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# Unusual Stabilities and Reactivities of Tris- and Bis(2,4,6-trimethoxyphenyl)carbenium Salts

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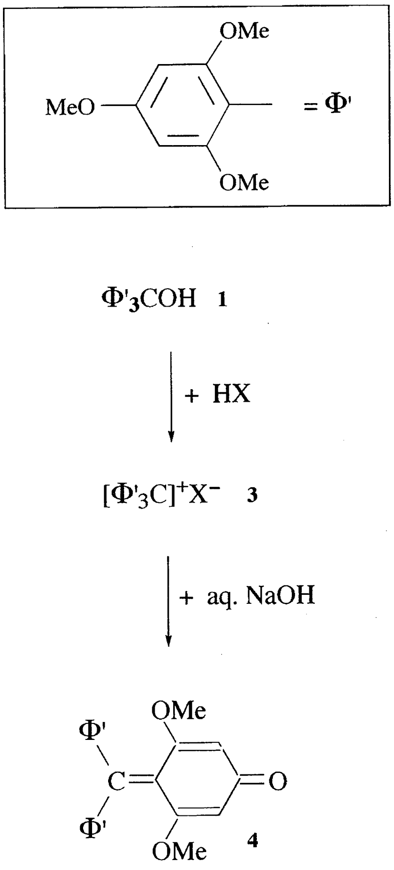
2,4,6-Trimethoxyphenyllithium, $\Phi'$Li[$\Phi' = 2,4,6-(\mathrm{MeO})_3\mathrm{C}_6\mathrm{H}_2$], reacted with diphenyl carbonate and with ethyl formate to give tris(2,4,6-trimethoxyphenyl)methanol, $\Phi'_3$COH (**1**), and bis(2,4,6-trimethoxyphenyl)methanol, $\Phi'_2$CHOH (**2**), respectively. Compound **1** reacted with a slight excess of perchloric acid in 2-propanol to give very dark-purple crystals of the triarylcarbenium salt, [$\Phi'_3$C]X (**3**, X = $\mathrm{ClO_4}$), which were inert even in hot ethanol. However, a treatment of **3** (X = Cl), prepared in situ in 1 M (1 M = 1 mol dm$^{-3}$) hydrochloric acid, with 1 M sodium hydroxide resulted to give 4-bis(2,4,6-trimethoxyphenyl)methylene-3,5-dimethoxy-2,5-cyclohexadienone. Compound **2** also reacted with a slight excess of perchloric acid in methanol to give dark-red crystals of the diarylcarbenium salt, [$\Phi'_2$CH]X (**5**, X = $\mathrm{ClO_4}$). Compound **5** was considerably inert even in hot methanol, but was easily reduced in primary and secondary alcohols to give bis(2,4,6-trimethoxyphenyl)methane, $\Phi'_2\mathrm{CH_2}$. Measurements of the half-lives of **5** in these alcohols showed that **5** was more labile in secondary alcohols, such as 2-propanol and 2-butanol, than in primary alcohols. When a suspension of **5** (X = Cl), prepared in situ in 1 M hydrochloric acid, was heated, tris(2,4,6-trimethoxyphenyl)methane, $\Phi'_3$CH (**7**), was obtained. Analogous reactions to give **7** were observed in methanol containing a slight excess of hydrochloric acid or nitric acid in place of perchloric acid. The possible paths of these reactions are discussed.

The chemical properties of triphenylmethanol vary drastically depending on the number and position of the methoxy substituent on the phenyl groups.[1,2] Triphenylmethanols bearing at least four *ortho*-methoxy groups, such as $\Phi_3$COH and Ph$\Phi_2$COH [$\Phi = 2,6-(\mathrm{MeO})_2\mathrm{C}_6\mathrm{H}_3$], were highly basic to form isolable triarylcarbenium salts, [Ar$\Phi_2$C]X, even in alcohols and water.[1] Since such substitutions on *ortho*-carbons would cause a decreased conjugation of the aromatic ring to carbenium carbon, due to a steric hindrance, the stabilization effect of 2,6-dimethoxy groups is astonishing. While (2-$\mathrm{MeOC_6H_4}$)$\Phi_2$COH also formed an analogous triarylcarbenium salt, (4-$\mathrm{MeOC_6H_4}$)$\Phi_2$COH reacted in 2-propanol containing a catalytic amount of acid to give 4-bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone caused by $\mathrm{S_N}$Ar hydrolysis.[2] Consequently, it is of interest to study the properties of 2,4,6-trimethoxyphenyl derivatives, such as $\Phi'_3$COH (**1**) and $\Phi'_2$CHOH (**2**) [$\Phi' = 2,4,6-(\mathrm{MeO})_3\mathrm{C}_6\mathrm{H}_2$]. We report here on the facile isolations of tri- and diarylcarbenium salts, [$\Phi'_3$C]X (**3**) and [$\Phi'_2$CH]X (**5**), which can be recrystallized even from methanol. Some unusual chemical properties of these carbenium salts are also reported, as summarized in Schemes 1 and 2, respectively.

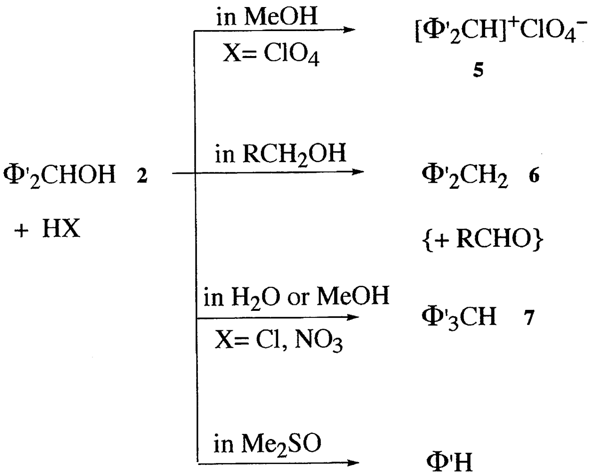
## Results and Discussion

**Preparation of Tris- and Bis(2,4,6-trimethoxyphenyl)methanols.** 2,4,6-Trimethoxyphenyllithium was most conveniently prepared by the reaction of 1,3,5-trimethoxybenzene ($\Phi'$H) and a 15% hexane solution of butyllithium in toluene or diethyl ether at 0 °C in the presence of a catalytic amount of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine. It reacted with diphenyl carbonate to give **1** as light-brown crystals. It also reacted with ethyl formate to give **2** as white crystals. It is advisable here that the use of an acid should be avoided to neutralize the reaction mixtures, since both **1** and **2** react with only a slight excess of acid to form the carbenium salts, as mentioned below.

**Tris(2,4,6-trimethoxyphenyl)carbenium Perchlorate.** When **1** was treated with a slight excess of perchloric acid in 2-propanol, very dark-purple crystals of **3** (X = $\mathrm{ClO_4}$) were obtained. The electronic spectrum (VIS) of **3** in 1,2-dichloroethane solution showed a well-formed absorption at $\lambda_{\mathrm{max}}$, 586 nm (log $\varepsilon$, 4.48) with a shoulder at ca. 450 nm. Though [$\Phi_3$C]$\mathrm{ClO_4}$ is slowly reduced in ethanol even at room temperature to give $\Phi_3$CH with a half-life of 18 h,[1] **3** was inert even in hot ethanol, and was recovered from a solution heated at 60 °C for 48 h.. This increased inertness of **3** may be attributed to the electronic effect of three 4-methoxy groups, which disperse the positive charge from the central carbon atom to the oxygen atoms to decrease the reactivity on the central carbenium carbon. Like $\Phi_3$COH, **1** dissolves in hot 1 M (1 M = 1 mol dm$^{-3}$) hydrochloric acid to form a dark-purple solution of **3** (X = Cl). With a hope to measure the p$K_{\mathrm{R^+}}$ value, 1 M sodium hydroxide was added to the acidic solution, but it resulted to form light-brown precipitates of a new compound **4** rather than the original compound **1**. Compound **4** was well characterized as 4-



Scheme 1.



Scheme 2.

bis(2,4,6-trimethoxyphenyl)methylene-3,5-dimethoxy-2,5-cyclohexadienone. The reaction is quite similar to that observed for (4-MeOC$_6$H$_4$)Φ$_2$COH to give 4-bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone, of which the formation was best understood in term of the S$_N$Ar substitution of 4-methoxy group by hydroxide ion followed by deprotonation.[2]

**Bis(2,4,6-trimethoxyphenyl)carbenium Perchlorate.** When **2** was treated with a slight excess of perchloric acid in methanol at room temperature, dark-red crystals of **5** ($X = ClO_4$) were obtained. Compound **5** was considerably inert, even in hot methanol, although the color faded upon prolonged heating. In primary and secondary alcohols, however, the color faded much faster than in hot methanol to give white crystals of bis(2,4,6-trimethoxyphenyl)methane, $\Phi'_2CH_2$ (**6**). Such a reduction by alcohols is one of the characteristic reactions observed for triarylcarbenium salts of type [ArΦ$_2$C]ClO$_4$, and the aldehyde or ketone were detected as the by-product.[1,2] The related reductions of common triarylcarbenium ions by alcohol have been known in some cases.[3,4] Olah and Svoboda further reported that triphenylcarbenium ion was reduced by a variety of organic compounds, such as ethers, aldehydes, amines, and formic acid.[5]

The electronic spectrum (VIS) of **5** in 1,2-dichloroethane solution showed a well-formed absorption at $\lambda_{max}$, 521 nm (log $\varepsilon$, 4.71). Analogous spectra were observed for **5** in some alcohols with no significant shift of $\lambda_{max}$ (518—520 nm), although the absorbance decreased during the spectral measurements due to reduction to form **6**. The half-lives ($t_{1/2}$) of **5** were measured in these alcohols (Table 3), which showed that **5** was more labile in secondary alcohols, such as 2-propanol and 2-butanol, than in primary alcohols. In other words, the reduction of **5** was not affected by the steric effect of alcohol, while those of [ArΦ$_2$C]ClO$_4$ were affected.[1]

With a hope to measure the p$K_{R^+}$ value, **2** was added to aqueous hydrochloric acid, and a dark-red suspension was obtained, immediately. When the suspension was heated in order to obtain the solution, the color gradually faded to give colorless crystals of tris(2,4,6-trimethoxyphenyl)methane, $\Phi'_3CH$ (**7**). Analogous reactions to give **7** were observed in methanol containing a slight excess of hydrochloric acid or nitric acid in place of perchloric acid. In contrast, when **2** was treated with hydrochloric acid in hot dimethyl sulfoxide, crystals of Φ'H were obtained.

The reactions of **2** with acid may be understood by Eqs. 1, 2, 3, and 4.

$$\underset{\mathbf{2}}{\Phi'_2CHOH} + H^+ \rightleftharpoons \{\Phi'_2CH\text{-}O^+H_2\} \rightleftharpoons \underset{\mathbf{5}}{\Phi'_2CH^+} + H_2O \quad (1)$$

$$\underset{\mathbf{2}}{\Phi'CHOH} + H^+ \rightleftharpoons \{\Phi'(\Phi'H^+)CHOH\} \rightarrow \Phi'H + \Phi'CHO + H^+ \quad (2)$$

$$\Phi'_2CHO + H^+ + H_2O \rightarrow \Phi'H + HCO_2H \quad (3)$$

$$\underset{\mathbf{5}}{\Phi'_2CH^+} + \Phi'H \rightarrow \underset{\mathbf{7}}{\Phi'_3CH} + H^+ \quad (4)$$

When perchloric acid is used in methanol or water, the salt of **5** separates from solutions due to poor solubility. When hydrochloric acid or nitric acids are used, the salts of **5** are more soluble in these solvents. The formation of **7** can be understood by Eqs. 2, 3, and 4. Cleavages of Φ–C or Φ'–C bonds by acid have been reported for Φ'(R)CO,[6] Φ'CHO [Eq. 3],[7,8] and Φ$_3$CH.[9] The formation of Φ'H was confirmed by isolation from a reaction mixture of **2** in hot dimethyl sulfoxide containing hydrochloric acid, as mentioned above. It also was confirmed that **2** reacted very fast with $\Phi'$H in methanol containing only a catalytic amount of hydrochloric acid (0.1 molar amount) to give **7** in a quantitative yield. The difference of reactivity of **2** between in methanol and in dimethyl sulfoxide may be attributed to a difference of the solvent basicity; more basic dimethyl sulfoxide would reduce the acidity of added acid, or it would coordinate to **5** to reduce the reactivity with $\Phi'$H. A related solvent effect of dimethyl sulfoxide has been observed for $\alpha,\alpha,\alpha',\alpha'$-tetrakis(2,6-dimethoxyphenyl)-1,4-benzenedimethanol, *p*-$HOC\Phi_2C_6H_4C\Phi_2OH$.[10]

It is worth noting here concerning our preliminary results that bis(2,6-dimethoxyphenyl)methanol, $\Phi_2CHOH$, did not form isolable diarylcarbenium salt in methanol, but reacted with acid to give mixtures containing $\Phi_2CHOMe$, $\Phi_2CH_2$, and/or $\Phi_2CHOH$. On the other hand, bis(2,4-dimethoxyphenyl)methanol reacted with acid to give a complex mixture of polymeric compounds.

**NMR Spectra.** The $^1$H NMR spectra of 2,4,6-trimethoxyphenyl derivatives (Table 1) were quite simple, giving three sharp singlets due to the phenyl protons. The 3,5-H proton resonance was observed in a region of $\delta$ =6.2—6.0. The 4-methoxy and 2,6-dimethoxy proton resonances were observed with a 3 : 6 ratio of the intensity in the region of $\delta$ = 4.1—3.4. Due possibly to the cationic property, these methoxy proton resonances of **3** were observed at lower magnetic fields than those of **1**. The spectrum of **4** showed, in addition to the resonances due to $\Phi'$-groups, a new singlet at such a high magnetic field as $\delta$ =5.49 due to 2,6-H, reflecting the alkenic property, and a singlet at $\delta$ =3.33 due to 3,5-dimethoxy protons. All of the resonances of **5** were observed at the lowest magnetic fields in accordance with the cationic property and with a number of $\Phi'$-groups less than **3**. The unique resonance observed at $\delta$ =8.90 must be assigned to the proton bonded to the central cationic carbon. The resonance of diphenylcarbenium ion ($Ph_2C^+$–*H*) has been observed at $\delta$ =9.81 (measured in fluorosulfonic acid solution).[11]

The $^{13}$C NMR spectra of 2,4,6-trimethoxyphenyl derivatives (Table 2) showed six resonances due to $\Phi'$-group carbon atoms. The *ortho*-carbon (C-2,6) and *para*-carbon (C-4) resonances were observed at such a low magnetic field as $\delta$ =170—154 owing to the presence of the methoxy substituent. The *ipso*-carbon (C-1) resonance was observed in a region of $\delta$ =121—112, the *meta*-carbon (C-3,5) resonances was observed in such a narrow region of $\delta$ =93—90, and the 4-methoxy and 2,6-dimethoxy carbon resonances were observed in the region of $\delta$ =58—55. The resonance attributable to the central cationic carbon of **3** could not be observed, although those of aryl-bis(2,6-dimethoxyphenyl)carbenium ions $(XC_6H_4)\Phi_2C^+$ have been observed at $\delta$ =192.1 (X=H), 189.3 (4-Cl), 185.7 (2-MeO), 176.5 (4-

Table 3. Half-Lives ($t_{1/2}$) of **5** in Alcohols

| RR′CHOH | $t_{1/2}$/min | RR′CHOH | $t_{1/2}$/min |
|---|---|---|---|
| MeOH | 300 | *i*-PrOH | <1 |
| EtOH | 55 | *n*-BuOH | 50 |
| *n*-PrOH | 85 | *s*-BuOH | 6 |

Condition: **5** ($8.0\times10^{-5}$ M) in RR′CHOH in UV cell at 20 °C; the reactions were followed by VIS spectra at 518—520 nm.

Table 1. $^1$H NMR Spectral Data[a] for 2,4,6-Trimethoxyphenyl Derivatives

| Compounds | 3,5-H[b] | 4-MeO[c] | 2,6-(MeO)$_2$[d] | Others |
|---|---|---|---|---|
| **1** | 6.06 | 3.76 | 3.46 | 6.66 (s, 1H, OH). |
| **2** | 6.09 | 3.77 | 3.74 | 6.51 (d, *J* = 10 Hz, 1H, C<u>H</u>OH),<br>5.38 (d, *J* = 10 Hz, 1H, CHO<u>H</u>). |
| **3** | 6.05 | 3.99 | 3.59. | |
| **4** | 6.04 | 3.80 | 3.54 | 5.49 (s, 2H, 2,6-H),<br>3.33 [s, 6H, 3,5-(MeO)$_2$]. |
| **5** | 6.19 | 4.12 | 3.97 | 8.90 (s, 1H, C$^+$–H). |
| **6** | 6.09 | 3.76 | 3.69 | 3.84 (s, 2H, CH$_2$). |
| **7** | 6.09 | 3.75 | 3.46 | 6.26 (s, 1H, Ar$_3$C–H). |

a) In CDCl$_3$ ($\delta$/ppm; s = singlet, d = doublet). b) Singlet. c) Singlet. d) Singlet.

Table 2. $^{13}$C NMR Spectral Data[a] for 2,4,6-Trimethoxyphenyl Derivatives

| Compounds | $\delta$/ppm | |
|---|---|---|
| **1** | 159.2, 158.3, 120.4, 92.5; | 77.8 (COH), 56.2 and 55.1 (MeO). |
| **2** | 159.8, 159.0, 114.0, 91.4; | 64.0 (CHOH), 56.0 and 55.2 (MeO). |
| **3** | 169.9, 164.1, 118.8, 91.2; | — (C$^+$), 56.7 and 56.5 (MeO). |
| **4** | 160.8, 158.6, 117.2, 90.9; | 188.0 (C=O), 165.2, 142.3, 125.8, 100.6,<br>56.3, 55.2, 55.1. |
| **5** | 166.6, 154.0, 115.5, 92.0; | 175.5 (C$^+$–H), 57.7 and 57.3 (MeO). |
| **6** | 159.3, 158.7, 112.1, 91.7; | 56.1 and 55.2 (MeO), 16.7 (CH$_2$). |
| **7** | 160.0, 158.2, 117.3, 93.0; | 56.9 and 55.1 (MeO), 28.8 (Ar$_3$<u>C</u>H) |

a) In CDCl$_3$; in order of C-2,6 and/or C-4, C-1, and C-3,5 of $\Phi'$-group; and others.

MeO), and 161.2 (4-$Me_2N$).[1,2] The resonance of **5** was observed at $\delta = 175.5$, which was $\delta = 24.7$ to a higher field than that of diphenylcarbenium ion ($\delta = 200.2$).[12] The higher field shift is consistent with a lower positive charge on the carbenium carbon in **5** than in the diphenylcarbenium ion.

The spectrum of **4** showed a resonance at such a low magnetic field as $\delta = 188$, which must be assigned to the carbonyl carbon.

## Experimental

**Physical Measurements.** The NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model 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. UV-vis spectra were recorded using a Shimadzu UV-160 spectrophotometer.

The $^1$H- and $^{13}$C NMR spectral data for compounds **1**—**7** are summarized in Tables 1 and 2.

**Preparation of Tris(2,4,6-trimethoxyphenyl)methanol (1).** To a solution of 1,3,5-trimethoxybenzene (17.2 g, 103 mmol) in toluene (100 ml) was added a 15% hexane solution of butyllithium (60 ml, 96 mmol) at 0 °C, followed by *N*,*N*,*N*′,*N*′-tetramethylenediamine (0.5 ml). The mixture was stirred at 0 °C for 2 h to give a white suspension of 2,4,6-trimethoxyphenyllithium. To this suspension was added diphenyl carbonate (6.72 g, 31 mmol) dissolved in toluene (100 ml). The mixture was heated at 80 °C for 12 h to give a brown solution. It was washed with water repeatedly, and hexane (200 ml) was added at −30 °C to precipitate light-brown crystals of **1** in 80% yield based on diphenyl carbonate; mp 147—149 °C. The analytical sample was obtained by recrystallization from ethanol to give yellow crystals; mp 147—148 °C; IR 3500 cm$^{-1}$ (OH). Found: C, 63.27; H, 6.54%. Calcd for $C_{28}H_{34}O_{10}$: C, 63.39; H, 6.46%. This compound is soluble in acetone, methanol, hot ethanol, hot 2-propanol, and hot toluene, and insoluble in diethyl ether, hexane, and water. It is soluble in 1 M hydrochloric acid (0.25 g/50 ml) on heating to form a dark-purple solution.

**Preparation of Bis(2,4,6-trimethoxyphenyl)methanol (2).** To a solution of 1,3,5-trimethoxybenzene (7.6 g, 45 mmol) in diethyl ether (30 ml) was added a 15% hexane solution of butyllithium (27 ml, 43 mmol) at 0 °C, followed by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.15 ml). The mixture was stirred at 0 °C for 2 h to give a white suspension of 2,4,6-trimethoxyphenyllithium. To this suspension was added ethyl formate (1.6 ml, 20 mmol) dissolved in dry diethyl ether (40 ml). The mixture was stirred at room temperature for 4 h to give a brown solution. Methanol (30 ml) was added, and the mixture was concentrated to ca. one third. Hexane (50 ml) was added, and the mixture was cooled to −30 °C to give white crystals of **2** in 67% yield; mp 150—151 °C after recrystallization from ethanol; IR 3500 cm$^{-1}$ (OH); MS *m*/*z* (%) 364 (M$^+$; 20), 168 ($\Phi'H^+$; 100). Found: C, 62.45; H, 6.62%. Calcd for $C_{19}H_{24}O_7$: C, 62.63; H 6.64%. This compound is very soluble in benzene, chloroform, and acetone, soluble in hot alcohols, and poorly soluble or insoluble in diethyl ether, hexane, 1 M aqueous sodium hydroxide, and water. It forms a dark-red suspension in 1 M hydrochloric acid.

**A Reaction of Tris(2,4,6-trimethoxyphenyl)methanol (1) with Perchloric Acid to Give Tris(2,4,6-trimethoxyphenyl)carbenium Perchlorate (3).** To a suspension of **1** (0.528 g, 1 mmol) in 2-propanol (10 ml) was added 60% perchloric acid (0.12 ml, 1.2 mmol). The resultant black suspension was stirred at room temperature for 2 h, or was heated for a short period to dissolve; the mixture was then cooled at −30 °C to give very dark-purple crystals of **3** in 97% yield. The analytical sample was obtained by recrystallization from 2-propanol in air; mp 174—175 °C; IR 1100 cm$^{-1}$ ($ClO_4$); UV-vis ($ClCH_2CH_2Cl$) 232 (log $\varepsilon$, 4.24), 286 (3.99), ca. 450 (shoulder), and 586 (4.48) nm. Found: C, 54.60; H, 5.33%. Calcd for $C_{28}H_{33}ClO_{13}$: C, 54.86; H, 5.43%. This salt was recovered from ethanol after heating at 60 °C for 48 h in 85% yield.

**A Reaction of Tris(2,4,6-trimethoxyphenyl)methanol (1) to Give 4-Bis(2,6-dimethoxyphenyl)methylene-3,5-dimethoxy-2,5-cyclohexadienone (4).** Compound **1** (0.528 g, 1 mmol) is soluble in 1 M hydrochloric acid (100 ml) to form a dark-purple solution. To this was added 1 M sodium hydroxide (100 ml) to give light-brown precipitates of **4** in 89% yield. The analytical sample was obtained by recrystallization from acetone; mp 216—218 °C; IR 1635 cm$^{-1}$ (C=O). Found: C, 64.81; H, 6.13%. Calcd for $C_{27}H_{30}O_9$: C, 65.05; H, 6.07%.

**A Reaction of Bis(2,4,6-trimethoxyphenyl)methanol (2) with Perchloric Acid to Give Bis(2,4,6-trimethoxyphenyl)carbenium Perchlorate (5).** To a suspension of **2** (0.364 g, 1 mmol) in methanol (10 ml) was added 60% perchloric acid (0.12 ml, 1.1 mmol). The resultant dark-red suspension was stirred at room temperature for 2 h to give dark-red crystals, which were separated by filtration in air to give **5** in 74% yield. Recrystallization from methanol gave the analytical sample; mp 201—202 °C; IR 1080 cm$^{-1}$ ($ClO_4$); UV-vis ($ClCH_2CH_2Cl$) 225 nm (log $\varepsilon$, 4.19), 258 (4.07), 283 (4.09), ca. 310 (shoulder), and 521 (4.71). Found: C, 51.11; H, 5.32%. Calcd for $C_{19}H_{23}ClO_{10}$: C, 51.07; H 5.19%. This salt is soluble in acetone, chloroform, 1,2,-dichloroethane, dimethyl sulfoxide, nitromethane, hot methanol, and hot ethanol, although it decomposes or reacts in some of these solvents.

In analogous manners, **5** was obtained in 77 and 69% yields from ethanol and 2-propanol, respectively.

**A Reaction of Bis(2,4,6-trimethoxyphenyl)methanol (2) to Give Bis(2,4,6-trimethoxyphenyl)methane (6).** A dark-red suspension of **2** (0.5 mmol) in 2-propanol (5 ml) containing 1 M hydrochloric acid (0.55 ml) was heated at 50 °C for 1 h to give light-yellow solution. Water (20 ml) was added to give white precipitates of **6** in 77% yield; mp 106—107 °C; MS *m*/*z* (%) 348 (M$^+$; 95), 151 (100). Found: C, 65.47; H, 6.99%. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94%. This compound is soluble in acetone, benzene, chloroform, diethyl ether, hot methanol, hot ethanol, hot 2-propanol, and hot hexane.

**Reactions of Bis(2,4,6-trimethoxyphenyl)methanol (2) to Give Tris(2,4,6-trimethoxyphenyl)methane (7). In 1 M Hydrochloric Acid.** When **2** (1 mmol) was added to 1 M hydrochloric acid (10 ml) at 60 °C, it formed a dark-red suspension. It was heated at 60 °C for 1 d to give crystals, which were recrystallized from acetone-hexane to give white crystals of **7** in 0.31 mmol; mp 204—206 °C; MS *m*/*z* (%) 514 (M$^+$; 50), 346 ($Ar_2C^+$; 100). Found: C, 65.20; H, 6.64%. Calcd for $C_{19}H_{24}O_6$: C, 65.36; H, 6.66%. This compound is soluble in acetone, benzene, chloroform, and hot methanol.

**In Methanol Containing Hydrochloric Acid or Nitric Acid.** To a suspension of **2** (1 mmol) in methanol (10 ml) was added 6 M hydrochloric acid (0.2 ml, 1.2 mmol). The resultant dark-red suspension was stirred at room temperature for 2 h to give a dark-red solution. It was cooled at −30 °C to give brown crystals of **7** in 0.20 mmol yield.

In an analogous manner as described above, a treatment of **2** (1 mmol) with 6 M nitric acid (0.2 ml, 1.2 mmol) resulted to give **7** in 0.26 mmol yield.

**In Presence of 1,3,5-Trimethoxybenzene.** To a suspension of **2** (5 mmol) in methanol (300 ml) was added 1,3,5-trimethoxybenzene (0.924 g, 5.5 mmol) and 1 M hydrochloric acid (0.5 ml). The resultant dark-red suspension was stirred at room temperature for 1 h and was cooled at −30 °C to give crystals of **7** in 92% yield (4.6 mmol).

**A Reaction of Bis(2,4,6-trimethoxyphenyl)methanol (2) in Dimethyl Sulfoxide Containing Hydrochloric Acid to Give 1,3,5-Trimethoxybenzene.** To a suspension of **2** (1 mmol) in dimethyl sulfoxide (10 ml) was added 1 M hydrochloric acid (1 ml) to give a dark-red suspension. It was heated at 60 °C to give a red solution. After 1 h, water (20 ml) was added to give brown crystals of 1,3,5-trimethoxybenzene in less than 0.7 mmol yield, which are contaminated with **2**, as characterized by $^1$H NMR and GC-MS spectra; MS of $\Phi'$H *m*/*z* (%) 168 (M$^+$; 98), 139 ($C_7H_8O_3$; 100).

When 12 M hydrochloric acid (1 ml) was used, crystals of 1,3,5-trimethoxybenzene were obtained in pure form in 0.5—0.7 mmol yield.

**Measurements of Half-Lives of Bis(2,4,6-trimethoxyphenyl)carbenium Perchlorate (5) in Alcohols.** VIS spectra at 520 nm of **5** in alcohols (MeOH, EtOH, PrOH, *i*-PrOH, BuOH, *s*-BuOH; $8\times10^{-5}$ M) were measured at 20 °C. The decreases of absorbance at 518—520 nm were analyzed to give the half-lives of **5** in these alcohols. The results are summarized in Table 3.

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