Triarylcarbenium Salts Highly Reducible by Primary Alcohols

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A series of triarylmethanols bearing *o*-methoxyl groups (**1a**: $[2,6\text{-}(MeO)_2C_6H_3]_3COH$, **1b**: $(2\text{-}MeOC_6H_4)[2,6\text{-}(MeO)_2C_6H_3]_2COH$, **1c**: $Ph[2,6\text{-}(MeO)_2C_6H_3]_2COH$, **1d**: $[2,5\text{-}(MeO)_2C_6H_3]_3COH$, **1e**: $Ph_2[2,6\text{-}(MeO)_2C_6H_3]COH$) were prepared. Corresponding carbenium salts, $[Ar_3C]X$ **2a**—**c**, were isolated by short-period treatments of Ar_3COH **1a**—**c** with a slight excess of acid in some bulky alcohols, such as 2-propanol or 2-methyl-1-propanol. The high basicity of **1a**—**c** was explained by through-space interactions of a pair of 2p electrons of an *o*-methoxyl oxygen with an empty 2p orbital of the resulting carbenium carbon. In ethanol, 1-butanol or 3-methyl-1-butanol, **1c**, as well as **2c**, was reduced under very mild conditions to triarylmethane, $Ar_3C\text{–}H$ **3c**, and in other bulkier alcohols it was reduced under more forcing conditions. The formations of aldehyde or ketone, the by-product, were confirmed in some cases. Compounds **1a**,**b**,**d**,**e**, as well as **2a**,**b**, reacted in analogous manners under more forcing conditions. The reaction rates in several alcohols increased in the order **2a**<**2b**<**2c**, and the reaction rates of alcohol for **2c** decreased in the order ethanol> 3-methyl-1-butanol> 1-butanol> 2-propanol> methanol> 2-butanol> 2-methyl-1-propanol. Compounds **2b**,**c** were also reduced in tetrahydrofuran, and formed xanthene derivatives in dimethyl sulfoxide or in water.

It is expected that triphenylcarbenium ions bearing an *o*-methoxyl substituent are stabilized by a π-electron resonance. In 1963, Martin and Smith studied tris(2,6-dimethoxyphenyl)methanol $[2,6\text{-}(MeO)_2C_6H_3]_3COH$ **1a**, and found its unusual basicity (pK_{R^+},>6.5) compared with those of tris(4-methoxyphenyl)methanol ($pK_{R^+}=0.82$) or 9-(2,6-dimethoxyphenyl)-9-xanthenol ($pK_{R^+}=2.5$).[1)] Later on, the carbenium salts, $[\{2,6\text{-}(MeO)_2C_6H_3\}_3C]X$ **2a** ($X=HCl_2$, ClO_4), were isolated and well-characterized;[2—5)] the radical $[2,6\text{-}(MeO)_2C_6H_3]_3C\cdot$ is also isolable.[6—8)]

In contrast, it is also expected that the presence of an *o*-methoxyl substituent in the phenyl group would sterically hinder the coplanar orientation of such *o*-methoxy-substituted phenyl groups to prevent any effective overlap of their π-orbitals with the p-orbital of the central cationic carbon. In relation to this expectation, Smith et al. have found that **2a** undergoes a very rapid exchange reaction of 3,5-protons with added protons.[3)] They reasoned this observation by the fact that two positive charges in the intermediate dication are separated into two π systems perpendicular to each other.

If the second expectation is also correct, there is a possibility that some triarylmethanol with a smaller number of *o*-methoxyl substituents is more basic than **1a**. In addition, while the high basicity of triarylmethanol is in favor of carbenium-ion stabilization, the carbenium ion must be both energetically stable and unfavorable for the following reactions, such as the one shown in Eq. 1. The steric effect can also influence the reactivity of the carbenium ion, and there are a variety of possibilities that some triarylmethanol with a certain number of *o*-methoxyl substituents is more reactive than **1a** and, at the same time, than common triphenylmethanol.

$$\underset{\mathbf{1}}{Ar_3C\text{–}OH}+H^+\rightleftharpoons\underset{\mathbf{2}}{[Ar_3C]^+}\xrightarrow{\text{in } RCH_2OH}\underset{\mathbf{3}}{Ar_3C\text{–}H}+RCHO \qquad (1)$$

As an extension of our own chemistry on 2,6-dimethoxyphenyl derivatives,[9)] we were originally interested in comparing the relative properties of such triarylmethanols. We report here in detail on the unexpected reactivity of some of these triarylmethanols in acidic solution. The preliminary results have been reported elsewhere.[10)]

Results and Discussion

Reactions of Triarylmethanol with Acid. Light-yellow crystals of **1a** dissolved in alcohols in air to form purple (methanol), light-purple (ethanol), or colourless (2-propanol) solutions; it formed a purple suspension in water. These properties are in accord with its high basicity,[1)] suggesting the formation of carbenium ion **2a** in equilibrium, even in neutral conditions. In fact, the colour of the solutions deepened on bubbling with carbon dioxide. Dark-purple crystals of **2a** ($X=ClO_4$) could be obtained from a 2-propanol solution of **1a** by adding only a slight excess of perchloric acid. The related triarylmethanols ($(2\text{-}MeOC_6H_4)[2,6\text{-}(MeO)_2C_6H_3]_2COH$ **1b**, $Ph[2,6\text{-}(MeO)_2C_6H_3]_2COH$ **1c**, $[(2,5\text{-}(MeO)_2C_6H_3]_3COH$ **1d**, and $Ph_2[2,6\text{-}(MeO)_2C_6H_3]COH$ **1e**) were treated with acid in 2-propanol. Both **1b** and **1c** also reacted immediately upon mixing with a slight excess of acid ($HClO_4$, HBF_4) to give dark-purple solutions, and crystals of the carbenium salts **2b** and **2c** ($X=ClO_4$, BF_4) were obtained in quantitative yields upon cooling the solutions. In contrast, we could not isolate the carbenium salts from **1d** or **1e**, even in cold alcohols, and mixtures containing the reduced compound, Ar_3CH **3d** or **3e**, were always obtained (see blow).

Compound **2a** ($X=ClO_4$) is hydrolytically stable, even in hot 2-propanol at 60 °C for 12 h. Both **2b** and **2c** are hydrolyzable in dilute solutions of polar solvents, or they react differently depending upon the solvent (see below). Compounds **2a**—**c** are inert in 1,2-dichloroethane at ambient temperature, and their UV spectra could be measured for this solution, as summarized in Table 1. The pK_{R^+} values for **1b** and **1c** were not measured because of the reactivity of **2b** and **2c** in polar solvents; however, since their carbenium salts are more labile toward hydrolysis than **2a**, it is apparent that **1b** and **1c** are less basic than **1a**.

The highest basicity of **1a** among **1a**—**e** is astonishing in spite of the expected steric disadvantage to prevent effective overlaps of their π-orbitals with the p-orbital of the central cationic carbon in the resulting carbenium ion. Consequently, we have to assume an alternative cause for such a basicity of **1a**. We assume that there is a through-space overlap of a pair of 2p electrons of a methoxyl oxygen with an empty 2p orbital of the central carbon in **2a**. If this assumption is correct, the basicity of **1a** is well-understood as caused by six such interactions on both sides of the coordination plane in **2a**. Kahr et al. reported that the crystal structure of **2a** ($X=BF_4$) is of a propeller shape with the three aryl groups twisted with angles of 32.6, 46.1, and 48.9° out of the coordination plane of the central atom.[5] An interesting observation (cited in the paper) is that the methoxyl groups are arranged in such a way that they form a pair of nucleophilic oxygen pockets situated on either side of the mean molecular plane with the lone-electron pairs projecting toward the center of small cavities. Using the atomic positional parameters reported there, we obtained the six MeO···C (central) distances of **2a** as 2.771, 2.769, 2.758, 2.757, 2.776, and 2.779 Å. These distances are all much shorter than the sum of the van der Waals' radii (3.22 Å), and have a sufficient range of distances to expect any through-space interaction.

The concept of a through-space overlap of a pair of 2p electrons of a methoxyl oxygen has been proposed by McEwen et al. to explain the unusually high nucleophilicity of (2,6-dimethoxyphenyl)diphenylphosphine, in which an empty d-orbital of phosphorus atom is used to overlap.[11]

Reduction of Triarylcarbenium Salts by Alcohols. The triarylmethanol **1d** is poorly soluble in alcohols at ambient temperature, and the addition of an acid to the suspension resulted in a momental green coloration, followed by decoloration to give a light-brown suspension. Mixtures of **1d** and the reduced compound, $[2,5\text{-}(MeO)_2C_6H_3]_3CH$ **3d**, were always isolated, of which the relative ratio varied depending upon the reaction conditions. Compound **1e** also reacted in acidic alcohols in analogous manners to give mixtures of **1e** and the reduced compound, $Ph_2[2,6\text{-}(MeO)_2C_6H_3]CH$ **3e**, but without any clear coloration during the reaction. Interestingly, **1d** was more reactive in hot methanol and ethanol than **1e**, giving **3d** in quantitative yield in 2 h at 50 °C, while **1e** was more reactive in hot 2-propanol than **1d** to give **3e** with a half-life time of ca. 2 h at 50 °C.

In methanol containing a small amount of acid, even **1a**, as well as **2a**, reacted very slowly upon heating to give the reduced compound $[2,6\text{-}(MeO)_2C_6H_3]_3CH$ **3a**. **1b** reacted at ambient temperature to give $(2\text{-}MeOC_6H_4)[2,6\text{-}(MeO)_2C_6H_3]_2CH$ **3b** in 12 h, while **1c** reacted to give $Ph[2,6\text{-}(MeO)_2C_6H_3]_2CH$ **3c** in less than 2 h in quantitative yields.

In hot ethanol containing acid, **1a** also reacted to give mixtures of **2a** and the reduced compound **3a** in a variety of ratios, depending upon the reaction conditions. Compound **1b** reacted in acidic ethanol even at ambient temperature to give dark-purple solutions, followed during 24 h by the gradual formation of colourless crystals of the reduced compound **3b**. The reactions of **1c** in acidic ethanol was apparently much faster than **1b**, giving **3c** in less than two hours at ambient temperature. In 2-propanol on heating, **1c** was again most reactive among **1a**—**c** to give **3c**. In the absence of an acid, both **1b** and **1c** did not react in these alcohols for a prolonged period.

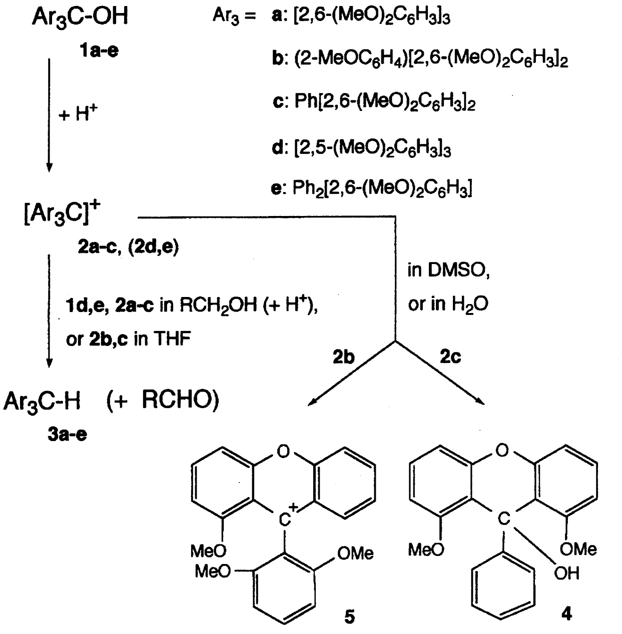
Inevitably, **2b** and **2c** also reacted in these alcohols in analogous manners to **1b** and **1c** to give **3b** and **3c**, respectively. Although compound **2c** ($X=ClO_4$) is less soluble in higher alcohols, it reacted in 1-butanol very fast when dissolved upon heating at 60 °C, and 1-butanal was found to be the sole by-product, as detected by GC and UV of the distillate. An analogous treatment of **2c** in 2-propanol gave **3c** and acetone in quantitative yields, as confirmed by UV and by the formation of 2,4-dinitrophenylhydrazone. The reactions together with those mentioned below are summarized in Scheme 1.

The related reduction of the arylcarbenium ion by alcohol has long been known.[12,13] Deeply related reductions have been either found or used in reactions with xanthene,[14] triphenylsilane,[2,15] ketone acetals,[16]

Table 1. The UV Spectral Data and the Half-Lives of **2a**—**2c** in Alcohols[a]

		2a	**2b**	**2c**
	λ_{max}/nm	525	532, (438)[b]	(525),[b] 479
Alcohols	$\log \varepsilon$	4.24	4.28	4.37
CH_3OH		72 h	83 min	20 min
CH_3CH_2OH		18 h	20 min	<5 min
$(CH_3)_2CHOH$		>300 h	200 min	12 min
$CH_3CH_2CH_2CH_2OH$		15 h	96 min	10 min
$CH_3CH_2(CH_3)CHOH$		No change	30 h	3 h
$(CH_3)_2CHCH_2OH$		No change	55 h	13 h
$(CH_3)_2CHCH_2CH_2OH$		No change	27 min	<5 min

a) At 25 °C. b) Shoulder.



Scheme 1.

ethers,[16,17] cycloheptatriene,[18] alkoxysilane,[19] formate anion,[20] anthracene,[21] and 1,1-diarylethylene.[21] The mechanism has been discussed by Olah and Svoboda,[22] in which they reported that the triphenylcarbenium ion also reacted with many ethers, aldehydes, amines, and formic acid.

Reactions of Triarylcarbenium Salt in Some Other Solvents than Alcohol. Both **2b** and **2c** reacted in tetrahydrofuran (THF) containing a small amount of acid to give **3b** and **3c** at ambient temperature, respectively. The reactivity of **2c** was faster than **2b**, such in alcohols, to complete in less than a few hours. The fate of an oxidized compound of THF is not clear at present; there is a possibility of the formation of a polymeric material.

In dimethyl sulfoxide (DMSO) containing acid, **2c** reacted at ambient temperature to give a mixture of 9-phenyl-1,8-dimethoxy-9-xanthenol **4** as the main product and **3c** in 30—40% yield. Analogous formations of 9-aryl-1,8-dimethoxy-9-xanthenol or 9-aryl-1,8-dimethoxy-9-xanthenium salt have been reported for **1a**, and the reaction mechanism has been discussed.[1—4] The formation of **3c**, the by-product, can be understood as resulting from the reduction of **2c** by dimethyl ether, which was produced during the formation of **4**. On the other hand, **2b** reacted much slower and in somewhat different ways to give dark-purple crystals of 9-(2,6-dimethoxyphenyl)-1-methoxy-9-xanthenium perchlorate **5**, a product derived by nucleophilic substitution of the 2-methoxyl group in the 2-methoxyphenyl group by one of the methoxyl oxygens in the 2,6-dimethoxyphenyl groups of **2b**. Due to the high π-electron density, the second 2,6-dimethoxyphenyl group in **2b** must be more inert than the 2-methoxyphenyl group. The predominant formation of **5**, rather than 9-(2-methoxyphenyl)-1,8-dimethoxy-9-xanthenium salt, thus supports the nucleophilic substitution mechanism proposed.[1—4] A small amount of **3b** was detected as the by-product.

In hot acidic water under atmospheric conditions, **2c** reacted slowly to give **4** in good yield. The dimethyl ether by-product must be removed into the atmosphere before it can react to reduce **2c**. Compound **1b** reacted in hot water to give **5**, also selectively.

Very interestingly, some preliminary results indicate that these reactions are somewhat accelerated in the dark. Detailed studies concerning the effect of light are in progress.

Consumption Rate of Carbenium Salts in Alcohols. For a better comparison, the consumption rates of carbenium salts **2a**—**c** in alcohols or of the triarylmethanols **1a**—**c** in alcohols containing acid ($HClO_4$ or CF_3COOH) were measured using the UV spectra; the results are summarized in Table 1 together with their spectral data. These reactions followed pseudo-first-order kinetics for **2a**—**c** or **1a**—**c**, and there was no essential difference in the rate between **2a**—**c** and **1a**—**c** in acidic alcohols. It was also found for **1c** in acidic methanol that the rate was affected little by the type of acid ($HClO_4$, HBF_4, HCl, H_2SO_4, HNO_3, CF_3COOH) or by the amount of perchloric acid between 1.2—5.0 equivalent. The latter observation indicates that **2c** formed almost quantitatively in the presence of a slight excess of acid, even in a large amount of methanol.

As observed above, rate measurements also showed that **2a** is least reactive, followed by **2b** and then **2c** in all of alcohols investigated. While the result can be easily understood in terms of a steric effect of the carbenium ion, it is also consistent with the stability order of these carbenium ions (as mentioned above). The rate ratio of **2a**,**b**,**c** is 216 : 4 : 1 in methanol and is 90 : 10 : 1 in 2-butanol, while it is >1500 : 17 : 1 in 2-propanol. For the smallest four alcohols listed in Table 1, the reactivity is in the order 1-butanol > ethanol > methanol > 2-propanol for **2a**, but it is in the order ethanol > methanol > 1-butanol > 2-propanol for **2b** and ethanol > 1-butanol > 2-propanol > methanol for **2c**. Noteworthy is the fact that methanol is less reactive than some other bulkier alcohols; it is expected that the electronic effect is a dominant factor for the reactions. On the other hand, 2-propanol is less reactive than primary alcohols, which may imply that a steric effect is also an important factor. In connection with the present investigation, we have recently reported on the properties of tris(2,6-dimethoxyphenyl)borane, an isoelectronic compound of **2a**, and its derivatives.[23] The borane formed isolable 1 : 1 adducts with ammonia and some primary amines, but not with tertiary amines, secondary amines or *s*-alkylamines. Since one of the *s*-alkylamines is isoelectronic with 2-propanol, the poor reactivity of **2a** with 2-propanol can undoubtedly be understood by a steric reason.

Among the three C_4-alcohols listed in Table 1, 1-butanol is apparently far more reactive than the other two alcohols. Interestingly, 2-butanol is more reactive with **2b** and **2c** than 2-methyl-1-propanol; this result may indicate that a steric effect at the 2-position of alcohol influences more dominantly than that at the 1-position, especially for the reaction with **2c**. To our great surprise, 3-methyl-1-butanol is highly reactive with **2c**. It is much more reactive than the other alcohols listed in Table 1, except for ethanol. Compound **2b** is also highly reactive in this alcohol, although **2a** did not react for several days. Its high reactivity was confirmed by a separate experimental: namely, when **2c** ($X=ClO_4$) was dissolved in this alcohol at 60 °C for only a short period (less than 30 min), **3c** was obtained in 94% yield. Under analogous conditions in 2-butanol (4 h), 2-methyl-1-propanol (24 h), and 2-methyl-1-butanol (4 h), mixtures of **2c** and **3c** were isolated in a variety of ratios. In 1,3-butanediol, which is isoelectronic with 3-methyl-1-butanol, **2c** also reacted very fast to give **3c** in 87% yield in 30 min. In 2-methyl-2-propanol (*t*-BuOH), **2c** was inert, even after 24 h of heating at 60 °C.

The mechanism proposed by Olah and Svoboda[22] involves an initial interaction of an *n*-donor atom with a phenyl ring followed by the formation of a two-electron, three-center bond at the carbenium center, $Ar_3C^{+}\cdots H{-}C$; it seems to be supported by Huszthy et al. for the reaction of **2a**.[4] For the present reductions of **2a**—**c**, we rather prefer a simple hydride transfer mechanism.[20] This is because the hydride-donating ability of alcohol must be reduced by such an interaction. In addition, if such an interaction could occur for **2a**, for example, solvent alcohols should react to give any derivatives in which some of the 2,6-dimethoxyl groups in **2a** were substituted by the alcohol alkoxide. The hydride source for the formation of 9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-9-xanthene reported by Huszthy et al.[4] must be free dimethyl ether, as mentioned above for the thermal reaction of **2b**,**c** in DMSO to produce **3b**,**c**.

An explanation for the reactivity order of primary alcohols, such as ethanol > 3-methyl-1-butanol (> methanol) > 1-butanol for **2b**, is quite difficult to make. For a detailed comparison, it seems necessary to use any suitable solvent for the reactions in order to make the solvation effect identical. The solvent must dissolve **2a**—**c** without decomposition, and it must be inert in the presence of an acid during the reaction of **2a**—**c** with alcohols.

Preparation of Triarylmethanols. It is worth noting here the preparations of triarylmethanol **1a**—**c**, since they have not always been successful.[24] Some of them have been prepared without any statement concerning special care.[8] It is advisable, first of all, that the use of alkyl esters as the starting compound should be avoided, since a variety of alkoxy derivatives, such as alcohols or ethers produced during the preparation, might react with **1a**—**c** in the presence of an acid or of carbon dioxide in air. Even though **1a** is the least reactive, the intermediate produced during the preparation should be reactive. We have been able to prepare **1a** most successfully using diphenyl carbonate as the starting compound. However, both **1b** and **1c** could be prepared using methyl *o*-anisate or ethyl benzoate in reasonable yields, where special care was paid, as follow. Namely, the use of ethers as the solvent should be avoided for the same reason as mentioned above. We have used hydrocarbons, such as benzene or toluene, as the solvent for the reaction of butyllithium in hexane with 1,3-dimethoxybenzene, although only a catalytic amount of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was added to accelerate the reaction. TMEDA might also reduce **1a**—**c**. Finally, the use of an acid should be avoided to neutralize the reaction mixture. In the presence of a catalytic amount of acid, **1a**—**c** are often soluble in water to form carbenium salt; they decompose to give xanthenium derivatives, and/or they react with a variety of organic compounds.

The solubility of triarylmethanols in alcohols decreases in the order **1a**≈**1c**>**1b**>**1e**>**1d**; they are less soluble in alcohols with a longer alkyl chain. In acetone and aromatic hydrocarbons, all of them are quite soluble. In diethyl ether, the solubility decreases in the order **1c**≈**1e**>**1a**>**1b**≈**1d**, and most of them are poorly soluble in paraffins and in neutral water.

Experimental

Physical Measurements. NMR spectra were recorded in CDCl$_3$ using a JEOL (JNM-GX-270) spectrometer. IR spectra were recorded for Nujol mull using a Shimadzu (FTIR-4200) spectrophotometer. UV spectra were recorded using a Shimadzu (UV-160) spectrophotometer.

The ^{1}H and ^{13}C NMR spectral data are shown in Tables 2 and 3, respectively.

Preparation of Triarylmethanols. [2,6-(MeO)$_2$C$_6$H$_3$]$_3$COH, 1a. A suspension of 2,6-dimethoxyphenyllithium, prepared from a 15% hexane solution of butyllithium (16 ml, 25.6 mmol), resorcinol dimethyl ether (3.5 ml, 27 mmol), and *N,N,N'N'*-tetramethylethylenediamine (TMEDA) (0.1 ml) at a temperature 0—20 °C under argon, was diluted with benzene (60 ml), and diphenyl carbonate (1.76 g, 8.2 mmol) was added. The mixture was heated to reflux for 28 h to give a light-orange solution. After it was washed with cold water (30 ml×3), the volatile materials were removed under reduced pressure. The residue was recrystallized from hexane to give light-yellow crystals of **1a** in 75% yield; mp 160—161 °C (reported, 165.2—165.9, 166 °C);[1,8] IR 3500 cm^{-1} (O–H). This compound is very soluble in methanol (to form a purple solution in air), ethanol (to form a pale-purple solution), acetone, chloroform, and benzene, soluble in hot 2-propanol, hot hexane, diethyl ether, and insoluble in hot water (light purple suspension).

(2-MeOC$_6$H$_4$)[2,6-(MeO)$_2$C$_6$H$_3$]$_2$COH, 1b. A 2,6-dimethoxyphenyllithium suspension was prepared as mentioned above. It was diluted with benzene (40 ml) and methyl *o*-anisate (1.5 ml, 10 mmol) was added. After the suspension was stirred at room temperature for 7 h, it was washed with cold water to give a clear organic solution. It was then concentrated under reduced pressure. The residue was washed with hexane and recrystallized from 2-propanol to give white crystals of **1b** in 80% yield; mp 152—153 °C; IR 3480 cm^{-1}. Anal. (C$_{24}$H$_{26}$O$_6$) C, H. Compound **1b** is very soluble in acetone, benzene, THF and methanol. It can be recrystallized from 2-propanol, and is poorly soluble in diethyl ether and hexane.

Ph[2,6-(MeO)$_2$C$_6$H$_3$]$_2$COH, 1c. A suspension of 2,6-dimethoxyphenyllithium, prepared as above, was diluted with benzene (30 ml) followed by the addition of ethyl benzoate (1.5 ml, 10 mmol) at 0 °C under argon. The mixture was stirred at room temperature for 16 h; the resultant mixture was washed with water. The organic layer was concentrated to dryness, the residue was washed with hexane, and the resultant white solid was recrystallized from 2-propanol or from hexane to give **1c** in 80—90% yield; mp 102—103 °C (reported,[8] 107 °C); IR 3480 cm^{-1} (OH); UV 241 (log *ε*, 3.32), 275 (3.40) nm. Anal. (C$_{23}$H$_{24}$O$_5$) C, H. This compound is very soluble in methanol, ethanol, acetone, tetrahydrofuran, diethyl ether, and chloroform, soluble in hot 2-propanol and hexane, and insoluble in hot water.

[2,5-(MeO)$_2$C$_6$H$_3$]$_3$COH, 1d. *p*-Dimethoxybenzene (4.84 g, 35 mmol), diethyl ether (35 ml), and 15% hexane solution of butyllithium (20.6 ml, 33 mmol) were mixed at 0 °C under argon, followed by the addition of TMEDA (0.15 ml). The mixture was stirred at room temperature for 2 h to give a yellow suspension. After diethyl carbonate (1.2 ml, 10 mmol) was added at 0 °C, the mixture was stirred at room temperature for 15 h. Methanol (35 ml) was added at 0 °C, and the mixture was concentrated to ca. a third volume. The resultant precipitates were recrystallized from 2-propanol to give white crystals of **1d** in 60—75% yield; mp 132—133 °C (reported,[25] 136 °C); IR 3500 cm^{-1} (OH). This compound is very soluble in benzene, acetone, and dichloromethane, soluble in hot methanol and ethanol, but poorly soluble in 2-propanol, diethyl ether, and hexane.

Ph$_2$[2,6-(MeO)$_2$C$_6$H$_3$]COH, 1e. To a suspension of 2,6-dimethoxyphenyllithium, prepared as above in a 30 mmol scale, was added dry diethyl ether (30 ml) followed by benzophenone (5.8 g, 32 mmol) at 0 °C under argon; the mixture was then stirred at room temperature for 2 h. Methanol (40 ml) was added, and the mixture was kept at −30 °C to give white crystals of **1e** in 80—70% yield; mp 131—132 °C (recrystallized from 2-propanol) (reported,[8] 137 °C); IR 3480 cm^{-1}. This compound is very soluble in benzene, acetone, and dichloromethane, soluble in methanol, ethanol, and 2-propanol, but poorly soluble in hexane and water.

Isolation of Triarylcarbenium Salts. [{2,6-(MeO)$_2$C$_6$H$_3$}$_3$C]ClO$_4$, 2a. A suspension of **1a** (0.880 g, 2 mmol) in 2-propanol (40 ml) containing 60% aqueous perchloric acid (0.24 ml, 2.2 mmol) was warmed for a minimum period to give a dark-purple solution. Upon cooling to −30 °C, it gave dark-purple crystals of **2a** in 94% yield; mp 188—189 °C; IR 1100 cm^{-1} (ClO$_4$); UV 525 nm (log *ε*, 4.24) [reported,[1] 522 nm (log *ε*, 4.25)]; ^{1}H NMR chemical shifts were quite close to those reported for [Φ_3C]HCl$_2$.[4]

[(2-MeOC$_6$H$_4$){2,6-(MeO)$_2$C$_6$H$_3$}$_2$C]ClO$_4$, 2b. This salt was obtained in an analogous manner as mentioned above using **1b** to give dark-purple crystals of **2b** in 93% yield; mp 150—152 °C; IR 1100 cm^{-1} (ClO$_4$); UV 438 (sh), 532 nm (log *ε*, 4.24). Anal. (C$_{24}$H$_{25}$O$_9$) C, H.

[Ph{2,6-(MeO)$_2$C$_6$H$_3$}$_2$C]ClO$_4$, 2c. This salt was obtained in an analogous manner as mentioned above using **1c** to give dark-black crystals of **2c** in 92% yield; mp 152—155 °C; IR 1100 cm^{-1} (ClO$_4$); UV 479 (log *ε*, 4.37), 525 (sh) nm. Anal. (C$_{23}$H$_{23}$O$_8$Cl$_1$) C, H.

Reductions of Triarylmethanols or Triarylcarbenium Salts in Acidic Alcohols. Each solution of **1a**—**e** or **2a**—**c** (1 mmol) in alcohol (10—20 ml) containing perchloric acid or trifluoroacetic acid (1.1—5 mmol) was treated under the conditions shown below. After the solution was cooled to −30 °C, the resultant white crystals were recrystallized from 2-propanol to give **3a**—**e**. The yields were almost quantitative under the conditions.

[2,6-(MeO)$_2$C$_6$H$_3$]$_3$CH, 3a, in ethanol at 50 °C for 48 h; mp 182—184 °C (reported,[2] 185.5—187 °C).

(2-MeOC$_6$H$_4$)[2,6-(MeO)$_2$C$_6$H$_3$]$_2$CH, 3b, in methanol or ethanol at room temperature for 24 h; mp 138—139 °C. Anal. (C$_{24}$H$_{26}$O$_5$) C, H.

Ph[2,6-(MeO)$_2$C$_6$H$_3$]$_2$CH, 3c, in methanol or ethanol at room temperature for 2 h or in 2-propanol, 1-butanol, 3-methyl-1-butanol or 1,3-butanediol at 60 °C for 1 h; mp 130—131 °C. Anal. (C$_{23}$H$_{24}$O$_4$) C, H.

[2,5-(MeO)$_2$C$_6$H$_3$]$_3$CH, 3d, in methanol or ethanol at 50 °C for 2 h; mp 148—149 °C (reported,[25] 151 °C).

Ph$_2$[2,6-(MeO)$_2$C$_6$H$_3$]CH, 3e, in ethanol or 2-propanol at 50 °C for 12 h; mp 90—91 °C. Anal. (C$_{21}$H$_{20}$O$_2$) C, H.

Characterization of Aldehydes and Ketones. Solutions of **2b** or **2c** (0.5 mmol) in 1-butanol (5 ml) were

Table 2. ^{1}H NMR Spectral Data[a] for Methoxyphenyl Derivatives

Compounds	4-H[b]	3,5-H[c]	2,6-MeO[d]	Other protons[e]
1a	7.03	6.48	3.43	6.83s (1H, *OH*).
1b	7.11	6.54	3.45	7.15t[8] (1H, 4′-*H*),[f] 6.92d[8](1H, 6′-*H*), 6.83d[8](1H, 3′-*H*), 6.73t[8] (1H, 5′-*H*), 6.67s (1H, *OH*), 3.64s (3H, *OMe*).
1c	7.13	6.53	3.38	6.54—7.53m (5H, *Ph*), 6.40s (1H, *OH*).
1d[g]	6.91—6.74m (9H, 3,4,6-*H*), 5.56s (1H, *OH*), 3.68s (9H, *OMe*), 3.42s (9H, *OMe*).			
1e	—[f]	6.57	3.37	6.25s (1H, *OH*), 7.26—7.19m (11H, *Ph*).
2a	7.60	6.54	3.60	
2b	7.69	6.59	3.58	7.70dt[7][2] (1H, 4′-*H*),[f] 7.10—6.97m (3H, 3′,5′,6′-*H*), 3.78s (3H, *OMe*).
2c	7.83	6.66	3.57	7.75t[8] (1H, 4′-*H*), 7.53—7.42m (4H, *Ph*).
3a	7.03	6.50	3.42	6.47s (Ar_3CH).[f]
3b	7.08	6.50	3.46	7.08t[8] (1H, 4′-*H*),[f] 6.86dd[8][2] (1H, 6′-*H*), 6.77d[8] (1H, 3′-*H*), 6.76t[8] (1H, 5′-*H*),[f] 6.40s (1H, Ar_3CH), 3.63s (3H, *OMe*).
3c	7.12	6.52	3.48	7.2—7.0m (5H, *Ph*), 6.37s (1H, Ar_3CH).
3d[g]	6.77d[9] (3H, 4-*H*), 6.68dd[9][3] (3H, 5-*H*), 6.40d[3] (3H, 6-*H*), 6.34s (1H, Ar_3CH), 3.65s (9H, *OMe*), 3.63s (9H, *OMe*).			
3e	—[f]	6.56	3.59	7.14—7.23m, 6.16s (1H, Ar_3CH).
4[g]	7.33d[8] (2H, 2′,6′-*H*), 7.22t[8] (2H, 3,6-*H*), 7.16t[7] (2H, 3′,5′-*H*), 7.06t[7] (1H, 4′-*H*), 6.82d[8] (2H, 4,5-*H*), 6.53d[8] (2H, 2,7-*H*), 4.79s (1H, *OH*), 3.54s (6H, *OMe*).			
5[h]	3.81s (3H, 1-*MeO*), 3.65s (6H, 2′,6′-*MeO*).			

a) In $CDCl_3$, δ/ppm; s=singlet, d=doublet, dd=double doublets, dt=double triplets, and m=multiplet. b) Doublet with $J_\mathrm{H}=8$—9 Hz. c) Doublet with $J_\mathrm{H}=8$—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) Overlapped. g) In the order of chemical shifts. h) Poorly soluble in $CDCl_3$.

Table 3. ^{13}C NMR Spectral Data[a] for Methoxyphenyl Derivatives

Compounds	δ/ppm; in $CDCl_3$
1a	127.3, 158.7, 106.2, 126.2, 56.4, 78.4 (central C).
1b	125.5, 158.6, 106.5, 127.1, 56.2, 159.1, 136.2, 127.1, 127.0, 119.0, 110.8, 80.0 (central C), 55.5.
1c	—[b] 158.2, 107.0, 127.3, 56.4, 149.4, 126.7, 126.6, 125.4, 79.6 (central C).
1d[c]	153.5 (C-2), 151.8 (C-5), 135.0, 116.2, 113.7, 112.9, 80.2 (central C), 56.4 (5-MeO), 55.9 (2-MeO).
1e	126.4, 158.3, 106.8, 128.7, 56.2, 148.1, 127.4, 127.3, — (C-1′),[b] 81.6 (central C).
2a	—,[b] 162.8, 105.1, 142.5, 57.0, — (central C).[b]
2b	124.6, 162.9, 105.1, 136.6, 56.8, 185.7 (central C), 163.0, 143.7, 141.9, 134.2, 121.9, 111.7, 56.7.
2c	124.9, 163.9, 105.6, 145.9, 56.9, 192.1 (central C), 144.7, 137.2, 134.7, 129.2.
3a	—,[b] 159.6, 106.5, 125.7, 56.8, 30.4 (central C).
3b	122.6, 159.5, 105.8, 125.6, 56.2, 157.7, 133.5, 129.2, 126.4, 119.8, 109.8, 55.7, 33.4 (central C).
3c	121.9, 159.5, 105.6, 128.0, 56.2, 145.2, 127.0, 126.9, 124.3, 38.2 (central C).
3d[c]	153.9 (C-2), 151.9 (C-5), 133.9, 116.9, 112.2, 110.7, 56.7 (5-MeO), 55.5 (2-MeO), 37.6 (central C).
3e	121.2, 158.6, 105.2, 129.2, 55.8, 143.9, 128.0, 127.6, 125.4, 45.6 (central C).
4[c]	158.2 (C-1,8), 149.4 (C-11,12), 129.1 (C-3,6), 126.4 (C-3′,5′), 126.2(C-2′,6′), 125.7 (C-4′), — (C-1′),[b] 115.8 (C-10,13), 109.5 (C-4,5), 106.8 (C-2,7), 70.7 (C-9), 56.0 (OMe).
5	(Poorly soluble for the measurement)

a) In the order of phenyl carbons (C-1, C-2,6, C-3,5, C-4) of 2,6-dimethoxyphenyl group, 2,6-MeO and others. b) The resonance was not observed due probably to the weakness or overlapping. c) In the order of chemical shift; a possible assingment shown in parenthesis.

heated to distill; the distillates were analyzed by GC and UV to detect butanal in >80% yields. The other higher aldehydes were detected in analogous manners.

An analogous solution in 2-propanol was heated to distill to ca. a half volume, and acetone was detected by the UV spectrum of the distillate in 80% yield and by the formation of 2,4-dinitrophenylhydrazone.

Reactions of Triarylmethanols of Triarylcarbenium Salts in Acidic Solvents Other than Alcohols. In Tetrahydrofuran (THF). A dark reddish-purple solution of **1c** (1 mmol) in THF (10 ml) containing 60% aqueous perchloric acid (1 ml) was stirred at room temperature for 3 h to give pale-purple solutions. The addition of water resulted in white precipitates of **3c** in 85% yield.

An analogous treatment of **2b** for 24 h resulted in **3b** in 76% yield.

In Dimethyl Sulfoxide (DMSO). A dark reddish-purple solution of **1c** (1 mmol) in DMSO (10 ml) containing 60% aqueous perchloric acid (1 ml) was stirred at room temperature for 42 h to give a white suspension of 9-phenyl-1,8-dimethoxy-9-xanthenol **4** in 60% yield; mp 219—220 °C (recrystallized from toluene). Anal. ($C_{21}H_{18}O_4$) C, H. To the filtrate of **4** was added water to give the precipitates of **3c** in 36% yield.

An analogous treatment of **1b** for 72 h resulted to give dark-purple crystals of 9-(2,6-dimethoxyphenyl)-1-methoxy-9-xanthenium perchlorate **5** in 50% yield; mp 275—276 °C (recrystallized from methanol). Anal. ($C_{22}H_{20}O_9Cl$) C, H. From the filtrate, a mixture of **2b** and **3b** (in ca. 10% yield by ^{1}H NMR) was obtained.

In Hot Water. Suspensions of **1c** (1 mmol) in water (10 ml) containing 60% aqueous perchloric acid (0.5 ml) or 35% aqueous hydrochloric acid (0.5 ml) were heated at 80 °C until the color disappeared (4—9 h) to give **4** in 74—85% yields.

An analogous treatment of **1b** for 24 h resulted to give **5** in 83% yield.

Measurements of Reaction Rates. Solutions containing **1a**—**c** (0.005 mmol) in alcohol (5 ml) were diluted with the same alcohol (95 ml, 25 °C) containing acid ($HClO_4$, 0.025 mmol, in general); the UV spectra were then measured immediately at 25 °C, or the supernatant solutions of **2a**—**c** in alcohol suspension (25 °C) were diluted for the measurement. The half-lives were reproducible within 5%.

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References

1) J. C. Martin and R. G. Smith, *J. Am. Chem. Soc.*, **86**, 2252 (1964).

2) F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **90**, 2578 (1968).

3) R. J. Smith, T. M. Miller, and R. M. Pagni, *J. Org. Chem.*, **47**, 4181 (1982).

4) P. Huszthy, K. Lempert, and G. Simig, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1351.

5) B. Kahr, J. E. Jackson, D. L. Ward, and S. -H. Jang, *Acta Crystallogr. Sect. B*, **B48**, 342 (1992).

6) M. J. Sabacky, C. S. Johnson, Jr., R. G. Smith, H. S. Gutowski, and J. C. Martin, *J. Am. Chem. Soc.*, **89**, 2054 (1967).

7) H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

8) K. Ishizu, K. Mukai, A. Shibayama, and K. Kondo, *Bull. Chem. Soc. Jpn.*, **50**, 2269 (1977).

9) M. Wada, K. Nishiwaki, and Y. Kawasaki, *J. Chem. Soc., Dalton Trans.*, **1982**, 1443; M. Wada, S. Higashizaki, and A. Tsuboi, *J. Chem. Res. (S)*, **1985**, 38; *J. Chem. Res. (M)*, **1985**, 467; M. Wada, M. Kanzaki, M. Fujiwara, K. Kajihara, and T. Erabi, *Bull. Chem. Soc. Jpn.*, **64**, 1782 (1991); M. Wada, K. Kajihara, T. Morikawa, and T. Erabi, *Chem. Express*, **6**, 875 (1991).

10) M. Wada, H. Mishima, T. Watanabe, S. Natsume, H. Konishi, S. Hayase, and T. Erabi, *J. Chem. Soc., Chem. Commun.*, **1993**, 1462.

11) W. E. McEwen, A. B. Janes, J. W. Knapczk, V. L. Kyllingstad, W. -I. Shiau, S. Shore, and J. H. Smith, *J. Am. Chem. Soc.*, **100**, 7304 (1978).

12) C. D. Nenitzescu, in "Carbonium Ions," ed by G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York (1970), Vol. 2, p. 482, and references therein.

13) M. E. Jung and R. W. Brown, *Tetrahedron Lett.*, **1978**, 2771.

14) N. Deno, G. Saines, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3295 (1962).

15) M. Kira, T. Hino, and H. Sakurai, *Chem. Lett.*, **1993**, 153.

16) D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 542.

17) M. P. Doyle, D. J. DeBruyn, and D. J. Scholten, *J. Org. Chem.*, **38**, 625 (1973).

18) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

19) M. E. Jung, *J. Org. Chem.*, **41**, 1479 (1976).

20) R. Stewart and T. W. Toone, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 1243.

21) S. Futamura, *Bull. Chem. Soc. Jpn.*, **65**, 1779 (1992).

22) G. A. Olah and J. J. Svoboda, *J. Am. Chem. Soc.*, **95**, 3794 (1973).

23) M. Wada, M. Kanzaki, H. Ogura, S. Hayase, and T. Erabi, *J. Organomet. Chem.*, in press.

24) R. Levine and J. R. Sommers, *J. Org. Chem.*, **39**, 3559 (1974).

25) H. Kauffman and I. Fritz, *Chem. Ber.*, **41**, 4423 (1908).