Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation and Silver Ion Assisted Solvolysis of *sym*-Tetraphenylethylene Dichloride¹

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Received May 23, 1995[®]

The reaction of 3-chloro-2,2,3,3-tetraphenylpropanenitrile (2) with $AgSbF_6$ or $SbCl_5$ below -55 °C in methylene chloride produces the stable, long-lived cation 2-cyano-1,1,2,2-tetraphenylethyl cation (5). Treatment of 5 with TMSCN affords a 98% yield of 2,2,3,3-tetraphenylsuccinonitrile. It was also found that cation 5 generated with $AlCl_3$ at 0 °C can undergo intramolecular aromatic substitution to give 9-(cyanodiphenylmethyl)fluorene (8). In the reactions of sym-tetraphenylethylethylethanone dimethyl ketal (9) can be synthesized in 91% yield. Because rearrangement occurred, 1-methoxy-1,2,2,2-tetraphenylethyl cation (15) is proposed as a reaction intermediate. In contrast, treatment of dichloride 1 with CF₃CO₂Ag in the presence of phenol or isopropyl or allyl alcohol did not produce the corresponding ketals but the 1,3-dioxolane ortho esters 19, 20, or 21 (2-alkoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolanes).

sym-Tetraphenylethylene dichloride (1) is a little studied, readily available stable compound which appears to be an ideal precursor for the synthesis of substituted tetraphenylethanes. Recently, we discovered that 1 undergoes substitution with trimethylsilyl cyanide (TM-SCN) in the presence of TiCl₄ to form 3-chloro-2,2,3,3tetraphenylpropanenitrile (2) which in turn can be converted into 2,2,3,3-tetraphenylsuccinonitrile (3) (see eq 1).²

$$\begin{array}{cccc} CI & CI & TICI_4 & CI & CN & TICI_4 & CN & CN \\ Ph_2C & -CPh_2 & TMSCN & Ph_2C & -CPh_2 & TMSCN & Ph_2C - CPh_2 & Eqn. 1 \\ 1 & 2 & 3 \end{array}$$

In the absence of TMSCN, dichloride 1 reacted with $AlCl_3$ or $TiCl_4$ at ambient temperatures or -78 °C in CH_2 - Cl_2 to give tetraphenylethylene, probably via the decomposition of the cationic intermediate, chlorotetraphenylethyl cation. The instability of the chlorotetraphenylethyl cation is surprising since one might expect such a highly phenylated ethyl cation to be stable. It then became the goal of this study to investigate the stability of the cyanotetraphenylethyl cation. In this paper we report the synthesis of a long-lived substituted tetraphenylethyl cation.

Parallel to the study of the Lewis acid catalyzed substitution reactions of dichloride 1 reported previously,² we have also undertaken the solvolysis reactions of 1 promoted by silver trifluoroacetate. Products isolated from these solvolysis reactions include a sterically hindered ketal tetraphenylethanone dimethyl ketal (9), as well as dioxolane ortho esters (2-alkoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolanes) 19-21. Structural features of both 9 and 19 were studied by X-ray crystal structure determinations.

Results and Discussion

Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (5). The treatment of nitrile 2 with CF_3CO_2Ag in benzene at 0 °C for 1 h gave a 77% yield of 3-(trifluoroacetoxy)-2,2,3,3-tetraphenylpropanenitrile (4) together with AgCl. This suggests the reaction as shown in Scheme 1 may involve the formation of the 2-cyano-



1,1,2,2-tetraphenylethyl cation (5), which is trapped by trifluoroacetate ion. When the same reaction was carried out in a CH₂Cl₂.MeOH solvent system, 3-methoxy-2,2,3,3tetraphenylpropanenitrile (6) was isolated in 98% yield. The possible rearrangement of cation 5 to 1-cyano-1,2,2,2tetraphenylethyl cation (7) by a 1,2-phenyl shift did not occur. In earlier work it was suggested that an α -cyano cation is more stable than a β -cyano cation because the cyano function can provide resonance stabilization when it is directly attached to the carbocation center.^{3,4} However, the rearrangement of 2-cyano-2-bicyclo[2.1.1]hexyl cation to 1-cyano-2-bicyclo[2.1.1]hexyl cation shows a β -cyano cation that is about 2–3 kcal/mol more stable

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[®] Abstract published in *Advance ACS Abstracts*, August 15, 1995. (1) Presented in part at the 207th National Meeting of the American Chemical Society, San Diego, CA, 1994; ORGN 486.

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Table 1. Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (5) with SbCl₅

entry	mole ratio SbCl ₅ :2	<i>T</i> , °C	rect time, h	6 yield, %	2 recovered, %
1	1.5:1	-75	2.5	25	68
2	1.5:1	-75	4.5	37	55
3	1.5:1	-75	6.5	45	51
4	1.5:1	-55	2.5	46	46
5	2.5:1	-75	2.5	66	23
6	2.5:1	-75	4.5	93	0

than its isomeric α -cyano cation.⁵ Because **5** is a doubly benzylic cation, it is unlikely to rearrange to a singly benzylic α -cyano cation like 7.6

To study cation 5 under conditions of lower nucleophilicity of the anion, $AgSbF_6$ was substituted for CF_3CO_2 -Ag. As shown in Scheme 2, treatment of 2 with AgSbF₆ in CH_2Cl_2 gave a red-colored reaction mixture at -55 °C. After 2 h, the reaction was quenched with MeOH and methoxy nitrile 6 was isolated in 75% yield. This strongly suggests that cation 5 is stable at -55 °C for at least 2 h. If the temperature is warmed to -35 °C, tetraphenylsuccinonitrile (3) is generated in 44% yield. It seems possible that cation 5 may dissociate at higher temperatures into diphenylmethyl radical cation⁷ and cyanodiphenylmethyl radical. The latter dimerizes to give $3.^8$

The preparation of cation 5 from 2 with strong Lewis acids such as SbCl₅ also was studied. It was found that 2.5 mol of $SbCl_5$ was needed per mol of 2 to raise the yield of 5 to 93%.⁹ See Table 1. Evidence for the formation and stability of 5 comes from a run which was quenched with TMSCN to produce tetraphenylsuccinonitrile (3) (98%).

When cation 5 was generated with $AlCl_3$ at 0 °C in benzene, 9-(cyanodiphenylmethyl)fluorene (8) was obtained. The structure of 8 was confirmed by comparison with a sample synthesized from 9-bromofluorene and sodiodiphenylacetonitrile in liquid NH_3 (see Scheme 3). The formation of fluorene derivative 8 is probably due to the delocalization of the positive charge into one of the phenyl rings (see resonance structures 5 in Scheme 3) which then attacks one of the ortho positions of the other phenyl ring attached to the same carbon to give a cyclized intermediate. This intermediate can lose a proton followed by a 1,3-hydrogen shift to give the observed product.10

(10) Similar cyclizations to 9-substituted fluorenes have been reorted for benzoyl- and acetyldiphenylmethyl cations by Ohwada, T.; Shudo, K. J. Am. Chem. Soc. 1988, 110, 1862.



Silver Ion Assisted Solvolysis of sym-Tetraphenylethylene Dichloride (1). Inspired by the ease of converting chloro nitrile 2 to methoxy nitrile 6 under the solvolytic conditions shown in Scheme 1, we attempted to replace both chlorine atoms in 1 with two methoxyl groups to give 1,2-dimethoxytetraphenylethane.¹¹

When the reaction of 1 with CF_3CO_2Ag was run in the presence of MeOH for 2 h, tetraphenylethanone dimethyl ketal (9) was formed in 67% yield together with 28% of tetraphenylethanone (10).¹² A possible reaction sequence leading to the formation of ketal 9 is outlined in Scheme 4. The reaction probably proceeds via intermediate 12,

Scheme 4



followed by the formation of cation 13. Since 1,2dimethoxytetraphenylethane (14) was not isolated, the rearrangement of 13 to α -methoxy cation 15 by a 1,2phenyl shift must have shifted the equilibrium away from 14. The cation 15 was trapped by methanol to afford ketal 9.

Since 2 mol of trifluoroacetic acid is formed for each mole of dichloride 1 which reacts, it is possible that ketone 10 was formed from 9 via an acid-catalyzed hydrolysis reaction. If that were the case, neutralization of the acid with a base such as Na₂CO₃ before the aqueous workup would increase the yield of ketal 9 and diminish the amount of 10. This was shown to be true by simple addition of anhydrous Na₂CO₃ before the aqueous workup, and the yield of ketal 9 is improved to 91% at the expense of 10. Similar results were obtained when the reactions were carried out with other silver salts such

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⁽¹²⁾ The yield of ketal 9 varies with the dryness of the CF_3CO_2Ag . Better yields were obtained when the silver salt was dried in vacuo overnight before use.

as Ag_2CO_3 and $AgOCN^{13}$ Ketal **9** is a new compound, and all attempts to synthesize it directly from tetraphenylethanone (10) by a reaction of trimethyl orthoformate with 10 or by transketalization of 10 and 2,2-dimethoxypropane were unsuccessful.¹⁴

Since dimethyl ketal 9 had been synthesized by treatment of dichloride 1 with CF_3CO_2Ag in the presence of methanol, we wondered whether or not tetraphenylethanone diphenoxy ketal (16) could be prepared similarly. When the reaction of dichloride 1 with CF_3CO_2Ag was carried out in the presence of phenol, a 90% yield of air stable 2-phenoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (19) was isolated. This reaction appears to involve the formation of chloronium ion 11, which suffers attack by trifluoroacetate ion to yield chloro ester intermediate 17 as outlined in Scheme 5. Ester 17 can





react with a second mole of CF₃CO₂Ag to generate cation 18 with neighboring group participation from the trifluoroacetoxyl group.¹⁵ Intermediates similar to cation 18 were first proposed by Winstein to account for the stereochemical results in the reactions of some dihalides and acetoxy halides with AgOAc.¹⁶ It is interesting that 18 undergoes attack by phenol at the carboxylate carbon of the trifluoroacetoxy moiety rather than at the ethane carbons.

With 2-propanol present, the reaction gave 2-isopropoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (20) in 77% yield accompanied with 15% of tetraphenylethylene oxide (22). In the presence of allyl alcohol, the reaction afforded 67% of 2-(allyloxy)-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (21), as well as epoxide 22 (10%) and ketone 10 (15%).

The formation of 22 could result from a trace of moisture present in the solvent. To prove this by experiment, dichloride 1 was treated with CF_3CO_2Ag in 10 mL of CH_2Cl_2 and 0.5 mL of H_2O . The epoxide 22 was obtained in 94% yield. It seems that the first-formed chloronium ion 11 undergoes preferential attack by H₂O rather than trifluoroacetate ion. As a result, chlorohydrin 23 may be formed as an intermediate (see Scheme 6), prior to removal of the second chlorine atom with a second mole of CF₃CO₂Ag. That this second chlorine atom departure must occur with neighboring group participation from the hydroxyl group is shown by the

Scheme 6



Table 2. ¹³C NMR Spectral Data for Dioxolanes 19, 20, and 21

	CF ₃ group		ortho ester carbon	
dioxolane	δ (ppm)	$J_{\mathrm{C-F}}\left(\mathrm{Hz}\right)$	δ (ppm)	$^{2}J_{\mathrm{C-F}}(\mathrm{Hz})$
19 20 21	120.4 120.4 20.7	291.6 291.3 291.6	$114.7 \\ 113.6 \\ 114.0$	36.4 35.9 35.5
		مرگ مر	-77.8 C3 - 51.6 67.9 C21 - 56.1 80.9	$ \begin{array}{c} 01 \\ 67.7 \\ - 50.1 \\ 66.7 \\ 02 \\ 02 \\ 44.2 \\ (b) \\ \end{array} $

Figure 1. (a) Spacial orientation of tetraphenylethanone dimethyl ketal (9). (b) Projection of ketal 9 molecule down the C2-C1 bond. Torsional angles about the bond and rotational angles of phenyl rings are shown.

absence of any rearrangement. Not surprisingly the literature records that epoxide 22 has been prepared by refluxing dichloride 1 in water.¹⁷

Structural assignments of the 1,3-dioxolane ortho esters 19, 20, and 21 were based on the ¹³C NMR spectroscopic data for the CF₃ group and the quaternary ortho ester carbon. As Table 2 indicates, the CF₃ group in each case shows a quartet near $\delta = 120$ ppm with a coupling constant (J_{C-F}) in the magnitude of 291 Hz. Furthermore, the quaternary ortho ester carbon also appears as a quartet around 114 ppm with a coupling constant $({}^{2}J_{CCF})$ in the range of 35–36 Hz.

Single-Crystal X-ray Structure Determination of Ketal 9 and 1,3-Dioxolane Ortho Ester 19. Structral assignments for ketal 9 and 1,3-dioxolane ortho ester 19 were verified with the aid of X-ray crystal structure determinations.¹⁸ Figures 1 and 2 show spacial orientations and torsion angle projections of 9 and 19, respectively. Bond distance data reveal that the central ethane carbon-carbon bond in ketal 9 has a length of 1.599(3)A while 1,3-dioxolane 19 has an ethane C-C bond length of 1.603(3) Å. These values compare favorably with literature data on pentaphenylethane (PPE) $(1.606 \text{ Å})^{19}$ and pentaphenylethane $-\pi$ -Cr(CO)₃ complexes [PPE- π -C1-Cr(CO)₃ 1.615(7); PPE-л-C2-Cr(CO)₃ 1.620(5) Å] studied earlier in our laboratories.²⁰ The ethane carboncarbon bonds in ketal 9 and 1,3-dioxolane 19 are significantly longer than those in their hydrocarbons

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Figure 2. (a) Spacial orientation of dioxolane ortho ester 19. (b) Projection of 19 molecule down the C2-C1 bond. Torsional angles about the bond and rotational angles of phenyl rings are shown. (c) Conformation of the dioxolane ring.

Table 3.Torsional Angles Involving the Ethane AtomsC1 and C2 in Tetraphenylethanone Dimethyl Ketal (9)

angle	deg	angle	deg
01-C2-C1-C15	67.7(2)	C9-C1-C3-C21 C2-C1-C3-C8	-56.1(2)
$O_2 - C_2 - C_1 - C_{15}$	-50.1(2)	C2-C1-C3-C8	-77.8(2)
$O_2 - C_2 - C_1 - C_9$	66.7(2)	C2-C1-C9-C10	-54.2(2)
O1-C2-C1-C3	-51.6(2)	C2-C1-C15-C16	-6.8(2)
C3-C1-C2-C21	67.9(2)	C1-C2-C21-C22	80.9(2)

Table 4. Torsional Angles and Bond Angles Involving the Ethane Carbon Atoms C1 and C2 in Dioxolane Ortho Ester 19

angle	deg	angle	deg
$\begin{array}{c} 01-C1-C2-O2\\ 01-C2-C1-C22\\ C10-C1-C2-C22\\ C10-C1-C2-C16\\ C4-C1-C2-C16\\ 02-C2-C1-C4\\ C1-C2-C22\\ \end{array}$	$\begin{array}{r} -32.4(2)\\ 83.0(2)\\ -30.7(2)\\ 100.5(2)\\ -31.2(2)\\ 82.2(2)\\ 52.1(2)\end{array}$	$\begin{array}{c} C1-C2-C16-C17\\ C2-C1-C4-C5\\ C2-C1-C10-C11\\ C2-C1-C4\\ C2-C1-C4\\ C2-C1-C10\\ C1-C2-C16\\ C1-C2-C22\\ \end{array}$	$\begin{array}{r} -80.9(2)\\ 36.3(3)\\ -87.5(2)\\ 119.4(2)\\ 114.9(1)\\ 117.0(2)\\ 117.5(2)\end{array}$

counterparts, 1,1,1,2-tetraphenylethane $(1.567~{\rm \AA})^{21a}$ and 1,1,2,2-tetraphenylethane $(1.540~{\rm \AA})^{.21b}$

The torsion angles about the ethane C-C bond displayed in Table 3 show that ketal **9** in its solid state exists as a nearly perfectly staggered conformation. On the other hand, the 1,3-dioxolane ring of **19** prevents the phenyl rings from adopting their normal staggered conformation. As shown by the torsion angles in Table 4 involving the ethane C-C bond, the dihedral angles C10-C1-C2-C22 and C4-C1-C2-C16 at 30 °C show phenyl groups approaching an eclipsed conformation. The resulting strong interaction between phenyl rings C10 and C22 and C4 and C16 is slightly relieved by the deformation of the bond angles of ethane carbons and ipso carbons [C1-C2-C22 117.5(2)°; C1-C2-C16 117.0-(2)°; C2-C1-C4 119.4(2)°; C2-C1-C10 114.9(1)°].

Another consequence of the bulky phenyl groups in 19 is that O1-C1-C2-O2 in the dioxolane moiety cannot be planar (torsion angle, -32.4°). Atoms C1, O1, C3, and O2 are almost coplanar, having a torsion angles of -5.4° . Thus the dioxolane ring looks like an envelope conformation of cyclopentane with C2 syn to the phenoxyl substituent.

In conclusion, we have shown that 2-cyano-1,1,2,2tetraphenylethyl cation (5) can be generated with silver hexafluoroantimony and SbCl₅ and that it is stable at -75 °C for at least 4.5 h. It is also observed that cation 5 generated with AlCl₃ at 0 °C reacted intramolecularly to form fluorene derivative 8. A novel sterically hindered ketal, tetraphenylethanone dimethyl ketal (9), was prepared by treatment of dichloride 1 with CF₃CO₂Ag in the presence of MeOH in 91% yield. 1-Methoxy-1,2,2,2tetraphenylethyl cation (15) was proposed as a reaction intermediate. 1,3-Dioxolane ortho esters 19, 20, and 21 isolated from the reaction of dichloride 1 with CF₃CO₂-Ag in the presence of phenol, isopropyl alcohol, or allyl alcohol indicate the existence of cationic intermediate 18.

Experimental Section

CH₂Cl₂ was distilled over CaH₂ prior to use. MeOH was dried over magnesium and distilled. Benzene was purified by stirring with Na and distilled. 2-Propanol and allyl alcohol were dried over K₂CO₃ and distilled. CF₃CO₂Ag was freshly prepared from CF₃CO₂H and Ag₂O according to the literature procedure.²³ AgSbF₆ and AlCl₃ were obtained from Aldrich Chemical Co. and used as supplied. *sym*-Tetraphenylethylene dichloride (1) was synthesized in CHCl₃ as described by Thorne et al. (mp 169–171 °C).²⁴ 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (2) was prepared from dichloride 1 and TMSCN as described previously.² Flash chromatography was performed on silica gel (230–400 mesh). Elemental analyses were done by Desert Analytics and National Chemical Consulting. All melting points are uncorrected.

Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (2) with CF₃CO₂Ag in Benzene. To a stirring solution of nitrile 2 (0.394 g, 1.0 mmol) in 20 mL of benzene was added CF₃CO₂Ag (0.442 g, 2.0 mmol) in one portion at 0 °C. After 1 h, the reaction mixture was poured into ice-cold water and filtered. The solid AgCl was washed with CH_2Cl_2 , and the filtrate was separated. The organic phase was washed with H₂O, dried over Na₂SO₄, and concentrated. The resulting solid was recrystallized from benzene-ligroin (or from acetonewater) and yielded 0.341 g (77% yield) of 3-(trifluoroacetoxy)-2,2,3,3-tetraphenylpropanenitrile (4), mp 120-125 °C dec. Compound 4 decomposed on prolonged standing in the air. ¹³C NMR (CDCl₃) δ : 63.9, 96.1, 114.5 (q, $J_{C-F} = 287.6 \text{ Hz}$), 121.0, 127.3, 127.9, 128.3, 129.2, 130.2, 130.4, 135.6, 136.8, 153.9 (q, ${}^{2}J_{CCF} = 42.9 \text{ Hz}$). IR (KBr, cm⁻¹): 2240, 1785, 1220, 1190, 1165, 1140.

Reaction of Nitrile 2 With CF₃CO₂Ag in a Mixture of CH₂Cl₂ and CH₃OH. To a solution of nitrile 2 (1.181 g, 3.0 mmol) in 30 mL of CH₂Cl₂ and 15 mL of MeOH was added CF₃CO₂Ag (0.991 g, 4.51 mmol) at 0 °C. After being stirred for 0.5 h, the reaction mixture was poured into ice-cold H₂O and the solid was filtered and washed with CH₂Cl₂. The filtrate was separated and washed with water, dried over Na₂SO₄, and concentrated. The resulting solid was recrystallized from CH₂Cl₂-petroleum ether and yielded 1.1515 g (98%) of 3-methoxy-2,2,3,3-tetraphenylpropanenitrile (6), mp 120–140 °C dec. ¹H NMR (CDCl₃) δ : 3.2 (s, 3H), 7.1–7.5 (m, 20H). ¹³C

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128.0, 130.3, 131.2, 138.1, 139.74. Anal. Calcd for $C_{28}H_{23}\text{-}$ NO: C, 86.34; H, 5.95. Found: C, 86.30; H, 5.71.

Reaction of Nitrile 2 with AgSbF₆ in CH₂Cl₂ at -55 °C. To a solution of 2 (0.394 g, 1.0 mmol) in 10 mL of CH₂Cl₂ was added AgSbF₆ (0.565 g, 1.64 mmol) at -78 °C. When the temperature was allowed to rise gradually to -55 °C over a 15 min period, the reaction mixture turned red. After 2 h, 10 mL of MeOH (prechilled to -78 °C) was added and the reaction mixture was poured into ice-cold H₂O and filtered. To the filtrate was added 20 mL of CH₂Cl₂, and the organic phase was separated, washed with H₂O, dried (Na₂SO₄), and concentrated. The resulting solid was recrystallized from CH₂-Cl₂-petroleum ether and gave 0.298 g (75% yield) of methoxy nitrile **6**.

Reaction of Nitrile 2 with AgSbF₆ in CH₂Cl₂ at -35 °C. To a solution of nitrile 2 (0.394 g, 1.0 mmol) in 10 mL of CH₂-Cl₂ was added AgSbF₆ (0.436 g, 1.27 mmol) at -78 °C. The temperature was allowed to rise gradually to -35 °C over a 20 min period, and during that time the reaction mixture turned red. After 1.5 h, 10 mL of MeOH (prechilled to -78°C) was added and the reaction mixture was poured into icecold H₂O and filtered. To the filtrate was added 20 mL of CH₂-Cl₂, and the organic phase was separated, washed with H₂O, dried (Na₂SO₄), and concentrated. The resulting residue was diluted with MeOH, and a pale yellow solid was precipitated. Recrystallization of the crude product from CH₂Cl₂-MeOH yielded 0.086 g (44%) of tetraphenylsuccinonitrile (**3**), mp 219– 222 °C (lit.⁸ mp 222–224 °C).

Reaction of Nitrile 2 with SbCl₅ (Table 1). SbCl₅ (1.0 M in CH₂Cl₂) was added to nitrile 2 (0.787 g, 2.0 mmol) in 20 mL of CH_2Cl_2 dropwise at the temperatures shown in Table 1. The reaction was terminated with 10 mL of MeOH (prechilled to $-78\ ^\circ C)$, followed by 20 mL of 10% $NaHCO_3$ solution. The product was extracted into 20 mL of CH₂Cl₂, and the organic layer was separated, washed with H₂O (2 \times 20 mL), dried over Na₂SO₄, and concentrated. The resulting residue was taken into 10 mL of MeOH, and solids were collected, dried, and subjected to NMR analyses. The product composition was determined by comparison of a reaction's ¹³C NMR spectrum with those of compound 2 and 6. The yields of **2** and **6** were determined by a ¹H NMR integration method: the methoxyl methyl group (from methoxynitrile 6) at 3.22 ppm vs the aromatic protons (from both 2 and 6) near 7.3 ppm. The results are summarized in Table 1.

Reaction of Nitrile 2 with AlCl₃ in Benzene. To a solution of **2** (0.577 g, 1.5 mmol) in 25 mL of CH₂Cl₂ and 10 mL of benzene was added dropwise a solution of AlCl₃ (0.399 g, 3.0 mmol) in 10 mL of CH₂Cl₂ at -78 °C. The reaction mixture was allowed to warm to 0 °C and was stirred for 2 h. It was poured into ice-water, and the organic layer was separated, dried over Na₂SO₄, and concentrated. The resulting residue was diluted with 10 mL of MeOH, and a pale yellow solid was obtained. Recrystallization of the crude product from acetone yielded 0.186 g (35%) of 9-(cyanodiphenylmethyl)-fluorene (8), mp 253-255 °C. ¹H NMR (CDCl₃) δ : 5.2 (s, 1H), 6.5 (d, 2H, J = 7.6 Hz, 2H). ¹³C NMR (CDCl₃) δ : 5.3.6, 57.2, 119.9, 120.5, 125.9, 126.7, 127.7, 128.3, 128.4, 128.8, 138.7, 142.0, 142.1. Anal. Calcd for C₂₇H₁₉N: C, 90.72; H, 5.36; N, 3.92. Found: C, 90.86; H, 5.35; N, 3.96.

Alternative Synthesis of Fluorene Derivative 8. NaNH₂ (0.447 g, 11.5 mmol) was dissolved in 30 mL of liquid NH₃, and diphenylacetonitrile (2.45 g, 10 mmol) was added in one portion. The resulting greenish-brown solution was stirred for 15 min, and a suspension of 9-bromofluorene (1.94 g, 10 mmol) in 20 mL of ether was added dropwise over a 10 min period. The reaction mixture was stirred for another 0.5 h, and liquid NH₃ was evaporated. The solid was filtered, washed with H₂O (4 × 40 mL), and recrystallized from acetone to give 3.39 g (95% yield) of 8, mp 253-255 °C. The ¹H and ¹³C NMR spectra were identical with those described above.

Reaction of Cation 5 with TMSCN. Cation **5** was prepared as described in Table 1, entry 6. After 4.5 h at -75 °C, TMSCN (0.521 g, 5.3 mmol) was added and stirring was continued for another 0.5 h, followed by quenching of the reaction with 10 mL of MeOH. After hydrolysis with 20 mL

of H₂O, the product was extracted into CH₂Cl₂ (80 mL), separated, washed with H₂O (3×15 mL), dried (Na₂SO₄), and concentrated. The resulting residue was recrystallized from CH₂Cl₂-MeOH to give 0.755 g of succinonitrile **3** in 98% yield, mp 218–221 °C.

Synthesis of Tetraphenylethanone Dimethyl Ketal (9) (Run 1). To a solution of dichloride 1 (0.806 g, 2.0 mmol) in 20 mL of CH₂Cl₂ and 10 mL of MeOH was added CF₃CO₂Ag (dried overnight) (1.133 g, 5.13 mmol) in one portion at 0 °C. A white solid precipitated immediately. The reaction mixture was stirred for 2 h, and 20 mL of 10% NaHCO3 solution was added. The solid was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was separated, washed with $H_2O\ (2\ \times\ 10$ mL), dried (Na_2SO_4) , and concentrated. The resulting residue was recrystallized from CH_2Cl_2 -EtOH, and 0.524 g (67% yield) of dimethyl ketal 9 was obtained as white crystals, mp 129-130.5 °C. The mother liquor was concentrated and recrystallized from EtOH-H₂O to give 0.193 g (28% yield) of tetraphenylethanone (10), mp 178–179 °C (lit.²⁵ mp 179–180 °C).¹³C NMR (CDCl₃) δ: 71.1, 126.7, 127.6, 127.8, 130.9, 131.1, 131.7, 137.5, 143.2, 198.7.

For ketal 9. ¹H NMR (CDCl₃) δ : 3.4 (s, 6H), 6.8 (d, J = 7.5 Hz, 2H), 7.0–7.5 (m, 18H). ¹³C NMR (CDCl₃) δ : 53.7, 70.0, 110.5, 125.6, 126.4, 126.6, 128.0, 131.1, 132.5, 136.0, 145.2. Anal. Calcd for C₂₈H₂₆O₂: C, 85.25; H, 6.64. Found: C, 85.58; H, 6.65.

Run 2. If the CF_3CO_2Ag was not dried overnight before use, the reaction gave the following results after flash chromatography: ketal **9**, 0.262 g, 33% yield, CH_2Cl_2 :hexane (30:70); ketone **10**, 0.464 g, 66% yield, CH_2Cl_2 :hexane (50:50).

Run 3. To a solution of dichloride 1 (0.806 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 10 mL of MeOH was added CF_3CO_2Ag (1.118 g, 5.06 mmol) at 0 °C. After 2 h, anhydrous Na_2CO_3 (1.622g, 15.3 mmol) was added and the stirring was continued for another 0.5 h. The solid was filtered and washed with CH_2 - Cl_2 (20 mL). The filtrate was washed with H_2O (2 × 10 mL), separated, dried (Na_2SO_4), and concentrated. Recrystallization of the resulting residue from CH_2Cl_2 -EtOH gave 0.716 g (91%) of ketal **9**. The mother liquor was concentrated and recrystallized from EtOH- H_2O to give 0.042 g (6%) of ketone **10**.

Run 4, Ag₂CO₃.To a solution of dichloride 1 (0.806 g, 2 mmol) in 20 mL of CH_2Cl_2 and 10 mL of MeOH was added Ag₂CO₃ (0.564 g, 2 mmol) at 20 °C. After 2 h, the reaction mixture was filtered and the solid was washed with CH_2Cl_2 (20 mL). The filtrate was washed with 20 mL of 10% NaHCO₃ and H₂O (2 × 10 mL), dried (Na₂SO₄), and concentrated. Recrystallization of the residue from CH_2Cl_2 -EtOH afforded 0.511 g of ketal **9** in 65% yield. Concentration of the mother liquor and recrystallization from EtOH-H₂O yielded 0.147 g of ketone **10** in 21% yield.

Run 5, AgOCN. Dichloride 1 (0.806 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 10 mL of MeOH was treated with AgOCN (0.904 g, 6 mmol) at room temperature. After 2 h, 20 mL of a 10% NaHCO₃ aqueous solution was added and the solid was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was separated, washed with H_2O (2 × 10 mL), dried (Na₂SO₄), and concentrated. The resulting residue was recrystallized from CH_2-Cl_2-EtOH , and 0.632 g of ketal **9** was obtained in 80% yield. The mother liquor was concentrated, and recrystallization of the residue from $EtOH-H_2O$ yielded 0.079 g of ketone **10** in 11% yield.

Run 6, AgOCN. The procedure of entry 5 was followed except anhydrous Na_2CO_3 (1.131 g, 10.7 mmol) was added before aqueous workup. After recrystallization from CH_2Cl_2 -EtOH, ketal 9 (0.727 g) was obtained in 92% yield and no ketone 10 could be detected.

Reaction of Dichloride 1 with CF_3CO_2Ag in the Presence of Phenol. To a solution of dichloride 1 (0.807 g, 2.0 mmol) and phenol (3.764 g, 40 mmol) in 20 mL of CH_2Cl_2 was added CF_3CO_2Ag (1.107 g, 5.0 mmol) at 0 °C. After 2.5 h, 40 mL of 10% NaHCO₃ was added. AgCl was filtered and washed (CH_2Cl_2), and the organic layer was washed with H_2O , dried (Na_2SO_4), and concentrated. Recrystallization of the resulting

⁽²⁵⁾ Gomberg, M.; Bachmann, W. E. J. Am. Chem. Soc. 1927, 49, 246.

residue from acetone gave 0.963 g (90% yield) of 2-phenoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (19) as white crystals, mp 185–189 °C dec. ¹³C NMR (CDCl₃) δ : 97.4, 114.7 (q, ²J_{CCF} = 36.4 Hz), 120.4 (q, J_{C-F} = 291.6 Hz), 121.0, 123.8, 127.12, 127.15, 127.36, 127.41, 128.53, 128.84, 129.3, 140.9, 141.1, 152.8. IR (KBr, cm⁻¹): 1180, 1115. Anal. Calcd for C₃₄H₂₅F₃O₃: C, 75.83; H, 4.68. Found: C, 75.59; H, 4.68.

Reaction of Dichloride 1 with CF₃CO₂Ag in the Presence of 2-Propanol. To a solution of dichloride 1 (0.807 g, 2.0 mmol) in 20 mL of CH₂Cl₂ and 5 mL of isopropyl alcohol was added CF₃CO₂Ag (1.105 g, 5.0 mmol) at 0 °C. After 2.5 h, Na_2CO_3 (1.164 g, 11 mmol) was added and the reaction mixture filtered. AgCl was filtered and washed (CH2Cl2), and the organic layer was washed with H_2O , dried (Na₂SO₄), and concentrated. The residue was separated by flash chromatography with a mixture of CH_2Cl_2 and petroleum ether (20: 80, v:v) as a eluent, and there was obtained 0.77 g (77% yield) of 2-isopropoxy-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (20), mp 138-140 °C, together with 0.105 g (15% yield) of tetraphenylethylene oxide (22), mp 205–206 °C (lit.¹⁷ mp 204–205 °C). For 20. ¹H NMR (\dot{CDCl}_3) δ : 1.0 (d, J = 6.1Hz, 6 H), 4.3 (septet, J = 6.1 Hz, 1 H), 7.1–7.3 (m, 20 H). ¹³C NMR (CDCl₃) δ : 23.1, 68.9, 94.7, 113.6 (q, ²J_{CCF} = 35.9 Hz), 120.4 (q, $J_{C-F} = 291.3$ Hz), 127.27, 127.30, 127.34, 127.45, 128.10, 128.40, 142.18, 142.62. Anal. Calcd for $C_{31}H_{27}F_3O_3$: C, 73.78; H, 5.40. Found: C, 73.52; H, 5.42. For 22. $^{13}\mathrm{C}$ NMR (CDCl₃) $\delta:$ 73.84, 127.03, 127.54, 128.24, 138.66.

Reaction of Dichloride 1 with CF_3CO_2Ag in the Presence of Allyl Alcohol. To a solution of dichloride 1 (0.807 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 5 mL of allyl alcohol was added solid CF_3CO_2Ag (1.111 g, 5.0 mmol) at 0 °C. After 2.5 h, Na₂CO₃ (1.100 g, 10 mmol) was added and the reaction mixture was filtered from unreacted Na₂CO₃ and AgCl. The solid was filtered and washed with CH_2Cl_2 , the filtrate was separated, and the organic layer was washed with H_2O , dried (Na₂SO₄), and concentrated. The resulting residue was separated by flash chromatography, and the following results were

obtained: 2-(allyloxy)-2-(trifluoromethyl)-4,4,5,5-tetraphenyl-1,3-dioxolane (**21**): 0.670 g, 67% yield, mp 106–108 °C, CH₂-Cl₂:petroleum ether (20:80); epoxide **22**, 0.073 g, 10% yield, CH₂Cl₂:petroleum ether (20:80); ketone **10**, 0.103 g, 15% yield, CH₂Cl₂:petroleum ether (50:50).

For 21. ¹H NMR (CDCl₃) δ : 4.1 (d, J = 5.0 Hz, 2 H), 5.0– 5.2 (m, 2 H), 5.59–5.63 (m, 1 H), 7.0–7.3 (m, 20 H). ¹³C NMR (CDCl₃) δ : 66.4, 97.1, 114.0 (q, ² $J_{CCF} = 35.5$ Hz), 116.7, 120.7 (q, $J_{C-F} = 291.6$ Hz), 127.01, 127.10, 127.26, 127.28, 128.64, 129.35, 133.00,142.18, 142.76. Anal. Calcd for C₃₁H₂₅F₃O₃: C, 74.08; H, 5.01. Found: C, 73.73; H, 5.07.

Reaction of Dichloride 1 with CF₃CO₂Ag in the Presence of H₂O. To a solution of dichloride 1 (0.404 g, 1.0 mmol) in 10 mL of CH₂Cl₂ and 0.5 mL of H₂O was added CF₃CO₂Ag (0.555 g, 2.5 mmol) at 0 °C. After 0.5 h, 20 mL of 10% NaHCO₃ solution was added. The solid was filtered and washed with CH₂Cl₂. The filtrate was separated, and the organic layer was washed with H₂O, dried (Na₂SO₄), and concentrated. The resulting residue was recrystallized from benzene–EtOH (1: 10) to give 0.329 g (94%) of epoxide **22**, mp 205–206 °C (lit.¹⁷ mp 204–205 °C).

Acknowledgment. This research was supported by the City University Faculty Research Award Program through PSC-CUNY Grant 6-63277. We gratefully acknowledge this support.

Supporting Information Available: ¹H and ¹³C NMR spectra for 4, 6, 8, 9, and 19-21 and X-ray crystallographic data and stereoviews of 9 and 19 (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9509364