a characteristic resonance at $\delta = 63.2$ ppm, in addition to at least fourteen sp^2 carbon resonances. These observations together with the results of an elemental analysis (C,H) and of the following reactions may suggest that **4a** is 3-(2,6-dimethoxybenzoyl)-3-(2,6-dimethoxyphenyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene. The ^{13}C NMR resonance at $\delta = 63.2$ ppm can be assigned to the sp^3 carbon at the 3-position, and the resonance at $\delta = 120.5$ ppm can be assigned to the 6-methylene carbon. The observation of four methoxy groups in both the ^{1}H and ^{13}C NMR spectra may be explained by the fact that the free rotation of two Φ-groups on the methylene carbon around the C–C bond is restricted by a steric hindrance. Evidence to support this is given below compared with the ^{1}H NMR spectra of related compounds.

The reaction of **2a** (1 mmol) in dimethyl sulfoxide was repeated under a variety of conditions. The yield of **4a** was almost quantitative after a two-hour reaction period at room temperature. The reaction was little affected by the amount of perchloric acid between 2.2—0.3 molar amounts, or by the use of another acid, such as aqueous hydrochloric acid (1 M and 12 M) or trifluoroacetic acid. These results indicate that the role of the acid is catalytic. In fact, **2a** was recovered unreacted in the absence of acid or in the presence of a weak acid, such as acetic acid. The reaction was accelerated upon heating, and no by-product formed, even at 80 °C, thus suggesting the high inertness of **4a** in dimethyl sulfoxide containing an acid. However, it seems that **4a** is thermally labile at much higher temperatures, since the GC-MS spectrum of **4a** showed decomposition to give (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)methane (**6a**) and 2′,6′-dimethoxy-4-biphenylyl 2,6-dimethoxyphenyl ketone, p-$\Phi C(O)C_6H_4\Phi$. A treatment of **4a** with bromine in carbon tetrachloride resulted in decoloration, supporting the presence of carbon-carbon double bonds.

A possibility of the intermolecular migration of an aryl group must be precluded, because 1) **2a** and **3a** are too bulky to approach each other enough to react; 2) the reaction is too fast to measure the reaction rate, even for dilute solutions; and 3) the formation of expected products, such as **1**, was not observed.

Quite recently, some 3-methylene-1,4-cyclohexadiene derivatives bearing 2,6-dimethoxyphenyl groups on the methylene carbon have been reported (**4d** and **4e** in Scheme 2). The ^{1}H NMR spectral data for the methoxy protons are given as $\delta = 3.40$ (s, 12H) and 3.58 (d, $J = 2$ Hz, 12H) for **4d** and $\delta = 3.13$ (s, 12H) and 3.52 (d, $J = 2$ Hz, 24H) for **4e**.[8] Since these methoxy protons have no proton to couple with magnetically, the doublet signals must be assigned separately. The spectra can best be explained if the free rotation of two Φ-groups on the methylene carbon around the C–C bond is restricted. In order to confirm this, we prepared 1-(2,6-dimethoxyphenyl)-4-[bis(2,6-dimethoxyphenyl)methylene]-2,5-cyclohexadien-1-ol (**4f** in Scheme 2). As expected, the ^{1}H NMR spectrum of **4f** showed three methoxy proton resonances in a 1 : 1 : 1 ratio and three 1 : 1 : 1 doublets due to 3,5-H. These observations strongly suggest that the free rotation of the Φ-groups on the methylene carbon in 3-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene derivatives is restricted. Due to the double-bond character of the bond between Φ_2C and the cyclohexadiene carbon, the four carbons around the bond are in a same plane, and a rotation of the Φ-groups around the Φ–C bond might cause a steric interaction between the methoxyl oxygen atom and the



Scheme 2.

cyclohexadiene proton.

The reaction of **2a** to give **4a** is most probably understood as being an initial formation of **3a**, of which the positive charge must be partly shared with the other end of the *p*-phenylene ring, as shown in Scheme 1, where one of the neighboring Φ-groups migrates. It is followed by the loss of a proton to give **4a**. Aryl migrations have long been observed for carbenium cations, such as 1-methyl-2-phenylpropylium,[9] 2-aryl-1-methylethylium,[10] and 9,10-dimethyl-10-phenyl-9,10-dihydro-9-phenanthrylium.[11] The present intramolecular migration may resemble the so-called "pinacol rearrangement".

In contrast to the reaction of **2a** in dimethyl sulfoxide, reactions with perchloric acid (2.2 molar amounts) in acetone resulted to give **4a** or dark-violet crystals of (2′,6′-dimethoxy-4-biphenylyl)bis(2,6-dimethoxyphenyl)carbenium perchlorate, $[(4\text{-}\Phi C_6H_4)C\Phi_2]ClO_4$ (**5a**), depending on the conditions. When a catalytic amount of perchloric acid was used, the formation of **4a** predominated. When an excess of acid was used, however, a mixture of **5a** and an uncharacterized by-product was obtained. The reaction came to completion very fast, less than 1 hour at room temperature. The by-product was poorly soluble in a common organic solvent, and we tentatively assumed that it was a polymeric material derived by 2,6-dimethoxybenzaldehyde ΦCHO, of which the IR spectrum showed no band attributable to C=O stretching vibration.

An analogous formation of **5a** was also observed by reactions with an excess of acid in cold 2-propanol or 1-butanol. Reactions in methanol, ethanol, or in hot 2-propanol resulted to give white crystals of a triarylmethane, $(4\text{-}\Phi C_6H_4)\Phi_2CH$ (**6a**), the reduced product of **5a** by alcohols, which is one of the characteristic reactions of this type of carbenium ion.[1,2] The related reduction of the triarylcarbenium ion by alcohol to form triarylmethane and aldehyde or ketone has long been known;[12,13] the mechanism has been discussed by Olah and Svoboda,[14] in which they reported that the triphenylcarbenium ion was also reduced by ethers, aldehydes, amines, and formic acid.

A characteristic observation concerning the ^{1}H NMR spectrum of **5a** is that the triplets due to 4-H of the Φ-groups were observed at such low magnetic fields as $\delta = 7.77$ and 7.36 ppm in a 2 : 1 ratio, supporting the cationic character of the compound. In the ^{13}C NMR spectrum, a resonance of the central cationic carbon (C^+) was observed at $\delta = 191.1$ ppm. The ^{1}H NMR spectrum of **6a** showed the presence of two kinds of Φ-groups in a 1 : 2 ratio, the phenylene proton resonance as a singlet, and the *tert*-C–H resonance as a singlet at $\delta = 6.41$ ppm. The ^{13}C NMR spectrum also showed two resonances due to the methoxy carbon and the *tert*-C resonance at $\delta = 38.1$ ppm.

The 1,4-benzenedimethanols, **2b** and **2c**, also reacted with acid in dimethyl sulfoxide to form deep-violet solutions, suggesting the formation of carbenium ions, **3b** and **3c**, respectively. The color degradation of **2b** was slower than those of **2a** and **2c**. From solutions kept at room temperature, the 3-methylene-1,4-cyclohexadiene derivatives, **4b** and **4c**, were obtained, respectively, although a pure separation of the former has not succeeded. There are two structures considered for these products, depending on whether the Ar or Φ group migrates. We can propose the structure **4b** and **4c** to be as shown in Scheme 1, which is based on the reaction of **4c** to give [bis(2,6-dimethoxyphenyl)](4′-methoxy-4-biphenylyl)carbenium salt (**5c**), as is mentioned in the next section. ^{1}H NMR spectrum of **4b** showed three methoxy protons in a 1 : 1 : 1 ratio, one of which could be assigned to the Φ-group bonded to the carbonyl carbon. The other two could be assigned to the two Φ-groups on the methylene carbon, of which the free rotation was assumed to be inhibited. Observations of two kinds of 4-H resonances of the Φ-groups in a 1 : 2 ratio, and of two kinds of two doublets, attributable to C_6H_4 protons, are also consistent with the structure. An analogous ^{1}H NMR spectrum was obtained for **4c**, except for the observation of four methoxy protons in a 2 : 2 : 2 : 1 ratio. The ^{13}C NMR spectrum of **4c** showed a resonance at $\delta = 206.2$ ppm, attributable to the carbonyl carbon, four kinds of methoxy carbons, and a characteristic resonance at $\delta = 61.6$ ppm attributable to the sp^3 carbon at the 3-position. One of the four methoxy carbons must be assigned to the *p*-methoxy carbon, and the other three to the 2,6-dimethoxy carbons of the Φ-groups.

Hoping to observe the formation and stability of intermediate carbenium ion **3a**, the reactions were followed by the ^{1}H NMR spectrum. When a small amount of 60% aqueous perchloric acid was added to a suspension of **2a** in DMSO-d_6, the spectrum showed only the formation of **4a**. In CD_2Cl_2, however, the spectrum showed only the formation of a new compound attributable to **3a** at an early stage (Table 1). The characteristic are the observations 1) that there are two kinds of Φ-groups in 1 : 1 ratio, 2) that the C_6H_4 proton resonances were observed as two doublets, and 3) that one of the triples due to the 4-H of the Φ-groups was observed at such a low magnetic field as $\delta = 7.67$ ppm. The last observation is characteristic of the formation of the carbenium ion.[1,2] An analogous spectrum was observed for **2a** in CD_3OD. Upon standing this solution at room temperature, however, the spectrum changed to that of **6a**.

The spectrum of **2b** in DMSO-d_6 also showed a new set of resonances attributable to the intermediate carbenium ion **3b** in addition to those of **2b** and **4b**. The 4-H resonances of the Φ-group in **2b**, **3b**, and **4b** were observed as two kinds of triplets with a 2 : 1 ratio of the intensity, respectively. The low-field shift of the 4-H resonance of the Φ-group ($\delta = 7.64$) of **3b** is indicative that the cation center localizes mainly at the Φ_2C moiety, rather than at the CArΦ moiety. Analogous results were observed for **2c** in DMSO-d_6 to show the formation of **3c** (Table 1).

Reactions of 3-(2,6-Dimethoxybenzoyl)-3-(2,6-dimethoxyphenyl)-6-[bis(2,6-dimethoxyphenyl)methylene]-1,4-cyclohexadiene (4a) and the Related Compounds. The difference in the reactivity of **2a** between in dimethyl sulfoxide and in acetone or alcohols is astonishing. It was confirmed that **4a** is stable in dimethyl sulfoxide, even in the presence of acid, at least for 24 h, and that **4a** reacted in acetone containing an excess of perchloric acid to give **5a** together with uncharacterized by-product. The difference is tentatively attributed to a difference of the solvent basicity; more basic dimethyl sulfoxide would reduce the acidity of added acid.

Compound **4c** also reacted with perchloric acid in acetone to give **5c**. The observation indicates that *p*-methoxyphenyl group migrates, rather than the Φ-group, during the reaction of **2c** to give **4c**, probably due to the higher proton affinity of the ΦC(O)-group than the 4-MeOC$_6$H$_4$C(O)-group.

Compound **4f** is quite labile in hot solutions, even in the absence of an acid. Recrystallization from acetone resulted to give isomer **5′a** (Scheme 2) and from ethanol to give the reduced compound **6a**.

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