Triarylcyclopropenium Ions and Diarylcyclopropenones from Trichlorocyclopropenium Ion

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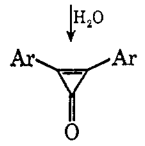
Abstract: Reaction of trichlorocyclopropenium tetrachloroaluminate with phenols or anisole at 30–80° yields symmetrical triarylcyclopropenium chlorides, with the aromatic rings substituted *para* to the hydroxyl or methoxyl group. At lower temperatures (0–10°) diarylchlorocyclopropenium ions are formed, which give diarylcyclopropenones after hydrolysis. Monoaryltrichloro- and diaryldichlorocyclopropenes can also be further substituted under Friedel–Crafts conditions with anisole or phenols, yielding unsymmetrical triarylcyclopropenium salts.

The preparation of the first cyclopropenium ion, triphenylcyclopropenium, by Breslow in 1957[1] was followed shortly by the synthesis of the first cyclopropenone, diphenylcyclopropenone.[2] Many additional examples of both kinds of substances have been reported during the last decade, prepared by various routes.[3] However, a synthetic method of wide applicability and generality has been lacking.

In 1964, we reported that trichlorocyclopropenium tetrachloroaluminate (**1**)[4] reacted with benzene or fluorobenzene to give after hydrolysis, the corresponding diarylcyclopropenone.[5] Further study of this reaction showed that it takes place stepwise; at low temperatures, a single chlorine atom on the $C_3Cl_3^+$ ion is replaced, whereas at room temperature, disubstitution takes place.[6] The substitution can be viewed as a

$$\mathrm{ArH} + \mathrm{C_3Cl_3^+AlCl_4^-} \xrightarrow{0^\circ} \mathrm{ArC_3Cl_2^+AlCl_4^-} + \mathrm{HCl}$$

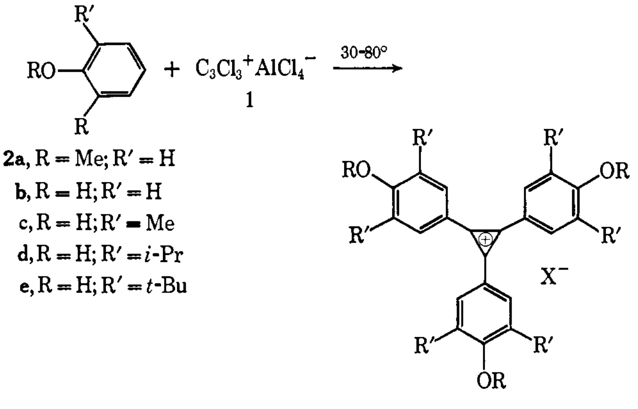
$$\mathrm{ArC_3Cl_2^+AlCl_4^-} + \mathrm{ArH} \xrightarrow{1} \mathrm{Ar_2C_3Cl^+AlCl_4^-} + \mathrm{HCl}$$



Ar = C_6H_5, p-FC_6H_4

Friedel–Crafts alkylation, involving electrophilic substitution on carbon of the benzene ring. The reaction to form symmetrical diarylcyclopropenone is general for aromatic hydrocarbons bearing weakly activating groups (alkyl) or weakly deactivating substituents (halogen);[7] trisubstitution is not observed. However, when trichlorocyclopropenium ion is allowed to react with aromatic hydrocarbons bearing strongly activating substituents, we find that the reaction continues until all three halogens have been replaced, as described below.

Symmetrical Triarylcyclopropenium Ion Salts. Reaction of **1** with anisole (neat), phenol (molten), 2,6-dimethylphenol (molten), 2,6-diisopropylphenol (chloroform solution), or 2,6-di-*t*-butylphenol (chloroform solution) at 30–70° gave the corresponding triarylcyclopropenium chloride (**2a–e**, X = Cl) after hydrolysis, in yields ranging from 20 to 80%. This reaction represents a new and highly convenient method for the synthesis of these interesting compounds. All the ions are new except **2a**, reported by Breslow and Chang as the bromide.[8]



2a, R = Me; R′ = H
b, R = H; R′ = H
c, R = H; R′ = Me
d, R = H; R′ = *i*-Pr
e, R = H; R′ = *t*-Bu

X = Cl, Br, ClO_4

In most cases, the crude triarylcyclopropenium chlorides isolated from these reactions were immediately converted to the corresponding perchlorate salts by adding perchloric acid to a solution of the chloride in methanol.[9] The triarylcyclopropenium perchlorates were white solids, most of which exploded at temperatures above 250°. They all possessed a very strong, broad, infrared band in the region 1400–1370 cm^{-1} characteristic of the cyclopropenium system. For example, the infrared spectrum of **2e** (X = ClO_4), shown in Figure 1, possesses a very intense, broad band at 1370 cm^{-1}. A similar band has been reported for other cyclopropenium ion salts,[4,10–12] and has been assigned to be mostly C–C ring expansion.[4] Note also in Figure 1, the strong, broad absorption band near 1050 cm^{-1}. This band is absent in the infrared spec-

[1] R. Breslow, *J. Amer. Chem. Soc.*, **79**, 5318 (1957).

[2] R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

[3] For a review through 1964 see A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

[4] R. West, A. Sadô, and S. W. Tobey, *J. Amer. Chem. Soc.*, **88**, 2488 (1966).

[5] S. W. Tobey and R. West, *ibid.*, **86**, 4215 (1964).

[6] R. West, D. C. Zecher, and S. W. Tobey, *ibid.*, **92**, 155 (1970).

[7] Numerous unpublished examples are described in A. R. Brause, M.S. Thesis, University of Wisconsin, 1964.

[8] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

[9] The perchlorates of the triarylcyclopropenium ions generally were easier to purify than the chlorides, and consequently most of the uv and nmr spectra, as well as elemental analyses, were performed on the perchlorates. However, **2b** and **4b** could not be converted to perchlorates by this method, and were never obtained analytically pure.

[10] R. Breslow, H. Hover, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).

[11] A. S. Kende, *ibid.*, **85**, 1882 (1963).

[12] (a) B. Föhlisch and P. Bürgle, *Tetrahedron Lett.*, 2661 (1965); (b) B. Föhlisch and P. Bürgle, *Ann. Chem.*, **701**, 67 (1967).

Table I. Ultraviolet and Nmr Spectra of Triarylcyclopropenium Salts and Diarylcyclopropenones

		Ultraviolet		Proton nmr, τ^b			
Compd[a]	Solvent	max, nm (log ϵ)	Har	J, cps	OR	$-$R′	J, cps
2a	CH$_3$CN[c]	238 (4.42), 280 (4.14), 343 (4.81), 362 (4.87)	1.63 (D)	9	6.90 (S)	2.60 (D)	9
2b	CH$_3$CN[c]	237 (4.06), 279 (3.75), 343 (4.38), 359 (4.40)[d]	1.60 (D)	9	5.90 (S)	2.60 (D)	9
2c	CH$_3$CN[c]	242 (4.57), 287 (4.26), 351 (4.76), 370 (4.81)	1.95 (S)		5.97 (S)	7.50 (S)	
2d	CH$_3$CN[c]	242 (4.56), 288 (4.19), 353 (4.76), 371 (4.83)	1.68 (S)		5.90 (S)	6.48 (SP) 8.46 (D)	7 7
2e	CH$_3$CN[c]	242 (4.53), 288 (4.17), 353 (4.76), 370 (4.82)	1.60 (S)			8.30 (S)	
3a	CH$_3$CN	224 (4.28), 229 (4.27), 252 (4.13), 295 sh (4.26), 321 (4.56), 338 (4.46)	1.80 (D)	9	5.92 (S)	2.67 (D)	9
3b	CH$_3$CN	223 (4.12), 230 (4.14), 245 (4.06), 304 sh (4.28), 319 (4.38), 336 (4.30)[d]	1.89 (D)	9	5.87 (S)	2.70 (D)	9
3c	CH$_3$OH	End Abs., 237 (4.33), 332 (4.57), 347 (4.58)	2.22 (S)		5.93 (S)	7.58 (S)	
3d	CH$_5$OH	End Abs., 239 (4.35), 333 (4.57), 348 (4.58)	2.03 (S)		5.90 (S)	6.62 (SP) 8.56 (D)	7 7
3e	CH$_3$OH	236 (4.26), 326 (4.40), 344 (4.36)	1.93 (S)		5.90 (S)	8.40 (S)	
4a	CH$_3$CN[c]	236 (4.38), 340 sh (4.75), 355 (4.81)	1.62 (M), 1.97 (M)		5.87 (S)	2.52 (D)	9
4b	CH$_3$CN[c]	236 (4.24),[d] 339 sh (4.55),[d] 353 (4.62)[d]	1.50 (M), 2.03 (M)			2.53 (D)	9
4c	CH$_3$CN[c]	240 (4.46), 347 sh (4.68), 362 (4.74)	1.53 (S), 2.03 (M)			8.29 (S)	
5a	CH$_3$CN[c]	236 (4.38), 340 sh (4.74), 355 (4.81)	1.62 (M), 1.97 (M)	9	5.87 (S)	2.52 (D)	
5b	CH$_3$CN[c]	236 (4.24), 339 sh (4.55), 353 (4.62)	1.50 (M), 2.03 (M)	9		2.53 (D)	
5c	CH$_3$CN[c]	240 (4.46), 347 sh (4.68), 362 (4.74)	1.53 (S), 2.03 (M)			8.29 (S)	
6a	CH$_3$CN[c]	242 (4.55), 287 (4.18), 352 (4.83), 371 (4.90)	1.58 (S), 1.72 (S)		5.90 (S)	8.28 (S) 6.54 (SP) 8.48 (D)	 7 7
6b	CH$_3$CN[c]	242 (4.50), 286 (4.08), 353 (4.76), 371 (4.81)	1.53 (S), 1.69 (S)		5.90 (S)	8.27 (S) 6.48 (SP) 8.46 (D)	 7 7
6c	CH$_3$CN[c]	242 (4.48), 286 (4.21), 352 (4.76), 372 (4.83)	1.63 (S), 1.83 (S)		5.95 (S)	7.48 (S) 8.32 (S)	

[a] All cyclopropenium ions were studied as perchlorates except **2b** and **4b** studied as chloride. [b] S = singlet, D = doublet, SP = septet, M = multiplet. [c] CH$_3$CN containing HClO$_4$, see Experimental Section. [d] Extinctions for this compound are probably low because of lack of purity of this compound.

trum of the corresponding chloride (**2e**, X = Cl), and can be assigned to the ClO$_4^-$ anion.[13] This is further evidence that these compounds exist as ionic salts, and not as their covalent counterparts, triarylchlorocyclopropenes.[2,3]

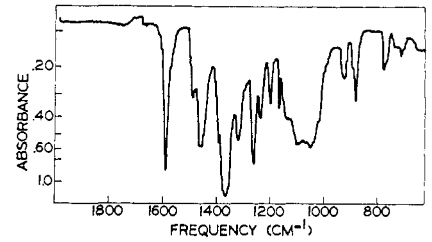


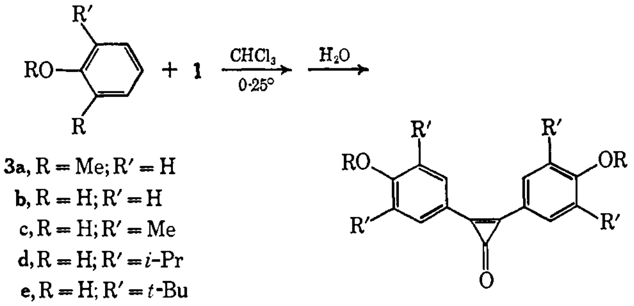
Figure 1. Infrared spectrum of **2e** as mull in Nujol.

The ultraviolet spectra of the symmetrical triarylcyclopropenium ion salts are given in Table I, and can be compared with that reported by Breslow and Chang for tris-*p*(anisyl)cyclopropenium bromide, 343 (sh) and 359 nm (log ϵ 4.86).[8] Note that the long wavelength maxima of the triarylcyclopropenium ions from 2,6-disubstituted phenols (**2c–e**) are bathochromically shifted by about 10 nm compared with the unsubstituted ions (**2a**, **2b**).

The proton nmr spectra of these salts were obtained in CF$_3$COOH and are also recorded in Table I. The aromatic protons of **2a** and **2b** appeared as two doublets (an A$_2$X$_2$ system), while those of **2c–2e** simply gave a single resonance, supporting the fact that alkylation of the aromatic compounds occurred *para* to the –OR groups as shown. In all cases, a low-field resonance was found near τ 1.60; the resonance of **2c** at τ 1.95 was exceptionally high. A similar low-field resonance has been observed for other triarylcyclopropenium ions, and is due to the protons *ortho* to the cyclopropenium nucleus.[10–12]

In addition, reaction of tribromocyclopropenium tetrabromoaluminate with anisole gave the known compound, tris-*p*(anisylcycl)opropenium bromide (**2a**, X = Br), the melting point and ultraviolet spectrum of which were very similar to those Breslow and Chang reported for the same compound.[8]

Diarylcyclopropenones. When **1** is allowed to react with anisole or phenols under mild conditions, only two aromatic nuclei are substituted onto the three-membered ring, and diarylcyclopropenones (**3a–e**) can be isolated after hydrolysis, in yields from 40 to 80%.



3a, R = Me; R′ = H
b, R = H; R′ = H
c, R = H; R′ = Me
d, R = H; R′ = *i*-Pr
e, R = H; R′ = *t*-Bu

The new compounds **3a–3e** are white solids,[14] most

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(13) H. Cohn, *J. Chem. Soc.*, 4282 (1952).

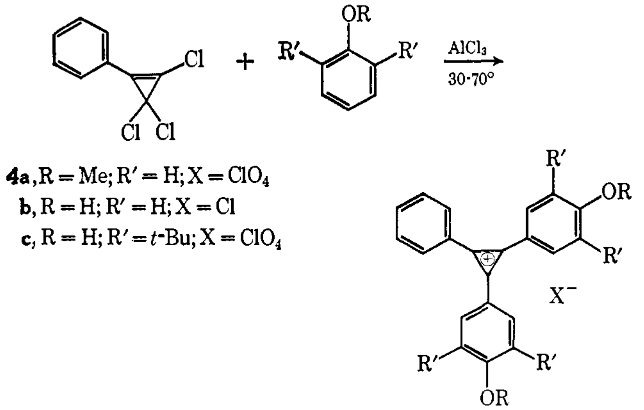
(14) Correct elemental analyses were obtained for all these compounds, except for the product from phenol, **3b**. However, **3b** did show mass spectral peaks at *m/e* 238 (M$^+$) and 210 (M$^+$ − CO). Furthermore, **3b** was converted to the diacetate derivative which was more soluble and easier to purify than **3b** itself, and for which a good elemental analysis was obtained.

of which melt with decomposition near 200°. They all possessed the two strong infrared absorption bands in the regions 1860–1840 and 1620–1590 cm^{-1}, which are diagnostic for the cyclopropenone system.[15,16] The ultraviolet spectra of **3a–e** are recorded in Table I. As shown, the long wavelength maxima occur near 338 nm for **3a** and **3b**, and at about 344 nm for **3c–e**. In contrast, the long wavelength absorption for unsubstituted diphenylcyclopropenone was reported as a shoulder at 310 nm.[16]

The proton nmr spectra of **3a–e** in trifluoroacetic acid, in which the cyclopropenones are expected to be protonated to diarylhydroxycyclopropenium ions, are also listed in Table I. Again the aromatic protons of **3a** and **3b** gave two doublets (an A_2X_2 system), while those of **3c–3e** appeared as singlets, indicating that alkylation of the original benzene derivatives had occurred *para* to the methoxy or hydroxy groups. Note also that the low-field resonances for the protons *ortho* to the three-membered ring for the diarylcyclopropenones are at higher fields (higher τ values) than the *ortho* protons for the corresponding triarylcyclopropenium ion salts listed in Table I. This is consistent with partial localization of the positive charge on the C–OH group, leading to less deshielding of the *ortho* protons on the attached benzene rings.

Unsymmetrical Triarylcyclopropenium Ions. The fact that arylation of trichlorocyclopropenium ion proceeds stepwise means that this reaction can be used to synthesize mixed triarylcyclopropenium ion salts. The final reaction must, however, involve an activated aromatic compound as reactant.

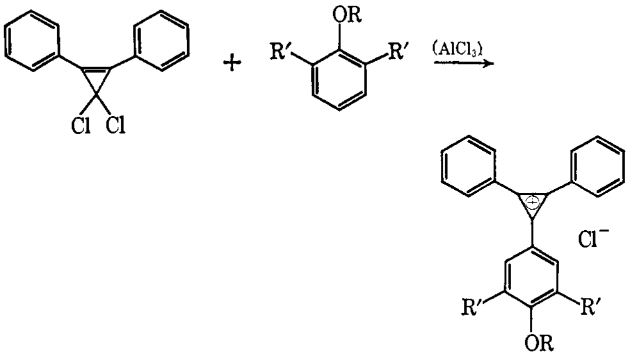
For example, consider the reactions of 1-phenyl-2,3,3-trichlorocyclopropene[6] (made from **1** and benzene under mild conditions) with anisole, phenol, or 2,6-di-*t*-butylphenol. In the presence of aluminum chloride at 30–70°, these reactions all led to the mixed triarylcyclopropenium salts **4a–4c**. The mixed triarylcyclopropenium chlorides were converted to and characterized as their perchlorate salts.[17] They all showed very strong, broad infrared bands in the region 1370–1410 cm^{-1} characteristic for cyclopropenium ions; strong multiplets in the region 1000–1120 cm^{-1} due to perchlorate anion,[13] and sharp bands near 770 and 680 cm^{-1} diagnostic for a monosubstituted benzene ring.[18] The ultraviolet spectra are reported in Table I; data for **4a** agree generally with those previously reported by Breslow and Chang for 1,2-bis(*p*-anisyl)-3-phenylcyclopropenium bromide, **4a** (X = Br).[8]



4a, R = Me; R' = H; X = ClO_4
b, R = H; R' = H; X = Cl
c, R = H; R' = *t*-Bu; X = ClO_4

The nmr spectra of these unsymmetrical triarylcyclopropenium ions, obtained in CF_3COOH, are also listed in Table I. The two substituted phenyl rings of **4a–c** gave proton resonances similar to those found for compounds **2a**, **2b**, and **2c**, respectively, while the unsubstituted ring gave an overlapping AB_2X_2 pattern. The net result was a low-field multiplet near τ 1.50 for all six protons *ortho* to the three-membered ring, and a multiplet near τ 2.02 for the *meta* and *para* protons of the unsubstituted phenyl ring.

If 1,2-diphenyl-3,3-dichlorocyclopropene is treated with the same three aromatic compounds under the usual conditions, the mixed triarylcyclopropenium chlorides **5a–5c** are produced.



5a, R = Me; R' = H
b, R = H; R' = H
c, R = H; R' = *t*-Bu

Prior to our investigation, **5a** and **5b** had been prepared *via* carbene addition reactions.[8,11] While our work was under waxy **5b** and later **5c** obtained by a method similar to ours, were reported by Föhlisch and Bürgle.[12] These workers found, and we confirm, that **5b** can be obtained from phenol and diphenyldichlorocyclopropene without a catalyst. To synthesize **5a** and **5c**, Föhlisch and Bürgle employed boron trifluoride etherate as a catalyst, isolating the ions as tetrafluoroborate salts. The spectral properties of **5a–c** agreed well those for the same ions prepared by others.[8,11,12]

Mixed cyclopropenium ion salts can also be prepared with hydroxyl substituents on all three rings. For instance, treatment of **1** with 2 equiv of 2,6-di-*t*-butylphenol in chloroform at 0°, followed by excess 2,6-diisopropylphenol at 50° led to the mixed triarylcyclopropenium ion salt **6a** (X = Cl); the reverse order of addition of phenols gave **6b** (X = Cl). Similarly, 1,2-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)-3,3-dichlorocyclopropene (**7**), prepared from **3e** and thionyl chloride,[5] reacts with 2,6-dimethylphenol in benzene without catalyst to give the mixed ion **6c**. Compounds **6a–c** are new.

Discussion

From the foregoing and information in the preceding paper, it is seen that reaction of **1** with aromatic compounds can proceed stepwise to give either mono-, di-,

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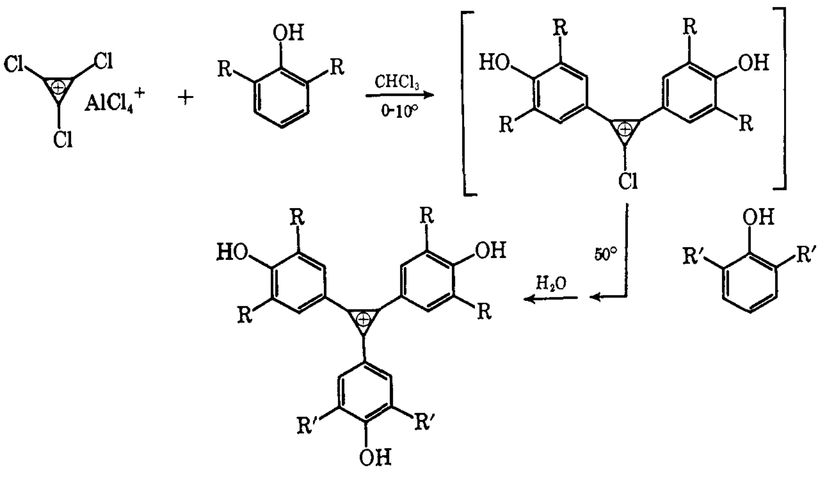
(15) E. V. Demlow, *Tetrahedron Lett.*, 2317, 4003 (1965).

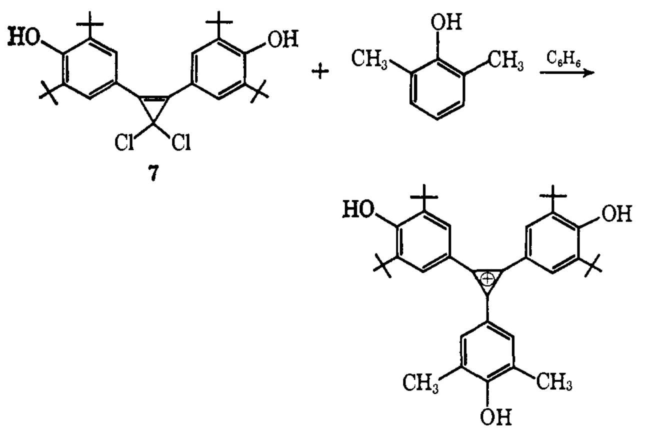
(16) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1376 (1965).

(17) Even the perchlorates were difficult to purify and only **4c** was obtained analytically pure. **4a** had properties agreeing with those of 1,2-bis(*p*-anisyl)-3-phenylcyclopropenium bromide, **4a** (X = Br), reported by Breslow and Chang.[8] Identification of **4b** follows from spectral evidence only.

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1958, p 65.



6a, R = *t*-Bu; R' = *i*-Pr
b, R = *i*-Pr; R' = *t*-Bu



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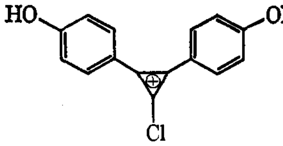
6c

or trisubstitution of chlorine by an aromatic ring, depending on the conditions used and on the aromatic hydrocarbon. To date, however, triarylcyclopropenium ions have been prepared only by the use of strongly activated aromatic compounds, at least in the final substitution step.

In determining the rate and course of the arylation reaction, the nucleophilicity of the aromatic substrate is clearly the most important factor. In the reaction of phenol with **1** to give the triarylcyclopropenium ion **2b** an intermediate must be the diarylchlorocyclopropenium ion, **8**. The final product in the reaction of **1** with benzene, before hydrolysis, is diphenylchlorocyclopropenium ion, **9**. The latter should be less stable and more electrophilic than **8**. Yet phenol reacts with **8**, whereas benzene, being much less nucleophilic than phenol, will not react under the same conditions with **9**,



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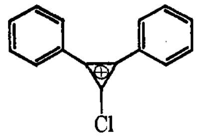

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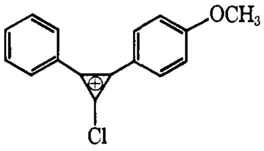
That the electrophilicity of the intermediate cyclopropenium ions may also be important is indicated by two reactions of anisole. Under the same conditions that tetrachlorocyclopropene and anisole give the bis-(*p*-anisyl)cyclopropenone **3a**, phenyltrichlorocyclopropene reacts with anisole to give the triarylcyclopropenium chloride **4a**. Evidently anisole, under these conditions, will react with the more electrophilic intermediate ion **10** but not with the less electrophilic analog **11**.



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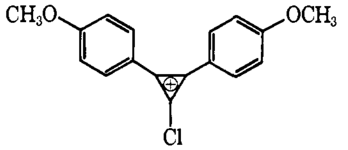

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Experimental Section

For general comments on the experimental procedures, and instruments used, see the accompanying paper.[6] In general, no effort was made to optimize yields. Infrared spectra were taken on mulls in Nujol and fluorocarbon oil as described previously.[6] Spectrograde solvents were used for ultraviolet spectra studies; when acetonitrile was used, it was acidified with 60% HClO$_4$ (*ca.* 0.1 vol %). Proton nmr spectra were determined in reagent grade trifluoroacetic acid. In every case, integration gave proton ratios corresponding to those calculated for the assignment given in Table I.

Tris(*p*-anisyl)cyclopropenium Chloride (2a, X = Cl). Tetrachlorocyclopropene (1.5 g, 8.4 mmol) was mixed with 1.1 g (8.4 mmol) of AlCl$_3$ and warmed momentarily at 80° to form tetrachlorocyclopropenium tetrachloroaluminate (1). Anisole (5 ml) was added and the reaction mixture was stirred for 30 min; occasional cooling was necessary to prevent the exothermic reaction from becoming too vigorous. The resulting deep violet reaction mixture was poured onto water and stirred until the color was discharged. A yellow precipitate formed; this was filtered and recrystallized from ethanol–ether to give 1.0 g (30%) of the product as an off-white solid, mp 190° dec. The infrared spectrum of this compound showed absorption at 1590 (vs), 1550 (m), 1460 (s), 1440 (s), 1390 (vs, br), 1310 (s), 1300 (m), 1260 (vs), 1170 (vs), 1010 (s), 840 (s), and 710 (m) cm^{-1}. The uv and proton nmr spectra, which agree with those reported by Breslow and Chang for the bromide,[8] are given in Table I.

Tris(*p*-anisyl)cyclopropenium Bromide (2a, X = Br). This compound was prepared in 25% yield by the reaction of tetrabromocyclopropene, AlBr$_3$, and anisole, as described above. The final product, an off-white solid, melted at 201° with decomposition (lit.[8] mp 210–212°). The infrared spectrum was the same as that stated above for **2a** (X = Cl).

Tris(*p*-anisyl)cyclopropenium Perchlorate (2a, X = ClO$_4$). This compound was prepared in 92% yield by dissolving **2a** (X = Cl or Br) in methanol and then adding 10% HClO$_4$ until precipitation was complete. This precipitate was filtered and recrystallized from ethanol–acetone to give a white solid, mp 274° dec. The infrared spectrum possessed all the bands of **2a** (X = Cl), plus an additional strong, broad band at 1090 cm^{-1}, which can be assigned to the perchlorate anion.[13] *Anal.* Calcd for $C_{24}H_{21}ClO_7$: C, 63.08; H, 4.63. Found: C, 62.29; H, 4.40.

Tris(3,5-dimethyl-4-hydroxyphenyl)cyclopropenium Chloride (2c). Reaction of 5.2 g (17 mmol) of **1** with 6.2 g (51 mmol) of 2,6-dimethylphenol at 70°, according to the method described above (except that chloroform was added after the initial reaction), gave, after washing with acetone, 4.2 g (55%) of crude yellow product (chloride). This was recrystallized from methanol–ether to give an off-white solid, with no defined melting point (slow decomposition over 200°). The infrared spectrum showed absorptions at 1600 (s), 1465 (m), 1400 (s), 1380 (vs), 1345 (vs), 1270 (s), 1240 (s), 1200 (s), 1110 (m), 1030 (w), 1000 (m), 955 (w), 930 (vw), 875 (m), 765 (vw), and 740 (w) cm^{-1}. The uv and nmr spectra are shown in Table I.

Anal. Calcd for $C_{27}H_{27}ClO_7$: C, 64.99; H, 5.46; Cl, 7.11. Found: C, 65.08; H, 5.52; Cl, 6.97.

Tris(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenium Ion Salts (2d). Reaction of 15 g (84 mmol) of tetrachlorocyclopropene, 11 g (84 mmol) of $AlCl_3$, and 50 g (280 mmol) of 2,6-diisopropylphenol in 75 ml of chloroform at 50°, according to the method described above, gave, after washing with acetone, 40.5 g (80%) of the chloride as an off-white solid. This was converted to the corresponding perchlorate, 272° dec. The infrared spectrum of the perchlorate showed absorptions in the region 4000–625 cm^{-1} at 3400 (m, br), 2955 (m), 2920 (m, sh), 2865 (m), 1595 (vs), 1490 (w), 1460 (m), 1385 (vs, br), 1335 (vs), 1320 (vs), 1290 (m), 1280 (m), 1260 (s), 1220 (m), 1205 (s), 1150 (s), 1115 (m), 1050 (s, br), 960 (w), 925 (m), 885 (m), 815 (w), and 775 (m) cm^{-1}. *Anal.* Calcd for $C_{39}H_{51}ClO_7$: C, 70.27; H, 7.66. Found: C, 70.17; H, 7.89.

Tris(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclopropenium Ion Salts (2e). Reaction of tetrachlorocyclopropene, $AlCl_3$, and 2,6-di-*t*-butylphenol in chloroform, according to the method described above, did not give a precipitate upon hydrolysis. Therefore, the organic material was extracted with several portions of chloroform, dried, filtered, and then stripped of solvent, leaving a solid mass which proved to be a mixture of **2e** (X = Cl) and its dehydrochlorinated derivative, a quinocyclopropene.[19]

Therefore, triethylamine was added during work-up of the reaction mixture to convert the entire product to the quinocyclopropene, which was washed with acetonitrile to give a 70% yield. Treatment of this with perchloric acid in benzene gave **2e** (X = ClO_4), 244–245° dec, while treatment with hydrogen bromide in ether precipitated **2e** (X = Br), mp 284–286 dec. The infrared spectrum of the perchlorate is shown in Figure 1. Only the bromide was analyzed. *Anal.* Calcd for $C_{45}H_{63}BrO_3$: C, 73.87; H, 8.62; O, 6.57; Br, 10.94. Found: C, 73.71; H, 8.71; O, 6.75; Br, 10.83 (diff).

Tris(*p*-hydroxyphenyl)cyclopropenium Ion Salts (2b). Reaction of 2.6 g (8.4 mmol) of trichlorocyclopropenium tetrachloroaluminate (**1**) with 6.0 g (63 mmol) of phenol at 70°, according to the method described above for the preparation of **2a** (X = Cl), gave 3.0 g (100%) of the crude chloride. Recrystallization from methanol–ether or large quantities of acetonitrile gave a yellow-brown solid showing the following bands in the infrared spectrum: 1855 (w, br), 1605 (vs), 1580 (s), 1400 (vs, br), 1300 (s, br), 1270 (s, sh), 1170 (s), 840 (m), 760 (w), and 720 cm^{-1}. The uv and proton nmr spectra are given in Table I.

The chloride was dissolved in hot formic acid and a slight excess of 60% aqueous perchloric acid was added. The perchlorate (**2b**, X = ClO_4) was obtained as an off-white powder, 320° dec, by addition of ether to the cold reaction mixture. The infrared spectrum was similar to that for **2b** (X = Cl) except that an additional band at 1080 typical for the perchlorate ion was found. *Anal.* Calcd for $C_{21}H_{15}ClO_7$: C, 60.80; H, 3.65; Cl, 8.55. Found: C, 60.71; H, 3.76; Cl, 8.73.

Bis(*p*-anisyl)cyclopropenone (3a). At −70°, 2.7 g (25 mmol) of anisole dissolved in 10 ml of chloroform was added to 2.6 g (8.4 mmol) of **1**. The reaction mixture was warmed rapidly to room temperature and then stirred for 30 min giving a purple suspension. Ice water was then added, discharging the color and forming a yellow precipitate. This was filtered and dried, giving 1.0 g (45%) of crude product. Two recrystallizations from methanol–water or benzene gave a white solid, mp 179–181°. The infrared spectrum supported the cyclopropenone structure with absorptions at 1845 (s), satellites at 1870 (m) and 1800 (w), and 1620 (s) cm^{-1}; other bands were observed at 1600 (vs), 1570 (m), 1510 (s), 1500 (m), 1440 (m), 1430 (m), 1350 (s), 1300 (s), 1270 (s), 1260 (s), 1195 (w), 1180 (m), 1170 (s), 1110 (w), 1020 (m), 1010 (s), 835 (s), 825 (s), 800 (w), and 750 (vw) cm^{-1}. *Anal.* Calcd for $C_{17}H_{14}O_3$: C, 76.69; H, 5.26; O, 18.05. Found: C, 76.49; H, 5.24; O, 18.17.

Bis(*p*-hydroxyphenyl)cyclopropenone (3b). Reaction of 2.6 g (8.4 mmol) of **1** and 1.6 g (16 mmol) of phenol in 10 ml $CHCl_3$, as described above, gave 0.2 g (10%) of yellow-brown **3b**. Much higher yields, but cruder products, could be obtained by heating the reaction mixture to reflux. The product was highly insoluble in most organic solvents and was never recrystallized successfully. It was reprecipitated several times by dissolving in aqueous sodium hydroxide and then adding hydrochloric acid, to finally give an off-white solid, mp 222–226° dec. The infrared spectrum showed characteristic cyclopropenone absorption at 1860 (s) and 1610 (vs), as well as bands at 1590 (s), 1560 (s) 1530 (m), 1510 (m), 1490 (s), 1380 (vs), 1300 (s), 1270 (s), 1260 (s), 1170 (s), 980 (w), 830 (s), and 760 (m) cm^{-1}. The uv and proton nmr spectra are given in Table I. The mass spectra showed a weak peak at *m/e* 238 (M^+) and a very strong peak at 210 ($M^+ - CO$).

This compound was converted to its diacetate for elemental analysis and proof of structure. **3b** (4.0 g, 16.7 mmol) was added to 5 ml of triethylamine and 6 ml of acetic anhydride. The mixture was heated at reflux for 15 min then cooled and added to 100 ml of 5% aqueous K_2CO_3, forming a precipitate. This was filtered and recrystallized twice from ethanol–water, giving 0.9 g (17%) of the product as a white solid, mp 177–180°. The infrared spectrum displayed typical cyclopropenone absorption bands at 1865 (s) and 1630 (s), an acetate carbonyl band at 1760 (s), and an acetate C–O stretching band at 1190 (vs, br) cm^{-1}. Other bands were formed at 1605 (s), 1500 (m), 1415 (w), 1370 (s), 1350 (s), 1300 (w), 1160 (s), 1100 (w), 1015 (s), 910 (s), and 850 (m) cm^{-1}. The proton nmr spectrum in $CDCl_3$ showed doublets at τ 2.02 (J = 8.5 cps) and τ 2.68 (J = 8.5 cps), and a singlet at τ 7.67, in the expected ratio of 2:2:3. In addition, the mass spectrum (heated inlet) showed a very strong peak at *m/e* 294 ($M^+ - CO$), as well as strong peaks at *m/e* 252 and 210 (due to successive loss of $CH_2 = C = O$). *Anal.* Calcd for $C_{19}H_{14}O_5$: C, 70.81; H, 4.35; O, 24.84. Found: C, 70.43; H, 4.49; O, 24.26.

Bis(3,5-dimethyl-4-hydroxyphenyl)cyclopropenone (3c). Reaction of 5.2 g (17 mmol) of **1** and 6.2 g (51 mmol) of 2,6-dimethylphenol in 30 ml of $CHCl_3$, as described above for the preparation of **3a**, gave 5.0 g (100%) of crude product as a light yellow solid. Several recrystallizations from methanol gave a white solid, mp 268° dec. The infrared spectrum showed typical cyclopropenone bands at 1840 (s) and 1600 (s) cm^{-1}; other bands occurred at 1560 (s), 1495 (m), 1375 (vs), 1335 (vs), 1265 (s), 1210 (vs), 1120 (m), 1105 (m), 1025 (m), 990 (vw), 935 (vw), 890 (m), 875 (sh, w), and 860 (sh, w) cm^{-1}. *Anal.* Calcd for $C_{19}H_{18}O_3$: C, 77.55; H, 6.12; O, 16.33. Found: C, 77.42; H, 6.21; O, 16.37 (diff).

Bis(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenone (3d). Reaction of 26 g (84 mmol) of **1** and 34 g (190 mmol) of 2,6-diisopropylphenol in 100 ml of $CHCl_3$ was carried out as described above, except that the reaction temperature was not allowed to go above 10°. The product (28.0 g, 82%) was obtained as an off-white solid. Recrystallization from methanol–water gave a white solid, mp 209–211° dec. The infrared spectrum in the 4000–625 cm^{-1} region showed absorption bands at 3200 (m, vbr), 2960 (m), 2920 (m, sh), 2870 (m), 1850 (s, sh), 1835 (vs), 1705 (w), 1595 (vs), 1560 (vs), 1460 (s), 1430 (s), 1370 (vs), 1335 (s), 1305 (vs, br), 1260 (s), 1200 (vs, br), 1245 (s), 1105 (m), 1045 (m), 1025 (w), 955 (vw), 935 (m), 885 (m), 820 (vw), 775 (w), and 745 (w) cm^{-1}. *Anal.* Calcd for $C_{27}H_{34}O_3$: C, 79.80; H, 8.38; O, 11.82. Found: C, 79.33; H, 8.51; O, 12.16 (diff).

Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclopropenone (3e). Reaction of tetrachlorocyclopropene, $AlCl_3$ and 2,6-di-*t*-butylphenol in chloroform at 0–10° as described above, did not give a precipitate upon hydrolysis. The organic material was therefore extracted with several portions of chloroform, dried, filtered, and stripped of solvent under vacuum, leaving the crude product (48%). Several recrystallizations from cyclohexane gave a white solid, mp 215° with gas evolution. The infrared spectrum gave absorption bands at 1840 (s), 1590 (s), 1580 (s, sh), 1560 (m, sh), 1415 (m), 1345 (vs), 1295 (m), 1255 (s), 1230 (m), 1195 (m), 1085 (m, br), 1020 (w), 920 (w, doublet), 890 (w, sh), 885 (m), 775 (w), and 720 (w) cm^{-1}. *Anal.* Calcd for $C_{31}H_{42}O_3$: C, 80.51; H, 9.09; O, 10.40. Found: C, 80.32; H, 9.30; O, 10.24.

Bis(*p*-anisyl)phenylcyclopropenium Ion Salts (4a). 1-Phenyl-2,3,3-trichlorocyclopropene (2.0 g, 9.1 mmol) was treated with 1.4 g (9.1 mmol) of $AlCl_3$ with 5 ml of anisole, resulting in an exothermic reaction with the evolution of HCl. The reaction mixture was

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(19) The chemistry of quinocyclopropenes derived from these compounds will be treated separately.

stirred for 30 min, then added to water, precipitating 1.5 g (45%) of **4a** (X = Cl) as a yellow solid. This was recrystallized from methanol–ether to give an off-white solid, which was then converted to and studied as the perchlorate, 238° dec. The infrared spectrum of the perchlorate showed bands at 1600 (vs), 1570 (m), 1490 (m), 1400 (vs), 1320 (s), 1280 (vs), 1170 (vs), 1090 (vs, br), 1010 (s), 830 (s), 770 (m), and 680 (m) cm^{-1}. The uv spectrum (Table I) is similar to that reported by Breslow and Chang.[8]

Bis(*p*-hydroxyphenyl)phenylcyclopropenium Salts (4b). This compound was prepared in 34% yield by the reaction of 1-phenyl-2,3,3-trichlorocyclopropene, $AlCl_3$, and phenol, according to the method described above, except that chloroform was used as a solvent for the reaction. The infrared spectrum showed bands at 1640 (s), 1600 (vs), 1580 (sh), 1490 (sh), 1395 (vs, br), 1300 (s), 1240 (m), 1160 (s), 840 (s), 760 (m), 730 (m), and 670 (m) cm^{-1}. The chloride was dissolved in warm formic acid and converted to the perchlorate by addition of 60% aqueous $HClO_4$. **4b** (X = ClO_4) was obtained (41%) as a white solid, 269° dec (explosion). The infrared absorption was identical with that for **4b** (X = Cl) except for the perchlorate band at 1080 cm^{-1}. *Anal.* Calcd for $C_{21}H_{15}ClO_6$: C, 63.24; H, 3.79; Cl, 8.89. Found: C, 62.89; H, 3.77; Cl, 8.95.

Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)phenylcyclopropenium Ion Salts (4c). The reaction of 1-phenyl-2,3,3-trichlorocyclopropene, $AlCl_3$, and 2,6-di-*t*-butylphenol in chloroform, as described above, gave a mixture of the mixed triarylcyclopropenium chloride, **4c** (X = Cl), and its dehydrochlorinated derivative, a quinocyclopropene.[19] Hence, triethylamine was added during work-up to convert all the product to the quinocyclopropene; a 55% yield was obtained. This was then treated with $HClO_4$ in benzene to form **4c** (X = ClO_4), 200–202° dec. The infrared spectrum of this perchlorate gave absorption at 1595 (s), 1495 (m), 1390 (s, sh), 1370 (vs, br), 1320 (s), 1260 (s), 1249 (m), 1200 (m), 1110 (m, br), 1030 (s, sh), 1020 (s, br), 930 (w), 895 (m), 880 (w), 770 (m), 750 (vw), 720 (w), and 685 (m), cm^{-1}. *Anal.* Calcd for $C_{37}H_{47}ClO_6$: C, 71.38; H, 7.56. Found: C, 71.33; H, 7.76.

Diphenyl-*p*-anisylcyclopropenium Ion Salts (5a). 1,2-Diphenyl-3,3-dichlorocyclopropene (2.2 g, 8.4 mmol), prepared by treatment of diphenylcyclopropenone with $SOCl_2$,[5] and 1.1 g (8.4 mmol) of $AlCl_3$ were added to 10 ml of anisole and heated to reflux for several minutes. The resulting deep red reaction mixture was added to water, discharging the color. A precipitate slowly formed in the aqueous layer. This was filtered to give 1.3 g (46%) of the crude chloride (**5a**, X = Cl) as a yellow solid. Recrystallization from methanol–ether gave the chloride as a white solid, mp 140° dec. This was converted to the corresponding perchlorate. The infrared spectrum of the perchlorate showed bands at 1500 (s), 1570 (w), 1490 (w), 1400 (vs), 1320 (m), 1280 (s), 1170 (s), 1080 (vs, br), 1010 (m), 830 (m), 770 (m), and 680 (m) cm^{-1}. The uv spectrum in acidic acetonitrile showed λ_{max} 236 nm (log ϵ 4.22), 273 (4.23), 328 sh (4.63), and 343 (4.74).

Diphenyl-*p*-hydroxyphenylcyclopropenium Salts (5b). These compounds were prepared by a method of similar to that of Föhlisch and Bürgle.[12a] 1,2-Diphenyl-3,3-dichlorocyclopropene (0.30 g, 1.15 mmol) was added to 0.3 g (3.2 mmol) of phenol in 4 ml of benzene. The mixture was heated to reflux for 7 min then cooled to room temperature. Ether was added to precipitate **5b** (X = Cl), 0.3 g (28%), as an off-white powder. The chloride was converted to the perchlorates[12b] in 60% yield. **5b** (X = ClO_4) was an off-white solid, 235° dec (lit.[12a] 237° dec). The infrared spectrum of the perchlorate showed bands at 1840 (w), 1600 (vs), 1580 (m), 1500 (m), 1490 (m), 1410 (vs, br), 1380 (s), 1320 (w), 1300 (s), 1270 (w), 1230 (m), 1180 (s), 1120 (s), 1100 (s), 1040 (s), 1000 (m), 920 (w), 850 (m), 770 (s), and 680 (s) cm^{-1}. The uv and nmr spectra are recorded in Table I. *Anal.* Calcd for $C_{21}H_{15}ClO_5$: C, 65.89; H, 3.95; Cl, 9.26. Found: C, 65.71; H, 3.90; Cl, 9.10.

Diphenyl(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclopropenium Perchlorate (5c). This compound was prepared in 33% yield by the reaction of 1,2-diphenyl-3,3-dichloropropene, $AlCl_3$, and 2,6-di-*t*-butylphenol in benzene, according to the method described above for **5a** (X = ClO_4). The final white solid perchlorate decomposed at 165–168°. The infrared spectrum of the perchlorate in the region 4000–625 cm^{-1}, showed absorption bands at 2950 (m), 2920 (sh), 2870 (sh), 1835 (w), 1600 (vs), 1580 (m), 1500 (s), 1395 (vs), 1380 (vs, br), 1330 (s), 1310 (sh), 1290 (m), 1270 (s), 1240 (m), 1200 (m), 1175 (m), 1160 (m), 1090 (vs, br), 1050 (s), 1020 (sh), 1000 (m), 930 (w), 890 (m), 760 (s), 730 (w), and 670 (s) cm^{-1}. See Table I for the uv and nmr spectra of this compound.

Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)-(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenium Ion Salts (6a). **1** (10.4 g, 33 mmol) and 14 g (68 mmol) of 2,6-di-*t*-butylphenol in 50 ml of chloroform were treated at 0–10° according to the method for the preparation of **3e** up to the point of addition of water. Instead, 12.0 g (67.5 mmol) of 2,6-diisopropylphenol was added and the mixture stirred at 50° for 30 more min. Then water was added, discharging the typical purple color of the reaction mixture. The organic material was extracted with chloroform, dried, filtered, and stripped to low volume by rotary evaporation, forming a precipitate. This was filtered and washed with chloroform, giving 13.0 g of the mixed triarylcyclopropenium chloride. This was then converted to and studied as the perchlorate, 244–245° dec. The infrared spectrum of the perchlorate in the region 4000–625 cm^{-1}, showed bands at 3520 (m), 3380 (m), 2965 (s), 2920 (sh), 2875 (m), 1590 (s), 1490 (w), 1470 (w), 1370 (vs, br), 1320 (s), 1260 (s), 1240 (m), 1200 (m), 1150 (m), 1110 (s), 1060 (s, br), 930 (w), 880 (m), 780 (w), and 755 (w) cm^{-1}. The uv spectrum (Table I) is very similar to that for **2d** and **2e**. The nmr spectrum is also given in Table I. The relative intensities indicate that the resonance at τ 1.58 is due to the *ortho* protons of the *t*-butyl substituted rings and that at 1.72 to the *ortho* protons of the isopropyl substituted rings. *Anal.* Calcd for $C_{43}H_{59}ClO_7$: C, 71.47; H, 8.17. Found: C, 70.86; H, 8.15.

Bis(3,5-diisopropyl-4-hydroxyphenyl)-(3,5-di-*t*-butyl-4-hydroxyphenyl)cyclopropenium Ion Salts (6b). A similar reaction between 10.4 g (33 mmol) of **1** and 17.0 g (68 mmol) of 2,6-diisopropylphenol in 50 ml of $CHCl_3$ at 0°, followed by 14 g (68 mmol) of 2,6-di-*t*-butylphenol at 50°, gave 16.0 g (74%) of the mixed triarylcyclopropenium chloride. This was converted to and characterized as the perchlorate, 248–249° dec. The infrared spectrum of the perchlorate exhibited bands at 3510 (s), 3400 (s), 2960 (s), 2925 (sh), 2865 (s), 1595 (vs), 1495 (m), 1465 (s), 1375 (vs, br), 1340 (vs), 1320 (vs), 1265 (s), 1225 (s), 1205 (s), 1150 (s), 1115 (s), 1055 (vs, br), 940 (m), 885 (m), 820 (w), 780 (m), and 720 (vw) cm^{-1}. The intensities in the nmr spectrum (Table I) allow assignment of the singlet at τ 1.53 to the *t*-butyl substituted ring and that at τ 1.69 to the isopropyl substituted ring. *Anal.* Calcd for $C_{41}H_{55}ClO_7$: C, 70.90; H, 7.92. Found: C, 70.76; H, 7.87.

Bis(3,5-di-*t*-butyl-4-hydroxyphenyl)-(3,5-dimethyl-4-hydroxyphenyl)cyclopropenium Ion Salts (6c). **3e** (3.2 g, 6.9 mmol) was treated with 5 ml of $SOCl_2$,[5] heated momentarily at 50°, and then placed under vacuum to remove the excess $SOCl_2$, leaving the crude *gem*-dichlorocyclopropene. The infrared spectrum of this solid showed no band at 1840 cm^{-1}, which would indicate unreacted **3e**. 2,6-dimethylphenol (1.7 g, 14 mmol) in 10 ml of benzene was added and the mixture was heated to reflux for 10 min, then cooled to room temperature. The precipitated product was filtered and washed with benzene to give 2.3 g (55%) of **6e** (X = Cl) as a light yellow solid. Several recrystallizations from methanol–ether gave an off-white solid (chloride), which was then converted to and studied as the perchlorate, 276° dec. The infrared spectrum of the perchlorate showed bands at 1600 (s), 1590 (s), 1480 (m), 1370 (vs, br), 1340 (s), 1260 (s), 1245 (s), 1200 (m), 1150 (m), 1130 (m), 1110 (s), 1080 (m), 1040 (s), 1020 (s), 1000 (s), 950 (m), 825 (w), 885 (m), 775 (w), and 720 (vw) cm^{-1}. From integrated intensities, the following assignments can be made for the nmr spectrum (Table I): τ 1.63, *ortho* protons of *t*-butyl substituted rings; 1.83, protons of methyl substituted rings; 7.48, CH_3 protons; and 8.32, *t*-butyl protons. *Anal.* Calcd for $C_{39}H_{51}ClO_7$: C, 70.28; H, 7.66. Found: C, 70.20; H, 7.68.

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