Facile Aromatic Nucleophilic Substitutions Observed for the Triarylcarbenium Ions, $[(4\text{-}YC_6H_4)\Phi_2C]^+$ [Φ=2,6-$(MeO)_2C_6H_3$; Y=MeO, Cl, Me_2N, HO]

Masanori Wada,* Tetsuya Watanabe, Satoko Natsume, Hisashi Mishima, Katsuhiko Kirishima, and Tatsuo Erabi

Department of Materials Science, Faculty of Engineering, Tottori University, Koyama, Tottori 680

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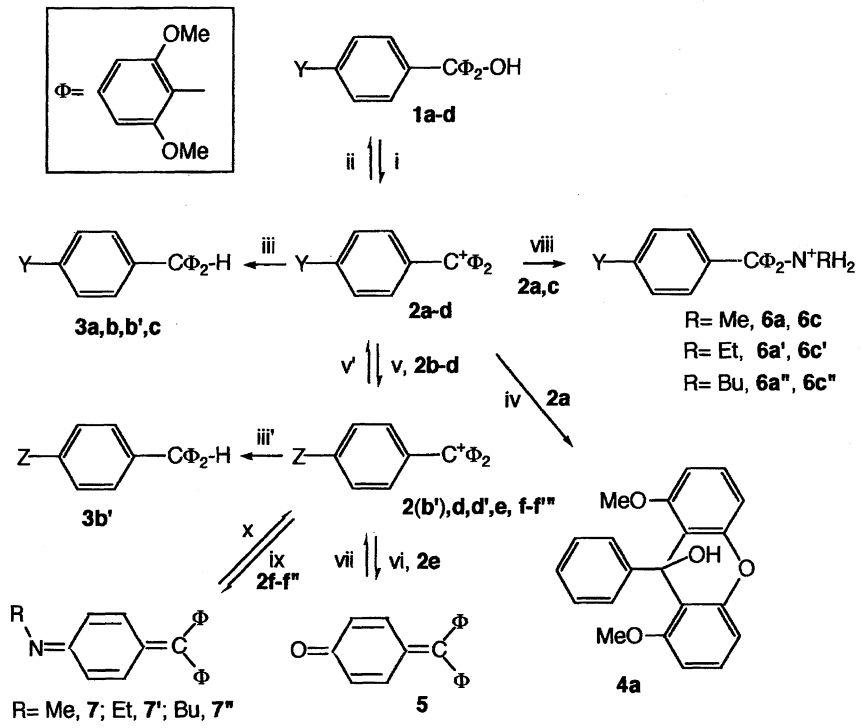
Triarylmethanols of type $(4\text{-}YC_6H_4)\Phi_2COH$ {Φ=2,6-$(MeO)_2C_6H_3$; Y=MeO, Cl, Me_2N} were prepared. The methanol, $(4\text{-}MeOC_6H_4)\Phi_2COH$, reacted with acids in a variety of solvents to give the triarylcarbenium salts, $[(4\text{-}MeOC_6H_4)\Phi_2C]X$ or $[(4\text{-}HOC_6H_4)\Phi_2C]X$, or 4-bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone, $O{=}C_6H_4{=}C\Phi_2$, depending on the conditions. These carbenium salts further reacted in alcohols, ROH, to give the triarylmethanes, $(4\text{-}ROC_6H_4)\Phi_2CH$ (R=Me, Et), where the *para*-substituent, MeO or HO, was substituted by the solvent, accompanied by a reduction at the central carbon. The methanol, $(4\text{-}ClC_6H_4)\Phi_2COH$, also reacted with acid to give the carbenium salt or the triarylmethane, depending on the conditions. While the methanol, $(4\text{-}Me_2NC_6H_4)\Phi_2COH$, also gave the carbenium salt, $[(4\text{-}Me_2NC_6H_4)\Phi_2C]$-X, it was inert against the formation of the triarylmethane under analogous conditions. It reacted with aqueous sodium hydroxide to give $O{=}C_6H_4{=}C\Phi_2$ rather than the original methanol. The *para*-substituent of $[(4\text{-}MeOC_6H_4)\Phi_2C]X$ was substituted by di- and monoalkylamines, RR′NH, to give $[(4\text{-}RR'NC_6H_4)\Phi_2C]$-X (R,R′=Me,Me; Et,Et; Me,H; Et,H; Bu,H). While $[(4\text{-}ClC_6H_4)\Phi_2C]X$ reacted with the dialkylamines to give $[(4\text{-}RR'NC_6H_4)\Phi_2C]X$, it reacted with monoalkylamines, RNH_2, to give $[(4\text{-}ClC_6H_4)\Phi_2C{-}NRH_2]X$. $[(4\text{-}Me_2NC_6H_4)\Phi_2C]X$ was hydrolyzed in the presence of diethylamine to give $O{=}C_6H_4{=}C\Phi_2$, but reacted with monoalkylamines to give $RN{=}C_6H_4{=}C\Phi_2$.

Triphenylmethanols bearing the 4-dimethylamino group have long been known to be highly basic to form stable triarylcarbenium salts,[1] and a variety of extending studies have been continued for such salts as crystal violet, $[(4\text{-}Me_2NC_6H_4)_3C]X$.[2] We have recently reported that triarylmethanols bearing at least two 2,6-dimethoxyphenyl groups, such as $Ph\Phi_2COH$ **1a** [Φ=2,6-$(MeO)_2C_6H_3$] and Φ_3COH, also show unusual high basicity to form isolable triarylcarbenium salt, even in secondary alcohols containing a slight excess of acid (path i in Scheme 1), that the carbeninum salt, $[Ph\Phi_2C]X$ **2a**, thus formed is quite reactive in primary alcohols, giving the reduced compounds, $Ph\Phi_2CH$ **3a** (path iii), and that **2a** decomposes in dimethyl sulfoxide to give the xanthenol **4a** (path iv).[3] The last reaction must involve an unusual aromatic nucleophilic substitution, S_NAr. In connection with these observations, we were interested in the properties of the related triarylmethanol bearing *para*-substituent, $(4\text{-}YC_6H_4)\Phi_2COH$ [Y=MeO (**1b**), Cl (**1c**), Me_2N (**1d**)], and their carbenium salts, $[(4\text{-}YC_6H_4)\Phi_2C]X$ **2b**—**d**. While the preparation of **1b** has been attempted by Levine and Sommers using 2,6-dimethoxyphenyllithium and methyl *p*-anisoate, they obtained a mixture of 2,4′,6-trimethoxybenzophenone and 4-bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone (**5** in Scheme 1).[4] We report here on the successful preparation of **1b**—**d** and of the carbenium salts **2b**—**d**, as well as facile S_NAr reactions of their *para*-substituent (path v).

Results and Discussion

Preparation of Aryl[bis(2,6-dimethoxyphenyl)]methanols. In an analogous manner to that used for **1a**,[3] the triarylmethanol **1b** could be prepared by the reaction of 2,6-dimethoxyphenyllithium with ethyl *p*-anisoate in good yield. The methanols, **1c** and **1d**, were prepared by the reactions of 4-chlorophenyllithium or 4-dimethylaminophenyllithium with bis(2,6-dimethoxyphenyl) ketone, also in good yields. The use of an acid must be avoided to neutralized these reaction mixtures, since compounds **1b**—**d** are quite reactive under acidic conditions, as mentioned below. The IR spectra of **1b**—**d** show very sharp absorption in the 3480—3450 cm^{-1} region due to the O–H stretching vibration, probably suggesting the absence of any hydrogen-bonding. Compounds **1b**,**c** were obtained as white crystals that are stable for a prolonged period in the solid state, and are soluble in common organic solvents, mostly without coloration. However, compound **1d** dissolves in methanol and ethanol to give light-pink solutions, or the



Y, Z= **a** H, **b** MeO, **b'** EtO, **c** Cl, **d** Me_2N, **d'** Et_2N, **e** HO,
f HMeN, **f'** HEtN, **f"** HBuN, **f'"** H(t-Bu)N.

i) + H^+; ii) + OH^-; iii), iii') + RCH_2OH, - RCHO; iv) in H_2O; v) + HZ; v') + HY;
vi) - H^+; vii) + H^+; viii) + NRH_2; ix) - H^+; x) + H^+.

Scheme 1.

crystals take an orange color upon storage in air, probably due to the formation of carbenium carbonate. An analogous coloration has been observed for Φ_3COH.[3]

Reactions of Aryl[bis(2,6-dimethoxyphenyl)]-methanols with Acid in Polar Solvents. Reactions of triarylmethanols, $(4\text{-}YC_6H_4)\Phi_2COH$ **1b—d**, and triarylcarbenium salts, $[(4\text{-}YC_6H_4)\Phi_2C]X$ (X= ClO_4 or BF_4) **2b—d**, are summarized in Table 1, as well as in Scheme 1. As Levine and Sommers have reported,[4] the decomposition of **1b** to **5** was commonly observed in a variety of polar solvents in the presence of an acid (Runs 1—4, 6, and 7 in Table 1). The reactions were, in general, very fast (less than 2 h) under the conditions given in the footnote of Table 1. Any acids, such as aqueous perchloric acid, hydrochloric acid, and trifluoroacetic acid, reacted in analogous manners to give **5**, although perchloric acid or tetrafluoroboric acid often gave mixtures containing **5** and the carbenium salts, $[(4\text{-}MeOC_6H_4)\Phi_2C]ClO_4$ **2b** and/or $[(4\text{-}HOC_6H_4)\Phi_2C]ClO_4$ **2e**, in a variety of ratios. The salt **2b** could best be obtained by reactions with these acids in benzene (Run 8). The salt **2e** could be obtained by the reaction of **1b** with acid in acetone, followed by the addition of benzene (Run 5), or by the reaction of **5** with acid in benzene. These salts, **2b** and **2e**, are deeply colored (dark red-purple), and easily decompose to give yellow crystals of **5** during recrystallization (Run 12, for an example).

When **2b** was kept standing in methanol at room temperature for a prolonged period (6 d), the reduced compound, $(4\text{-}MeOC_6H_4)\Phi_2CH$ **3b**, was obtained (Run 10, path iii). On the other hand, an analogous treatment of **2b** in ethanol gave another triarylmethane, $(4\text{-}EtOC_6H_4)\Phi_2CH$ **3b'**, where the *para*-methoxy group of **2b** was substituted by ethanol (Runs 9 and 11; path v, Y=EtO) accompanied by reduction (path iii'). The formations of **3b** and **3b'** were also observed using **2e**, where the 4-hydroxy group in **2e** was substituted by the solvent alcohols (Runs 23 and 24; paths vii, v', and iii), although **2e** did not react with 2-propanol nor with 1-butanol (Runs 25 and 26). These reactions can be best understood in term of the S_NAr mechanism, where the *para*-substituents (Y=MeO, EtO, HO) are mutually exchangeable with the solvent alcohol or water.

Deeply related S_NAr reactions have been reported for (4-bromophenyl)diphenylmethyl halides by silver to give (4-hydroxyphenyl)diphenylmethanol,[5,6] for tris(4-methoxyphenyl)methyl chloride by methanol-d_3,[7] for dichlorobenzenes by sodium thiolate or methoxide,[8] and for α-substituted 4-methoxybenzyl derivatives by ethanol or amines.[9—12] Feutrill and Mirrington found during the demethylation of aryl methyl ethers that 4-

Table 1. Representative Reactions of Triarylmethanols **1b—d** and Triarylcarbenium Salts **2a—f**

Run	Starting compound[a]	Reagent and conditions[b]	Product	Yd/%
1	**1b**	in MeOH, $+CF_3COOH$[c]	**5**	94
2	**1b**	in EtOH, $+HClO_4$[c]	**5**	86
3	**1b**	in *i*-PrOH, $+CF_3COOH$[c]	**5**	76
4	**1b**	in Me_2CO, $+CF_3COOH$[c]	**5**	90
5	**1b**	in Me_2CO, $+HClO_4$, 3 h, $+C_6H_6$	**2e**	80
6	**1b**	in MeCN, $+HClO_4$[c]	**5**	96
7	**1b**	in $MeNO_2$, $+CF_3COOH$[d]	**5**	90
8	**1b**	in C_6H_6, $+HBF_4$	**2b**	82
9	**1b**	in EtOH, $+HClO_4$, 3—5 days[c]	**3b′**	40
10	**2b**	in MeOH, 6 days[c]	**3b**	54
11	**2b**	in EtOH, 3 days[c]	**3b′**	78
12	**2b**	in DMSO[d]	**5**	78
13	**1c**	in MeOH, $+HClO_4$[c]	**3c**	70
14	**1c**	in EtOH, $+HClO_4$[c]	**3c**	89
15	**1c**	in *i*-PrOH, $+HClO_4$[c]	**2c**	92
16	**2c**	in *i*-PrOH, 60 °C, 16 h[c]	**3c**	84
17	**1c**	in THF, $+HClO_4$ (an excess)[d]	**3c**	75
18	**2c**	in DMSO, $+H_2O$, 6 h[d]	**5**	76
19	**1d**	in 1 M HCl (20 ml), +1 M $HClO_4$	**2d**	91
20	**1d**	in MeOH, $+HClO_4$[c]	**2d**	86
21	**1d**	in 1 M HCl, +1 M NaOH (12 ml)	**5**	88
22	**2d**	in DMSO, +0.1 M NaOH (2 equiv)	**5**	94
23	**2e**	in MeOH, 6 days[c]	**3b**	62
24	**2e**	in EtOH, 3 days[c]	**3b′**	85
25	**2e**	in *i*-PrOH, 2 days[c]	**5**	83
26	**2e**	in BuOH, 2 days[c]	**5**	53
27	**2e**	in THF, 24 h[c]	**2e**	57
28	**2a**	in *t*-BuOH, $+MeNH_2$	**6a**	88
29	**2a**	in *t*-BuOH, $+EtNH_2$	**6a′**	80
30	**2a**	in *t*-BuOH, $+BuNH_2$	**6a″**	83
31	**2b**	in *t*-BuOH, $+Me_2NH$	**2d**	91
32	**2b**	in *t*-BuOH, $+Et_2NH$	**2d′**	79
33	**2b**	in *t*-BuOH, $+MeNH_2$	**2f**	79
34	**2b**	in *t*-BuOH, $+EtNH_2$	**2f′**	77
35	**2b**	in *t*-BuOH, $+BuNH_2$	**2f″**	73
36	**2b**	in *t*-BuOH, $+t$-$BuNH_2$	**2f‴**	81
37	**2c**	in *t*-BuOH, $+Me_2NH$	**2d**	52
38	**2c**	in *t*-BuOH, $+Et_2NH$	**2d′**	60
39	**2c**	in *t*-BuOH, $+MeNH_2$[e]	**6c**	69
40	**2c**	in *t*-BuOH, $+EtNH_2$[e]	**6c′**	75
41	**2c**	in *t*-BuOH, $+BuNH_2$[e]	**6c″**	71
42	**2d**	in DMSO, $+Et_2NH$[d]	**5**	55
43	**2d**	in DMSO, $+MeNH_2$[d]	**7**	86
44	**2d**	in DMSO, $+EtNH_2$[d]	**7′**	84
45	**2d**	in DMSO, $+BuNH_2$[d]	**7″**	83
46	**2e**	in *t*-BuOH, $+Me_2NH$	**5**	97
47	**2f′**	in DMSO, +0.1 M NaOH	**7′**	70
48	**7**	in H_2O,[f] $+HClO_4$	**2f**	75

a) For **2a—f′**, the perchlorate or tetrafluoroborate were used. b) General procedure: to a solution or suspension of the starting material (0.5 mmol) in 5—10 ml of the solvent was added a slight excess of reactant (0.5—0.6 mmol), and the mixture was kept stirring at room temperature for 1—2 h to give the product as precipitate. c) The mixture was cooled to −30 °C to give crystals of the product. d) To the mixture was added water to give precipitates of the product. e) To the mixture was added hexane, and it was cooled to −30 °C to give crystals of the product. f) Suspension.

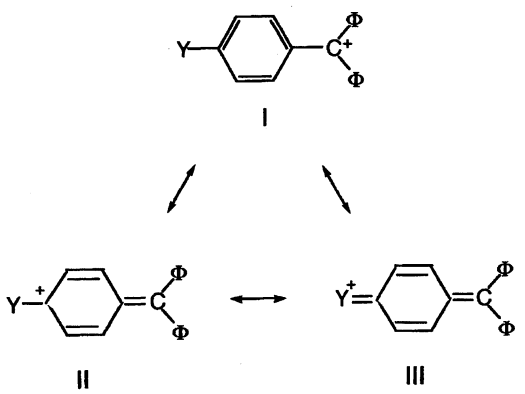
bromo-3-methylanisole reacted with sodium ethanethiolate to give 4-ethylthio-*m*-cresol.[13] Hattori et al. have recently applied the S_NAr substitutions of the methoxy group in 2-methoxybenzoates by an aryl Grignard reagent to the preparation of biphenyl-2-carboxylic acids.[14] Yeager and Schissel also reported on the preparation of 2-aroylbenzaldehydes by reactions of 2-fluorobenzaldehyde with phenols.[15]

The triarylmethanol **1c** also reacted with perchloric acid in 2-propanol to give dark-purple crystals of the carbenium salt, $[(4\text{-}ClC_6H_4)\Phi_2C]ClO_4$ **2c**, (Run 15); and it reacted in hot 2-propanol to give the reduced compound, $(4\text{-}ClC_6H_4)\Phi_2CH$ **3c**, (Run 16). It was confirmed that the salt **2c** reacted in methanol and ethanol to give **3c** even at room temperature, in less than 2 h (Runs 13 and 14). While the hydrolysis of **2c** to **1c** occurred rapidly in the presence of a large amount of water, it also decomposed during 6 h to give **5** in aqueous dimethyl sulfoxide (Run 18).

Like Φ_3COH,[3] the triarylmethanol **1d** is soluble, even in 0.1 M hydrochloric acid (1 M=1 mol dm^{-3}), to give an orange aqueous solution of the carbenium salt, $[(4\text{-}Me_2NC_6H_4)\Phi_2C]Cl$ **2d** (Run 19). Salts **2d** with another counter anion were commonly obtained by the reaction of **1d** with the corresponding acid in a variety of solvents. Salts **2d** are quite inert to hydrolysis (path ii), to the reduction to triarylmethane (path iii), or to the formation of xanthenol (path iv) under acidic and neutral conditions, such as in aqueous dimethyl sulfoxide (24 h at room temperature), in tetrahydrofuran (80 °C, 24 h), in 1 M hydrochloric acid (80 °C, 4 h) or in alcohols (60 °C, 36 h). The stability can be understood in terms of the reduced positive charge on the central carbon atom. In quite contrast, when an aqueous solution of **2d**, prepared in 1 M hydrochloric acid, was treated with aqueous sodium hydroxide, the immediate precipitation of **5** rather than **1d** resulted (Run 21), where the dimethylamino group was substituted by the hydroxide ion. The same fast reaction of **2d** to give **5** was also observed in dimethyl sulfoxide (Run 22). The high reactivity may be understood by increased positive charge on the 4′-carbon and/or on the nitrogen atoms (Scheme 2). It is worth adding here that crystal violet in 1 M hydrochloric acid reacted with 1 M sodium hydroxide to give the triarylmethanol.

While **2a**[3] and **2c** (Run 17) were reduced in tetrahydrofuran, **2e** was inert in the solvent (Run 27).

Reactions of Aryl[bis(2,6-dimethoxyphenyl)]-carbenium Ions with Alkylamines. Salt **2b** reacted with dimethylamine in 2-methyl-2-propanol quite easily at room temperature to give the *para*-substituted product **2d** (Run 31); it reacted with diethylamine to give $[(4\text{-}Et_2NC_6H_4)\Phi_2C]X$ **2d′** (Run 32) (path v). Salt **2c** also reacted quite easily with these dialkylamines to give **2d** and **2d′** (Runs 37 and 38). Salt **2b** also reacted with monoalkylamines, RNH_2, quite easily to give *para*-substituted products, $[(4\text{-}HRNC_6H_4)\Phi_2C]X$



Scheme 2.

(R=Me **2f**, Et **2f′**, Bu **2f″**, t-Bu **2f‴**) (Runs 33—36; path v), while the carbenium salts, **2a** and **2c**, reacted with these monoalkylamines to give the alkyl(triarylmethyl)ammonium salts, $[Ph\Phi_2C\text{–}NRH_2]X$ **6a—a″** (Runs 28—30) or $[(4\text{-}ClC_6H_4)\Phi_2C\text{–}NRH_2]X$ **6c—c″** (Runs 39—41) (R=Me, Et, Bu) (path viii). Salts **2** are, in general, highly colored, while salts **6** are almost colorless. Salt **2d** also reacted with monoalkylamines at the 4-carbon atom, but gave a deprotonated product, $4\text{-}RN{=}C_6H_4{=}C\Phi_2$ (R=Me **7**, Et **7′**, Bu **7″**; Runs 43—45), probably caused by the dimethylamine by-product (path ix). In contrast, these salts **2d,d′** were easily hydrolyzed in the presence of dialkylamines to give **5** (Run 42; path vi). It was confirmed that salts **2f—f″** were deprotonated by bases to give **7—7″**, rather than to give **5** (Run 47; path ix), and that the reactions are reversible (Run 48). Salt **2e** was also deprotonated by dimethylamine to give **5** (Run 46).

These reactions at the 4-carbon atom are of interest, since they show that the electron-donating *para*-substituent reduced the electrophilicity at the central carbon, though the electrophilicity at the 4-carbon still remained. The different reactivity of **2c** between mono- and dialkylamines may be explained by a steric effect. The relative reactivities among paths v, viii, and ix thus vary depending largely on the *para*-substituent, as well as on the reagent.

^{1}H NMR Spectra and the Conformation of 2,6-Dimethoxyphenyl Derivatives. The ^{1}H NMR spectra (Table 2) of 2,6-dimethoxyphenyl derivatives (Φ-derivatives) obtained here show, in general, a triplet due to 4-H, a doublet due to 3,5-H, and a sharp singlet due to 2,6-MeO protons of the Φ-group. Like **1a**,[3] the chemical shift of the 4-H resonance of neutral compounds **1b—d** and **3b—c** is observed in such a narrow region of δ=7.10—7.13, irrespective of the change of the *para*-substituent Y. The 4-H resonance of all the carbenium salts **2a—f‴** was observed at a much lower magnetic field, as expected, and it was quite sensitive to a change of Y, shifting to a higher magnetic field when the *para*-substituent Y is more electron donative: **2a** (δ=7.83)[3] ≈**2c**<**2b**<**2e**<**2d,d′,f—f‴**. The

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

Compounds	4-H[b]	3,5-H[c]	2,6-MeO[d]	Others[e]
1b	7.12	6.55	3.40	7.36d[9] (2H), 6.77d[9] (2H), 6.37s (1H, OH), 3.78s (3H, 4′-MeO).
1c	7.12	6.53	3.40	7.39d[8] (2H), 7.17d[8] (2H), 6.49s (1H, OH).
1d	7.10	6.55	3.40	7.29d[9] (2H), 6.66d[8] (2H), 6.28s (1H, OH), 2.89s (6H, Me_2N).
2b	7.56	6.61	3.58	7.92d[9] (2H), 7.22d[9] (2H), 4.27s (3H, 4′-MeO).
2c	7.83	6.67	3.60	7.47d[8] (2H), 7.41d[8] (2H).
2d	7.35	6.57	3.60	7.54d[10] (2H), 6.97d[10] (2H), 3.63s (6H, Me_2N).
2d′	7.36	6.58	3.62	7.56d[10] (2H), 6.95d[10] (2H), 3.91q[7] (4H, Et_2N), 1.42t[7] (6H, Et_2N).
2e	7.48	6.58	3.58	7.58d[9] (2H), 7.24d[9] (2H).
2f	7.35 and 7.34	6.58 and 6.57	3.61	9.73brs (HN), 7.58dd[10] (1H), (7.37?),[f] 7.05d[10] (1H), 6.75d[10] (1H), 3.33s (3H, MeN).
2f′	7.35	6.58 and 6.57	3.61	9.55brs (1H, HN), 7.59dd[10] (1H), 7.38dd[10] (1H),[f] 7.04dd[10] (1H), 6.74dd[10] (1H), 3.66q[8] (2H, Et), 1.43t[7] (3H, Et).
2f″	7.35	6.58 and 6.57	3.61	9.5brs (1H, HN), 7.58dd[10] (1H), 7.38dd[10] (1H),[f] 7.06dd[10](1H), 6.75dd[10] (1H), (3.61)[f] 1.79qn[7] (2H), 1.43m[7] (2H), 0.95t[7] (3H).
2f‴	7.34	6.57 and 6.56	3.62	9.35brs (1H, HN), 7.56dd[10] (1H), 7.37dd[10] (1H),[f] 7.12dd[10] (1H), 6.98dd[10] (1H), 1.60s (9H, *t*-Bu).
3b	7.12	6.52	3.50	6.98d[9] (2H), 6.72d[9] (2H), 6.30s (1H, Ar_3CH), 3.45s (3H, 4′-MeO).
3b′	7.11	6.52	3.50	6.97d[8] (2H), 6.70d[9] (2H), 6.30s (1H, Ar_3CH), 3.97q[7] (2H, Et), 1.36t[7] (3H, Et).
3c	—[f]	6.50	3.50	7.16—7.09m (3H), 6.97d[8] (2H), 6.31s (1H, Ar_3CH).
5	7.30	6.55	3.63	7.23d[9] (2H), 6.30d[9] (2H).
6a	7.28	6.57	3.57	7.37—7.17m (Ph),[f] 2.73s (3H, NMe).
6a′	7.28	6.57	3.58	7.39—7.16m (Ph),[f] 3.06q[7] (2H, Et), 1.30t[7] (3H, Et).
6a″	7.28	6.57	3.58	7.40—7.16m (Ph),[f] 3.00t[8] (2H), 1.62dt[7] (2H), 1.20m[7] (2H), 0.77t[7] (3H).
6c	7.30	6.58	3.59	8.7brs (2H, NH_2), 7.32d[9] (2H),[f] 7.21d[9] (2H), 2.71s (3H).
6c′	7.30	6.58	3.60	8.65brs (NH_2), 7.34d[9] (2H),[f] 7.21d[9] (2H), 3.03q[7] (2H), 1.30t[7] (3H).
6c″	7.31	6.58	3.60	7.35d[9] (2H),[f] 7.21d[9] (2H), 2.97t[8] (2H), 1.62qn[8] (2H), 1.19m[7] (2H), 0.76t[7] (3H).
7	7.22 and 7.21	6.54 and 6.53	3.63	6.87dd[10], 6.75dd[10], 6.59[10], 6.43dd[10], 3.36s (3H, MeN).
7′	7.22 and 7.21	6.54 and 6.53	3.63	6.84dd[10], 6.73dd[10], 6.57dd[10], 6.41dd[10], 3.57q (2H), 1.29t[7] (3H).
7″	7.21 and 7.20	6.54 and 6.53	3.64	6.83dd[10] (1H), 6.72dd[10], 6.58dd[10], 6.41dd[10], 3.54t[7] (2H), 1.67qn[7] (2H), 1.39m[7] (2H), 0.93t[7] (3H).

a) In $CDCl_3$ (δ/ppm; s=singlet, d=doublet, t=triplet, q=quartet, qn=quintet, brs=broad singlet and m=multiplet). b) Triplet with J_H=8—9 Hz. 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) Overlapped.

pronounced high-field chemical shift of the latter compounds is best understood as being due to a reduction of the positive character on the central carbon and/or in 2,6-dimethoxyphenyl groups due to the contribution of resonances II and/or III in Scheme 2. The observation of two well-defined 4-H resonances for **2f** and **7**—**7″** indicates that the two Φ-groups are magnetically nonequivalent, and, thus, the compound must take a quinonoidal configuration, where the *para*-HRN and RN groups exist in the same plane as the phenylene group, as shown in Scheme 1. In accordance with this observation, two 3,5-H resonances are observed, and the four phenylene protons are nonequivalent. The spectra of **2f′**—**f‴** can also be understood by the coplanar configuration of the *para*-HRN group with the phenylene group, of which the four aromatic protons of the 4-YC_6H_4 group are also nonequivalent. It is also expected that both **2d** and **2d′** take analogous coplanar configurations.

Some neutral compounds show the 2,6-MeO proton resonance at higher magnetic fields (δ=3.40 for **1b**—**d**

and δ=3.50 for **3b**—**c**) than any of the cationic compounds **2b**—**f'''**, **6a**—**a''**, and **6c**—**c''** (δ=3.62—3.58), as expected. Those of neutral compounds **5** and **7**—**7''** are also observed at such low magnetic fields as δ= 3.64—3.63, though the reason for this is unknown.

Experimental

Physical Measurements. NMR spectra were recorded in $CDCl_3$ using a JEOL model 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 NMR spectral data are summarized in Table 2.

Preparation of Triarylmethanols, (4-YC$_6$H$_4$)Φ_2COH, (Y=MeO, Cl, Me$_2$N). (4-MeOC$_6$H$_4$)Φ_2COH, 1b. A suspension of 2,6-dimethoxyphenyllithium ΦLi was prepared as reported[3] from a 15% hexane solution of butyllithium (7.4 ml, 12 mmol), resorcinol dimethyl ether (1.6 ml, 12 mmol), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.2 ml) at 0 °C under argon. It was diluted with benzene (40 ml), and ethyl *p*-anisoate (0.82 ml, 5 mmol) was added. The mixture was stirred at room temperature for 3 h to give a pale-yellow suspension. After it was washed with cold water, the volatile materials were removed under reduced pressure. The residue was recrystallized from hexane to give white crystals of bis(2,6-dimethoxyphenyl)(4-methoxyphenyl)methanol **1b** in 78% yield; mp 109—111 °C; IR 3450 (O–H) cm^{-1}; ^{13}C NMR δ=126.9 (C-1), 158.2 (C-2,6), 107.0 (C-3,5), 127.3 (C-4), 56.6 (2,6-MeO); 157.5, 141.7, 127.8, 112.1 79.3 (central C), 55.2 (4'-MeO). Found: C, 69.93; H, 6.39%. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38%. Compound **1b** is very soluble in chloroform, benzene, acetone, and methanol (pink solution); soluble in ethanol, hot 2-propanol, diethyl ether, and hot hexane; and insoluble in hot water.

(4-ClC$_6$H$_4$)Φ_2COH, 1c. A solution of 4-chlorophenyllithium was prepared by mixing a 15% hexane solution of butyllithium (4.5 ml, 7 mmol) and 4-bromochlorobenzene (1.53 g, 8 mmol) in diethyl ether (10 ml) at room temperature for 2 h under argon. It was added to a solution of bis(2,6-dimethoxyphenyl) ketone (1.51 g, 5 mmol) in diethyl ether (10 ml); the mixture was then stirred at room temperature for 7 h to give a white suspension. Benzene (10 ml) was added, the mixture was washed well with water, and the volatile materials in the organic layer were removed under reduced pressure. The residue was recrystallized from 2-propanol or hexane to give white crystals of 4-chlorophenyl[bis(2,6-dimethoxyphenyl)]methanol **1c** in 78% yield; mp 125—126 °C; IR 3450 (O–H) cm^{-1}; ^{13}C NMR δ=126.1 (C-1), 158.0 (C-2,6), 106.8 (C-3,5), 128.2 (C-4), 56.3 (2,6-MeO);148.1, 130.9, 127.5, 126.6, 79.2 (central C). Found: C, 66.59; H, 5.54%. Calcd for $C_{23}H_{23}ClO_5$: C, 66.59; H, 5.59%. Compound **1c** is very soluble in chloroform, benzene, and acetone; soluble in methanol, hot ethanol, hot 2-propanol, diethyl ether, and hot hexane; and insoluble in hot water.

(4-Me$_2$NC$_6$H$_4$)Φ_2COH, 1d. A solution of 4-dimethylaminophenyllithium was prepared by mixing a 15% hexane solution of butyllithium (4.5 ml, 7 mmol) and 4-bromo-*N,N*-dimethylaniline (1.6 g, 8 mmol) in diethyl ether (10 ml) at room temperature for 2 h under argon. It was added to a suspension of bis(2,6-dimethoxyphenyl) ketone (1.51 g, 5 mmol) in a benzene (10 ml); the mixture was then stirred at room temperature for 7 h to give a white suspension. The mixture was washed well with water, and the volatile materials in the organic layer were removed under reduced pressure. The residue was recrystallized from 2-propanol or hexane to give white crystals of bis(2,6-dimethoxyphenyl)(4-dimethylaminophenyl)methanol **1d** in 80% yield; mp 113—115 °C; IR 3480 (O–H) cm^{-1}; ^{13}C NMR δ=128.4 (C-1), 158.3 (C-2,6), 107.2 (C-3,5), 127.1 (C-4), 56.7 (2,6-MeO); 148.9, 138.1, 127.5, 111.8, 79.4 (central C), 41.1 (4'-Me$_2$N). Found: C, 70.98; H, 7.04; N, 3.36%. Calcd for $C_{25}H_{29}NO_5$: C, 70.90; H, 6.90; N, 3.31%. Compound **1d** is very soluble in chloroform, benzene, acetone, and methanol; soluble in ethanol, hot 2-propanol, diethyl ether, and hot hexane; and insoluble in hot water.

Preparation and Reactions of Triarylcarbenium Salts, [(4-YC$_6$H$_4$)Φ_2C]X (X=ClO$_4$ or BF$_4$; Y=MeO, Cl, Me$_2$N, HO). The procedures are summarized in the footnote of Table 1. The characterization data other than ^{1}H NMR spectral data (Table 2) are given here, together with the procedures for some typical products.

[(4-MeOC$_6$H$_4$)Φ_2C]BF$_4$, 2b. To a solution of **1b** (10.5 g, 10 mmol) in benzene (30 ml) was added 42% aqueous tetrafluoroboric acid (1.76 ml, 11 mmol); the resultant dark purple suspension was stirred for 10 min, and the resultant precipitates were well washed with diethyl ether to give dark green crystals of bis(2,6-dimethoxyphenyl)(4-methoxyphenyl)carbenium tetrafluoroborate, **2b**, in 82% yield; mp 133—137 °C; IR 1060 (BF$_4$) cm^{-1}; ^{13}C NMR δ=160.7 (C-2, 6), 104.9 (C-3,5), 136.9 (C-4), 56.4 (2,6-MeO); 176.5 (central C), 145.8, 138.9, 120.2, 117.6, 58.7 (4'-MeO). Attempts of recrystallization of **2b** resulted to give yellow crystals of 4-bis(2,6-dimethoxyphenyl)methylene-2,5-cyclohexadienone **5**.

***p*-O=C$_6$H$_4$=CΦ_2, 5.** Yellow crystals; mp 206—208 °C (recrystallized from acetone) (reported, 216—216.5 °C);[4] IR 1630 (C=O) cm^{-1}; UV 391 nm (logε 4.27); ^{13}C NMR δ=130.3 (C-1), 158.5 (C-2,6), 104.3 (C-3,5), 132.9 (C-4), 56.0 (2,6-MeO); 188.0 (C=O), 145.8, 139.6, 127.5, 117.8.

[(4-ClC$_6$H$_4$)Φ_2C]ClO$_4$, 2c. To a suspension of **1c** (0.415 g, 1 mmol) in 2-propanol (10 ml) was added 60% aqueous perchloric acid (0.12 ml) to give a dark-reddish purple solution, followed by the precipitation of dark green-red crystals (purple in solution) of 4-chlorophenyl[bis(2,6-dimethoxyphenyl)]carbenium perchlorate, **2c**, in 92% yield; mp 155—156 °C (from 2-propanol); IR 1100 and 620 (ClO$_4$) cm^{-1}; UV 493 nm (logε 4.47); ^{13}C NMR δ=124.5 (C-1), 163.8 (C-2,6), 105.5 (C-3,5), 146.2 (C-4), 57.0 (2,6-MeO); 189.3 (central C), 144.2, 142.7, 135.7, 129.6. Found: C, 55.30; H, 4.38%. Calcd for $C_{23}H_{22}Cl_2O_8$: C, 55.55; H, 4.46%.

[(4-Me$_2$NC$_6$H$_4$)Φ_2C]ClO$_4$, 2d. To a suspension of **1d** (0.423 g, 1 mmol) in methanol (10 ml) was added 60% aqueous perchloric acid (0.12 ml); the resulting deep-red suspension was stirred at room temperature for 2 h to give dark-red crystals (orange-red in solution) of bis(2,6-dimethoxyphenyl)(4-dimethylaminophenyl)carbenium perchlorate, **2d**, in 86% yield; mp 265—267 °C (from ethanol); IR 1620 (C=N) and 1100 (ClO$_4$) cm^{-1}; UV 484 nm (logε 4.09); ^{13}C NMR δ=133.4 (C-1), 163.6 (C-2,6), 104.6 (C-3,5), 143.6 (C-4), 56.2 (2,6-MeO); 161.2 (central C), 158.8, 132.8, 117.5, 116.3, 42.8 (4'-Me$_2$N). Found: C, 59.14; H, 5.62; N, 2.81%.

Calcd for $C_{25}H_{28}ClNO_8$: C, 59.35; H, 5.58; N, 2.77%. This salt **2d** is soluble in chloroform, acetone, dimethyl sulfoxide, hot methanol, hot ethanol, and hot 2-propanol to form a red solution, but is insoluble in water. Salt **2d** was recovered unchanged from aqueous dimethyl sulfoxide, from alcohols heated at 60 °C for 36 h, and from a water suspension heated at 60 °C for 4 h, but gave **5** upon a treatment with 0.1 M sodium hydroxide (2 molar amounts) in dimethyl sulfoxide.

[(4-Et$_2$NC$_6$H$_4$)Φ_2C]ClO$_4$, 2d′. To a suspension of **2b** (0.493 g, 1 mmol) in 2-methyl-2-propanol (10 ml) was added diethylamine (0.11 ml, 1.2 mmol) to give a clear solution followed by precipitation of dark-red crystals of **2d′** in 79% yield; mp 268—269 °C (from ethanol); IR 1620 (C=N) and 1100 (ClO_4) cm^{-1}. Found: C, 60.46; H, 6.07; N, 2.53%. Calcd for $C_{27}H_{32}ClNO_8$: C, 60.73; H, 6.04; N, 2.62%. This compound is obtained also from **2c** in 60% yield.

[(4-HOC$_6$H$_4$)Φ_2C]ClO$_4$, 2e. To a solution of **1b** (5 mmol) in acetone (50 ml) was added 60% aqueous perchloric acid (0.6 ml, 6 mmol); the resultant purple solution was stirred at room temperature for 3 h, followed by the addition of benzene (50 ml). The mixture was concentrated under reduced pressure to ca. half volume to give dark-red-purple crystals of bis(2,6-dimethoxyphenyl)(4-hydroxyphenyl)-carbenium perchlorate [(4-HOC$_6$H$_4$)Φ_2C]ClO$_4$, **2e**, in 80% yield; mp 230—231 °C. Found: C, 57.60; H, 4.74%. Calcd for $C_{23}H_{23}ClO_9$: C, 57.69; H, 4.84. This compound could be obtained also on treatment of **5** with 60% aqueous perchloric acid in benzene.

[(4-HMeNC$_6$H$_4$)Φ_2C]ClO$_4$, 2f. Orange crystals; mp 289—291 °C, decomposed (from ethanol); IR 3280 (N–H), 1630 (C=N), and 1110 (ClO_4) cm^{-1}.

[(4-HEtNC$_6$H$_4$)Φ_2C]ClO$_4$, 2f′. Orange crystals; mp 286—288 °C, decomposed (from ethanol); IR 3300 (N–H), 1625 (C=N), and 1110 (ClO_4) cm^{-1}. Found: C, 59.27; H, 5.63; N, 2.73%. Calcd for $C_{25}H_{28}ClNO_8$: C, 59.35; H, 5.58; N, 2.77%.

[(4-HBuNC$_6$H$_4$)Φ_2C]ClO$_4$, 2f″. Orange crystals; mp 241—243 °C, decomposed (from ethanol); IR 3300 (N–H), 1625 (C=N), and 1110 (ClO_4) cm^{-1}. Found: C, 60.81; H, 6.12; N, 2.49%. Calcd for $C_{27}H_{32}ClNO_8$: C, 60.73; H, 6.04; N, 2.62%.

[(4-H(*t*-Bu)NC$_6$H$_4$)Φ_2C]ClO$_4$, 2f‴. Orange crystals; mp 284—286 °C, decomposed (from ethanol); IR 3300 (N–H), 1625 (C=N), and 1110 (ClO_4) cm^{-1}; ^{13}C NMR δ= 158.7, 104.4, 132.3, 56.1, 162.2 (C=N), 144.9, 141.7, 122.5, 115.3, 29.6 (Me_3). Found: C, 60.61; H, 6.04; N, 2.54%. Calcd for $C_{27}H_{32}ClNO_8$: C, 60.73; H, 6.04; N, 2.62%.

(4-MeOC$_6$H$_4$)Φ_2CH, 3b. White crystals; mp 121—123 °C (from methanol); ^{13}C NMR δ=122.2 (C-1), 159.3 (C-2,6), 105.5 (C-3,5), 129.1 (C-4), 56.4 (2,6-MeO); 156.7, 137.1, 126.8, 112.7, 55.2 (4′-MeO), 37.4 (central C). Found: C, 72.92; H, 6.69%. Calcd for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64%.

(4-EtOC$_6$H$_4$)Φ_2CH, 3b′. White crystals; mp 98—100 °C (from acetone); ^{13}C NMR δ=122.1 (C-1), 159.0 (C-2,6), 105.6 (C-3,5), 129.0 (C-4), 56.3 (2,6-MeO); 156.1, 137.2, 126.9, 113.3, 63.4 (Et), 37.5 (central C), 15.0 (Et). Found: C, 73.54; H, 6.92%. Calcd for $C_{25}H_{28}O_5$: C, 73.51; H, 6.91%.

(4-ClC$_6$H$_4$)Φ_2CH, 3c. White crystals; mp 175—176 °C (from 2-propanol); ^{13}C NMR δ=120.9 (C-1), 159.2 (C-2,6), 105.2 (C-3,5), 129.3 (C-4), 56.0 (2,6-MeO), 143.7, 129.7, 127.1, 127.0, 37.5 (central C). Found: C, 69.16; H, 5.76%. Calcd for $C_{23}H_{23}ClO_4$: C, 69.26; H, 5.81%.

[PhΦ_2C–NMeH$_2$]BF$_4$, 6a. White crystals; mp 164—167 °C, decomposed; IR 3200 (N–H), 1030—1080 (BF_4) cm^{-1}; ^{13}C NMR δ=130.0 (C-1), 157.5 (C-2,6), 104.8 (C-3,5), 127.5 (C-4), 56.3 (2,6-MeO); 141.3, 124.3, 114.0, 106.8, 72.0 (central C), 55.5 (MeN). This compound decomposed partly to give **1a** during the recrystallization.

[PhΦ_2C–NEtH$_2$]BF$_4$, 6a′. White crystals; mp 161—163 °C, decomposed; IR 3200 and 3160 (N–H), 1030—1080 (BF_4) cm^{-1}. This compound decomposed partly to give **1a** during the recrystallization.

[PhΦ_2C–NBuH$_2$]BF$_4$, 6a″. White crystals; mp 130—131 °C, decomposed; IR 3200 and 3160 (N–H), 1030—1080 (BF_4) cm^{-1}. This compound decomposed partly to give **1a** during the recrystallization.

[(4-ClC$_6$H$_4$)Φ_2C–NMeH$_2$]BF$_4$, 6c. Light brown crystals; mp 104—105 °C, decomposed; IR 3200 (N–H), 1030—1100 (BF_4) cm^{-1}; ^{13}C NMR δ=130.2 (C-1), 157.3 (C-2,6), 104.8 (C-3,5), 127.6 (C-4), 56.2 (2,6-MeO); 140.0, 125.9, 113.5, 106.6, (overlapped or weak, central C), 55.5 (MeN). This composed decomposed partly to give **1c** during the recrystallization.

[(4-ClC$_6$H$_4$)Φ_2C–NEtH$_2$]BF$_4$, 6c′. Light brown crystals; mp 115—116 °C, decomposed; IR 3200 (N–H), 1030—1110 (BF_4) cm^{-1}. This compound decomposed partly to give **1c** during the recrystallization.

[(4-ClC$_6$H$_4$)Φ_2C–NBuH$_2$]BF$_4$, 6c″. Light brown crystals; mp 107—108 °C, decomposed; IR 3200 (N–H), 1030—1100 (BF_4) cm^{-1}. This compound decomposed partly to give **1c** during the recrystallization.

***p*-MeN=C$_6$H$_4$=CΦ_2, 7.** Yellow crystals; mp 179—180 °C, decomposed.

***p*-EtN=C$_6$H$_4$=CΦ_2, 7′.** Yellow crystals; mp 179—180 °C, decomposed; ^{13}C NMR δ=130.2 (C-1), 158.7 (C-2,6), 104.4 (C-3,5), 132.0 (C-4), 56.1 (2,6-MeO); 160.4 (C=N), 134.8, 133.4, 129.1, 118.5, 116.2, 45.1 (Et), 16.4 (Et).

***p*-BuN=C$_6$H$_4$=CΦ_2, 7″.** Yellow crystals; mp 147—149 °C, decomposed.

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