12, 83-13-6; 14, 607-81-8; 16, 37434-59-6; 19, 57197-29-2; 20, 21239-22-5; 21, 77-24-7; 22, 57197-30-5; 23, 4167-77-5; 24, 5453-85-0; 25, 133-13-1; 27, 75-67-5; 28, 119-43-7.

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Preparation and Reactions of 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone

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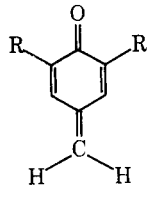
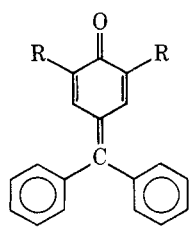
2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (**3**) was prepared from 2,6-di-*tert*-butyl-1,4-benzoquinone and fluorenylidenetriphenylphosphorane at 200°. In contrast to its α,α-diphenylmethylene analogue (**2b**), the 9-fluorenylidenequinone **3** smoothly undergoes electrophilic substitution reactions with phenols to give bisphenols. With anions as well as with amines, **3** reacts by 1,6 addition, yielding the correspondingly substituted phenols. Fluorenylidenequinone **3** was found to undergo a unique one-electron reduction with both hydrogen in the presence of platinum and with phenylmagnesium bromide. The acetyl derivative of the resulting 9-substituted fluorenyl radical was characterized by its ESR spectrum.

p-Methylenequinones of structure **1** play an important role as reactive intermediates in phenol oxidation.[1] Generally, they are easily reduced to the corresponding *p*-alkylphenols, they can dimerize by disproportionation, and they can undergo nucleophilic 1,6 addition resulting in aromatization.[1c] In the case of α,α-diphenylmethylene-substituted *p*-quinones (**2**, henceforth called fuchsones), disproportionation is structurally impossible, and reductive dimerization has not been encountered yet, probably because of the instability of the resulting hexaphenylethanes. Aromatization of fuchsones by acid-catalyzed 1,6 addition, however, occurs quite readily. For example, fuchsone itself (**2a**) rapidly adds water to give 4-hydroxytriphenylcarbinol.[2]



1

e.g., R = CH_3



2a, R = H

b, R = *tert*-butyl

c, R = CH_3

The chemistry of 3,5-di-*tert*-butylfuchsone (**2b**) has been the subject of detailed investigations.[3] This compound is easily reduced to give 3,5-di-*tert*-butyl-4-hydroxytriphenylmethane, and it readily aromatizes by addition of carbanions[4] as well as by photoinduced free-radical addition.[5] In contrast to **2a**, however, 3,5-di-*tert*-butylfuchsone does not add any nucleophiles in acid-catalyzed reactions and it does not undergo any electrophilic reactions with aromatic compounds such as phenols.[5b] Presumably, impaired protonation of the sterically hindered carbonyl group in conjunction with the steric hindrance of the methylene carbon caused by the out-of-plane position of the phenyl substituents may be responsible for the observed lack of reactivity. To test the validity of this assumption, it appeared interesting to replace the diphenylmethylene moiety in **2b** by the 9-fluorenylidene group and compare the chemistry of **2b** with that of its 9-fluorenylidene analogue. We have, therefore, prepared 2,6-di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (**3**) and studied the effect of the rigidity of the fluorenylidene moiety and inherent planarity of **3** on its chemical properties.

Results and Discussion

A. Preparation of 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone. In contrast to the large number of known fuchsones, the synthesis of 9-fluorenylidenebenzoquinones has not been described before. The only 9-fluorenylidenequinones known are those derived from 1,4-naphthoquinone,[6] 9,10-anthraquinone,[7] and 9,10-phenanthrenequinone,[6] though little has been reported about their chemistry. The desired 2,6-di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone was most conveniently prepared in

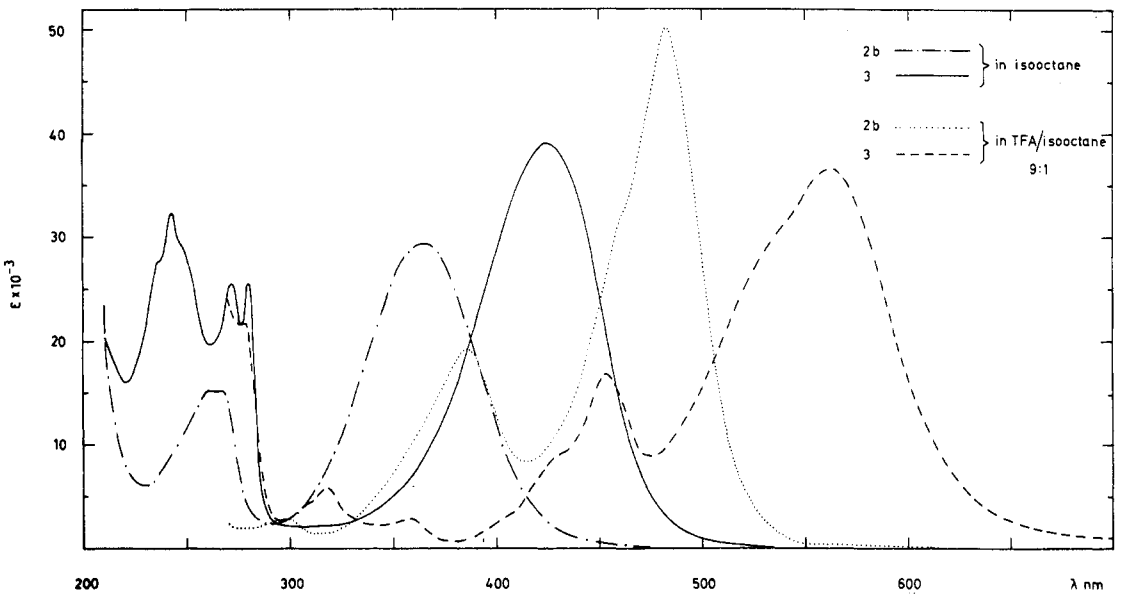
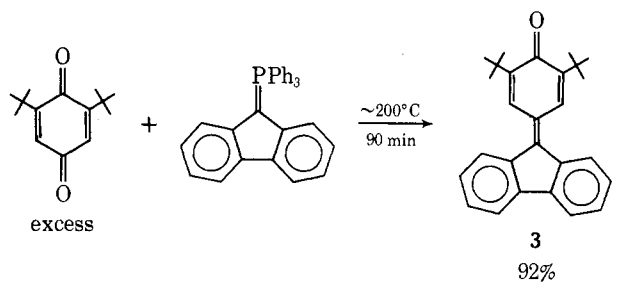


Figure 1. Electronic absorption spectra of **2b** and **3**.

Table I
Substitution of Aromatic Compounds by 3

4/5	Ar	Yield of 5, %
a	3,5-Di-*tert*-butyl-4-hydroxyphenyl	95
b	3,5-Dimethyl-4-hydroxyphenyl	82
c	3-*tert*-Butyl-4-hydroxy-5-methylphenyl	92
d	3,5-Diphenyl-4-hydroxyphenyl	95
e	3,5-Di-*tert*-butyl-2-hydroxyphenyl	91
f	3,5-Dimethoxy-4-hydroxyphenyl	56
g	4-Methoxyphenyl	65

92% yield from 2,6-di-*tert*-butyl-1,4-benzoquinone and fluorenylidenetriphenylphosphorane at 200° (reaction 1). The



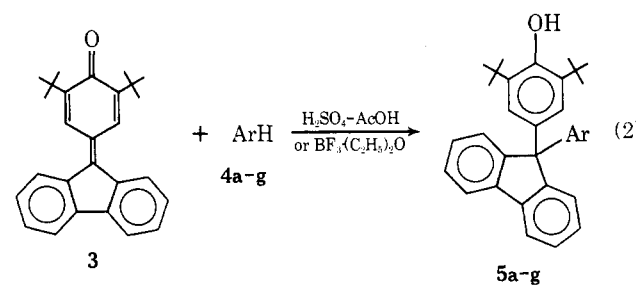
(1)

compound forms deep purple crystals which melt without decomposition at 227–228°. Its electronic absorption spectrum in the visible region exhibits its longest wavelength maximum at 424 nm, while a maximum at 364 nm is observed for 3,5-di-*tert*-butylfuchsone. The visible spectra of **2b** and **3** in trifluoroacetic acid, i.e., those of the corresponding triarylmethyl cations,[8] reveal a similar bathochromic shift (see Figure 1).

In the ir spectrum of **3** the strongest absorption attributed to the carbonyl group appears at 1592 cm^{-1} while the corresponding absorption in **2b** is found at 1602 cm^{-1}.[9]

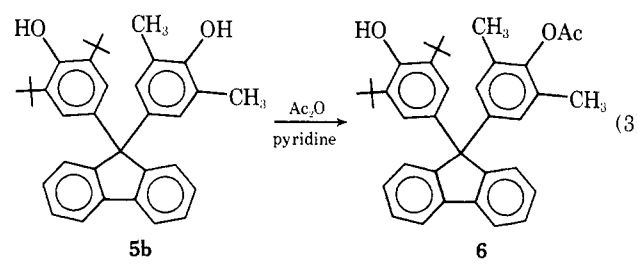
The NMR spectrum of **3** is in perfect agreement with the proposed structure. Different from the protons in the 3 and 5 positions of the 2,5-cyclohexadienone moiety in 3,5-di-*tert*-butylfuchsone at 7.20 ppm, the corresponding protons in the planar **3** give rise to a downfield singlet at 8.06 ppm since they are subject to the deshielding effect of the aromatic rings.[10] In its 270-MHz spectrum the protons of the fluorenylidene moiety give rise to a pair of doublets at 7.91 and 7.66 ppm and a pair of triplets centered at 7.36 and 7.29 ppm (see Experimental Section).

B. Acid-Catalyzed Additions to 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone. The reaction of fluorenylidenequinone **3** with 2,6-di-*tert*-butylphenol in acetic acid in the presence of sulfuric acid smoothly gives the symmetrical bisphenol **5a** which precipitates from the reaction mixture and can be isolated in 95% yield. The heretofore unknown asymmetrically 9,9-diaryl-substituted fluorenes **5b–g** were obtained by electrophilic substitution of **4b–g** under similar conditions (see Table I).



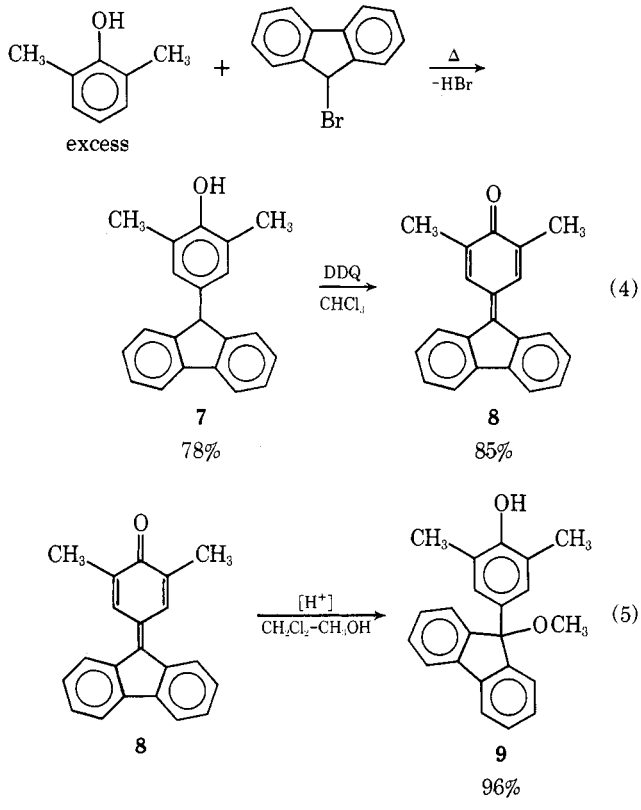
(2)

The structures of all new compounds are supported by their analytical and spectroscopic data (see Experimental Section) and by their chemical reactions. Bisphenol **5b**, for example, can be selectively acetylated at the less hindered phenolic site to give the corresponding monoacetate **6** (92% yield) (reaction 3).



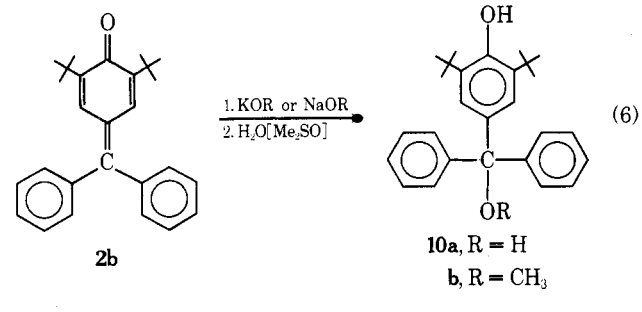
(3)

The driving force for the acid-catalyzed additions (reaction 2) most likely is due to the strained planarity of fluorenylidenequinone **3**, though the bulky *tert*-butyl substituents actually impair protonation of the carbonyl oxygen. The sterically less hindered 2,6-dimethyl-4-(9-fluorenylidene)-1,4-benzoquinone (**8**), which we prepared for comparison purposes (reaction 4), was found to undergo the 1,6



addition with methanol to give **9** (reaction 5) even in the absence of acid. Comparing the rates of the acetic acid catalyzed addition of methanol to fluorenylidenequinones **3** and **8** and the corresponding fuchsones **2b** and **2c**, the following order of relative reactivity was observed:[11] **8** ≫ **2c** > **3** ≫ **2b** (stable).

C. Anionic Additions to 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone. The reactions of anions with fluorenylidenequinone **3** were found to be analogous to the reactions of anions with 3,5-di-*tert*-butylfuchsone. Thus, with both water and methanol **2b** as well as **3** underwent base-catalyzed 1,6 additions in dimethyl sulfoxide solution to give the carbinols **10a** (reaction 6) and **11a**, and



their corresponding methyl ethers **10b** and **11b**, respectively. Similar 1,6 additions to **3** were observed with cyanide ion, methylsulfonyl carbanion, and 9-fluorenyl anion (reaction 7; see Table II).[12]

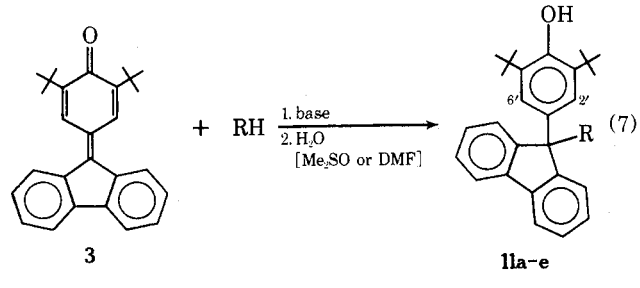


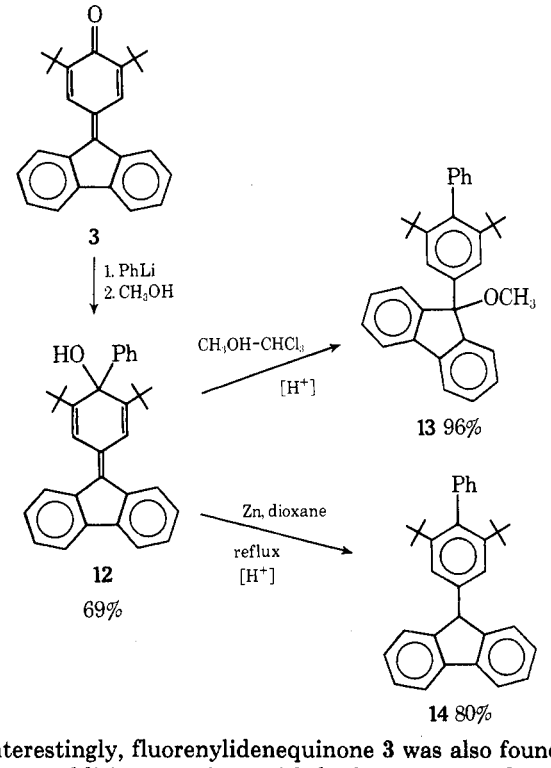
Table II
Base-Catalyzed Additions to 3 (Reaction 6)

11a–e	R	Yield, %
a	OH	86
b	OCH_3	85
c	CN	92
d	$CH_2SO_2CH_3$	75
e	9-Fluorenyl	81

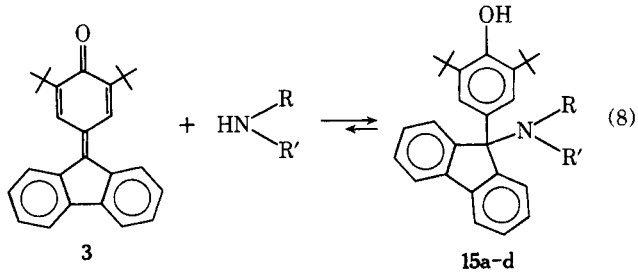
It is worth noting that in the NMR spectrum of the 9-aryl-9-fluorenylfluorene **11e**, two protons, most likely those in the 2′ and 6′ position, give rise to broad singlets at 6.05 and 6.18 ppm. Inspection of a Dreiding molecular model of **11e** suggests nonequivalence of the 2′,6′ protons because of hindered rotation about the aryl–C_9 bond.[13]

The 1,2 addition of phenyllithium to **3** followed the same exceptional course as had been found for 3,5-di-*tert*-butylfuchsone.[4] The structure of the 1,2-addition product **12** was established by its conversion into **13** and **14** (Scheme I). In the NMR spectrum of both **13** and **14** (see Experimental Section) the *tert*-butyl groups give rise to a singlet below 1 ppm, due to shielding by the phenyl substituent.

Scheme I



Interestingly, fluorenylidenequinone **3** was also found to undergo addition reactions with both primary and secondary amines (reaction 8; see Table III). The amine adducts

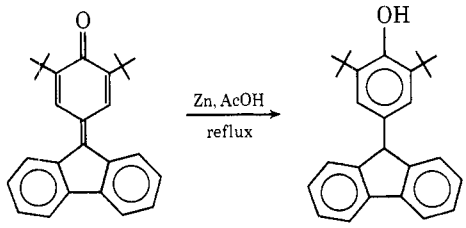


15a–d are colorless, crystalline compounds which are obtained in good yields when the amines are used as solvents. However, in chloroform solution and at elevated temperature the aminophenols **15** readily dissociate into their precursors.[14]

Table III
Addition of Amines to 3 (Reaction 8)

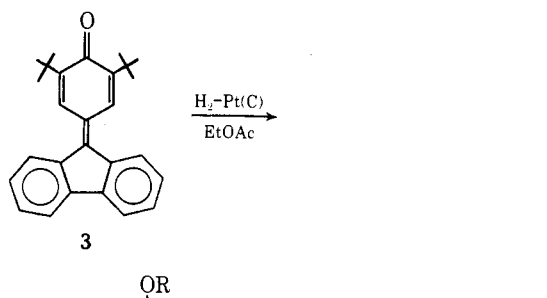
15a–d	R	R′	Yield, %
a	H	$CH(CH_3)_2$	87
b	H	c-C_6H_{11}	63
c		$-(CH_2)_2O(CH_2)_2-$	99
d		$-(CH_2)_4-$	91

D. Reductive Dimerization of 2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone. Interesting and unexpected results were obtained when we studied the reduction of **3**. Zinc in boiling acetic acid smoothly reduces **3** to give the fluorenyl-substituted phenol **16** in 95% yield (reaction 9). During the course of the reaction, however, the

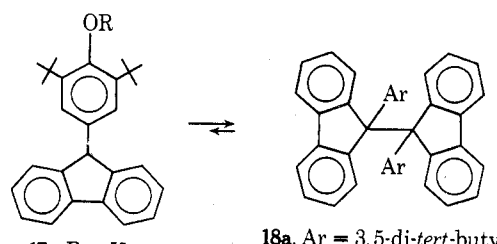


3 16 (9)

transient appearance of a colorless precipitate, which we presumed to be an unstable precursor of **16**, was noticed.[15] Upon catalytic hydrogenation at room temperature fluorenylidenequinone **3** indeed only consumed 0.5 molar equiv of hydrogen to give a colorless, crystalline product for which spectroscopic data (ir, NMR) are in agreement with the dimer **18a**. The NMR spectroscopic investigation revealed that the dimmer **18a** in solution decomposed to the fluorenylidenequinone **3** and the phenol **16**. Conceivably, the decomposition involves free-radical dissociation of dimer **18a** at the central carbon–carbon bond to give the fluorenyl radical **17a** which, because of the phenolic hydroxy group, is prone to undergo disproportionation. Perchloric acid catalyzed acetylation of dimer **18a** gives the



3



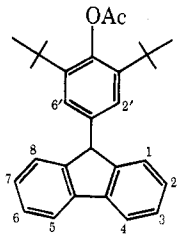
17a, R = H
b, R = Ac

18a, Ar = 3,5-di-*tert*-butyl-4-hydroxyphenyl
b, Ar = 3,5-di-*tert*-butyl-4-acetoxyphenyl (10)

fairly stable diaryl disubstituted 9,9′-bifluorenyl **18b**. Its structure was established by its conventional[16] preparation from fluorenylphenol **16** according to the following sequence of reactions (eq 11).

The equilibrium of dimer **18b** with the free radicals **17b** was studied by ESR spectroscopy.[17] The calculated spectrum of radical **17b**, based on coupling constants listed in Table IV, is in excellent agreement with the experimentally found spectrum in xylene at 98° (see Figure 2). Based on the temperature dependence of the radical concentration,

Table IV
Coupling Constants in 17b



17b

Position	a_H, G
1,8	3.27
2,7	0.62
3,6	3.40
4,5	0.83
2′,6′	1.95

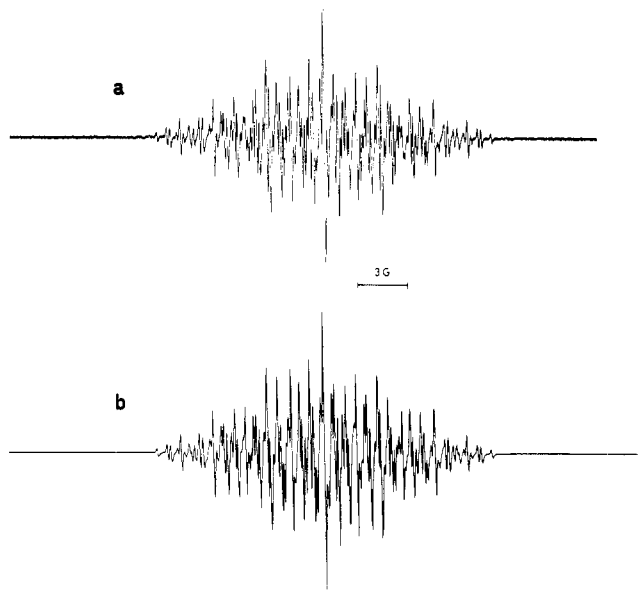
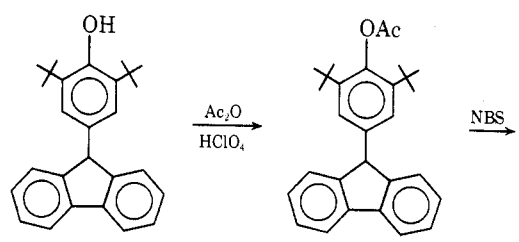
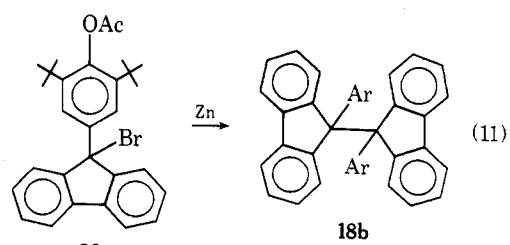


Figure 2. (a) ESR spectrum of radical **17b**; (b) simulated spectrum based on coupling constants in Table IV.



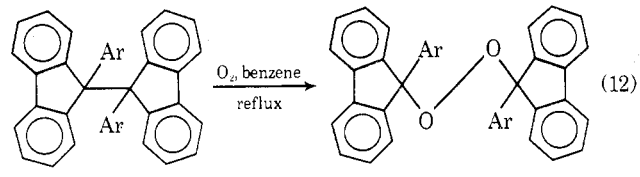
16 19 90%



20 67% 18b 77% (11)

the ΔH of equilibrium in anisole was found to be 25.8 ± 0.9[18] kcal/mol. For the equilibrium of the 9-phenylfluorenyl radical with its dimer a ΔH of 26.6 kcal/mol was observed.[17a]

As characteristic[16] for a 9-aryl substituted fluorenyl radical, **17b** rapidly reacts with oxygen to give the crystalline peroxide **21** whose structure is supported by analytical and spectroscopic data (see Experimental Section).



(12)

18b 21

90%

Quite unexpectedly, the reductive dimerization of fluorenylidenequinone **3** was also accomplished by phenylmagnesium bromide. This result is surprising in view of the 1,2 addition we observed with phenyllithium. The reductive dimerization indicates that **3** oxidizes the Grignard reagent by one-electron transfer[19] rather than undergoing the expected nucleophilic addition. This is of particular interest in view of the very recent discussion on the involvement of electron transfer steps in the Grignard reaction with ketones.[20]

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Analyses were performed by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark. Infrared spectra, in KBr pellets, were recorded on a Beckman IR9 instrument. Electronic absorption spectra were taken on a Beckman DK2 spectrophotometer. NMR spectra were recorded on Varian A-60 or Bruker WH 270 spectrometers using chloroform-*d*; chemical shifts are given in parts per million downfield from Me_4Si. ESR spectra were taken on a Varian E-9 instrument equipped for variable-temperature experiments.

2,6-Di-*tert*-butyl-4-(9-fluorenylidene)-1,4-benzoquinone (3). A stirred mixture of 2,6-di-*tert*-butyl-1,4-benzoquinone[21] (22.0 g, 0.1 mol) and fluorenylidenetriphenylphosphorane[22] (21.3 g, 0.05 mol) was kept for 90 min at 190–200°. The solid mixture obtained on cooling the red melt to room temperature was dissolved in warm methylene chloride. Addition of methanol gave a red crystalline precipitate. It was filtered off, washed with methanol, and dried at 120° to give 17.1 g (92%) of red-colored crystals, mp 227–228° (rods changing to plates at 215–218°). Recrystallization by dissolving in hot methylene chloride and adding methanol did not raise the melting point; ir 1590 (s), 1622 (w), 1640 cm^{-1} (w); uv (isooctane) λ ($\epsilon \times 10^{-3}$) 243 (32.4), 272 (25.4), 280 (25.4), 424 nm (39.0); NMR (270 MHz) 8.06 (s, 2), 7.91 (d, J = 7.5 Hz, 2), 7.66 (d, J = 7.3 Hz, 2), 7.36 (t, J = 7.3 Hz, 2), 7.29 (t, J = 7.5 Hz, 2), 1.41 ppm (s, 18).

Anal. Calcd for $C_{27}H_{28}O$ (368.49): C, 88.00; H, 7.66. Found: C, 87.77; H, 7.69.

Standard Procedure for the Preparation of Bisphenols 5a–f. Concentrated sulfuric acid (0.5 ml) was added dropwise to a stirred suspension of the phenol (3 mmol) and **3** (1.11 g, 3 mmol) in acetic acid (15 ml). The stirred reaction mixture was kept overnight at room temperature, yielding a colorless precipitate which was removed by filtration through a sintered glass funnel.

9,9-Bis(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)fluorene (5a): yield 1.64 g (95%); mp 274–275° (from petroleum ether, bp 80–110°) (lit.[23] 272–273°); ir 3640 cm^{-1}; NMR 7.85–7.65 (m, 2), 7.46–7.21 (m, 6), 6.98 (s, 4), 5.04 (s, 2), 1.30 ppm (s, 36).

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(3″,5″-dimethyl-4″-hydroxyphenyl)fluorene (5b): yield 1.22 g (82%); mp 229–230° (from boiling ethanol and drying for 1 hr at 140°); ir 3630, 3600 cm^{-1}; NMR 7.85–7.63 (m, 2), 7.51–7.21 (m, 6), 7.05 (s, 2), 6.77 (s, 2), 5.03 (s, 1), 4.44 (s, 1), 2.07 (s, 6), 1.30 ppm (s, 18).

Anal. Calcd for $C_{35}H_{38}O_2$ (490.69): C, 85.67; H, 7.81. Found: C, 85.83; H, 7.77.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(3″-*tert*-butyl-4″-hydroxy-5″-methylphenyl)fluorene (5c): yield 1.48 g (92%); mp 208–209° (from acetic acid); ir 3620, 3570 cm^{-1}; NMR 7.85–7.65 (m, 2), 7.40–7.10 (m, 7), 7.01 (s, 2), 6.57 (m, 1), 5.02 (s, 1), 4.55 (br s, 1), 2.00 (s, 3), 1.30 ppm (s, 27).

Anal. Calcd for $C_{38}H_{44}O_2$ (532.77): C, 85.67; H, 8.32. Found: C, 85.39; H, 8.29.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(3″,5″-diphenyl-4″-hydroxyphenyl)fluorene (5d): yield 1.76 g (95%); mp 232–233° (by dissolving in hot methylene chloride and adding ethanol); ir 3630, 3540 cm^{-1}; NMR 7.85–7.65 (m, 2), 7.52–7.10 (m, 20), 5.28 (s, 1), 5.04 (s, 1), 1.30 ppm (s, 18).

Anal. Calcd for $C_{45}H_{42}O_2$ (614.84): C, 87.91; H, 6.89. Found: C, 87.78; H, 6.86.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(3″,5″-di-*tert*-butyl-2″-hydroxyphenyl)fluorene (5e). This compound was prepared from **3** (1.11 g, 3 mmol) and 2,4-di-*tert*-butylphenol (1 g, 4.85 mmol) in acetic acid (15 ml) and sulfuric acid (1 ml): yield 1.57 g (91%); mp 224–225° (from acetic acid); ir 3640, 3460 cm^{-1}; NMR 7.85–7.18 (m, 11), 6.73 (d, J = 2.5 Hz, 1), 5.25 (s, 1), 5.21 (s, 1), 1.40 (s, 9), 1.28 (s, 18), 1.08 ppm (s, 9).

Anal. Calcd for $C_{41}H_{50}O_2$ (574.85): C, 85.67; H, 8.77. Found: C, 85.62; H, 8.79.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(3″,5″-dimethoxy-4″-hydroxyphenyl)fluorene (5f). The reaction according to the standard procedure resulted in an orange solution which was diluted with water and shaken with ether. The organic layer was washed with water and dried (magnesium sulfate) and the solvent was vacuum evaporated to give an oil which crystallized when treated with ether–*n*-hexane. Recrystallization from petroleum ether (bp 80–110°) gave 0.88 g (56%) of colorless crystals: mp 163–165°; ir 3640, 3540 cm^{-1}; NMR 7.89–7.69 (m, 2), 7.52–7.21 (m, 6), 7.05 (s, 2), 6.40 (s, 2), 5.40 (s, 1), 5.07 (s, 1), 3.67 (s, 6), 1.30 ppm (s, 18).

Anal. Calcd for $C_{35}H_{38}O_4$ (522.69): C, 80.43; H, 7.33. Found: C, 80.23; H, 7.60.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(4″-methoxyphenyl)fluorene (5g). Boron trifluoride etherate (0.3 ml) was added to a suspension of **3** (1.11 g, 3 mmol) in anisole (15 ml). The stirred reaction mixture was kept for 1 hr at 75–80° and then diluted with benzene and washed with water. The organic layer was dried (magnesium sulfate) and the solvent was removed by evaporation in vacuo to give an oily residue which crystallized when treated with petroleum ether (bp 60–70°). Recrystallization by dissolving in hot ethanol and adding some drops of water gave 0.93 g (65%) of colorless crystals: mp 180–182°; ir 3640 cm^{-1}; NMR 7.85–7.65 (m, 2), 7.48–7.00 (m, 10), 6.72 (d, J = 9 Hz, 2), 5.05 (s, 1), 3.67 (s, 3), 1.29 ppm (s, 18).

Anal. Calcd for $C_{34}H_{36}O_2$ (476.66): C, 85.67; H, 7.61. Found: C, 85.48; H, 7.66.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(4″-acetoxy-3″,5″-dimethylphenyl)fluorene (6). Pyridine (0.3 ml) was added to a stirred suspension of **5b** (500 mg) in acetic anhydride (10 ml). The solution thus obtained was kept for 10 hr at room temperature and then diluted with methanol. Vacuum evaporation of solvent gave a colorless, crystalline residue. It was triturated with aqueous methanol, removed by filtration, and recrystallized by dissolving in ether and adding petroleum ether (bp 80–110°): yield 500 mg (92%); mp 228–229°; ir 3610, 1755 cm^{-1}; NMR 7.83–7.65 (m, 2), 7.50–7.20 (m, 6), 7.03 (s, 2), 6.85 (s, 2), 5.06 (s, 1), 2.22 (s, 3), 2.00 (s, 6), 1.28 ppm (s, 18).

Anal. Calcd for $C_{37}H_{40}O_3$ (532.73): C, 83.42; H, 7.57. Found: C, 83.61; H, 7.57.

9-(3′,5′-Dimethyl-4′-hydroxyphenyl)fluorene (7). A molten mixture of 9-bromofluorene[24] (12.25 g, 50 mmol) and 2,6-dimethylphenol (30.5 g, 0.25 mol) was stirred for 16 hr at 45–50° and for an additional 24 hr at 80–90°. Excess 2,6-dimethylphenol was removed by vacuum sublimation at room temperature (0.1 mm) and the residue was recrystallized from methylene chloride–cyclohexane in the presence of charcoal: yield 11.1 g (78%) of colorless crystals; mp 158–160°; ir 3420 cm^{-1}; NMR 7.88–7.62 (m, 2), 7.51–7.18 (m, 6), 6.70 (s, 2), 4.90 (br s, 1), 4.48 (s, 1, exchangeable with D_2O), 2.13 ppm (s, 6).

Anal. Calcd for $C_{21}H_{18}O$ (286.37): C, 88.08; H, 6.34. Found: C, 87.87; H, 6.30.

2,6-Dimethyl-4-(9-fluorenylidene)-1,4-benzoquinone (8). A suspension of **7** (716 mg, 2.5 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (567 mg, 2.5 mmol) in ethanol-free chloroform (15 ml, filtered through activated basic alumina) was shaken for 3 hr under nitrogen. The precipitated hydroquinone was filtered off and washed with chloroform and the solvent was evaporated in

vacuo from the combined filtrates to give a red-colored crystalline residue which was recrystallized by dissolving in hot chloroform and addition of ether: yield 606 mg (85%) of red plates, mp 210–212°; ir 1595 (s), 1602 (s), 1628 cm^{-1} (w); uv (isooctane) λ ($\epsilon \times 10^{-3}$) 243.5 (30.8), 272.5 (25.0), 281 (24.8), 425 nm (38.2); NMR (270 MHz) 8.03 (s, 2), 7.91 (d, J = 7.5 Hz, 2), 7.64 (d, J = 7.4 Hz, 2), 7.36 (t, J = 7.4 Hz, 2), 7.28 (t, J = 7.5 Hz, 2), 2.19 ppm (s, 6).

Anal. Calcd for $C_{21}H_{16}O$ (284.36): C, 88.70; H, 5.67. Found: C, 88.63; H, 5.72.

9-(3′,5′-Dimethyl-4′-hydroxyphenyl)-9-methoxyfluorene (9). Acetic acid (1 ml) was added to a stirred solution of 8 (284 mg, 1 mmol) in methylene chloride (10 ml) and methanol (10 ml). After stirring for 45 min the pale yellow reaction mixture was concentrated by partial evaporation of solvent in vacuo. Addition of some drops of water gave a crystalline precipitate. It was recrystallized by dissolving in hot methylene chloride and addition of *n*-pentane: yield 303 mg (96%); mp 174–176°; ir 3460 cm^{-1}; NMR 7.80–7.25 (m, 8), 6.98 (s, 2), 4.51 (s, 1), 2.95 (s, 3), 2.13 ppm (s, 6).

Anal. Calcd for $C_{22}H_{20}O_2$ (316.40): C, 83.51; H, 6.37. Found: C, 83.16; H, 6.42.

3,5-Di-*tert*-butyl-4-hydroxytriphenylcarbinol (10a). This compound was prepared from **2b** (370 mg, 1 mmol) in the same way as described for **11a**. Recrystallization from petroleum ether (bp 80–110°) gave 255 mg (65%) of colorless crystals: mp 151–152° (lit.[25] 151–152°); ir 3635, 3575 cm^{-1}; NMR 7.28 (m, 10), 7.03 (s, 2), 5.20 (br s, 1), 2.76 (s, 1), 1.33 ppm (s, 18).

α,α-Diphenyl-α-methoxy-2,6-di-*tert*-butyl-*p*-cresol (10b). This compound was prepared from **2b** as described for **11b**. Recrystallization from methanol gave 330 mg (82%) of colorless to pale yellow crystals: mp 121–122°; ir 3640 cm^{-1}; NMR 7.58–7.13 (m, 12), 5.16 (s, 1), 3.06 (s, 3), 1.37 ppm (s, 18).

Anal. Calcd for $C_{28}H_{34}O_2$ (402.58): C, 83.54; H, 8.51. Found: C, 83.63; H, 8.43.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-fluorenol (11a). **3** (368 mg, 1 mmol) was added under nitrogen to a stirred solution of potassium hydroxide (2 g) in dimethyl sulfoxide (25 ml) and water (5 ml). After 30 min at 90–95° traces of unreacted starting material were removed by filtration. The filtrate was diluted with water (200 ml) and neutralized with acetic acid. The precipitate thus obtained was filtered off and dissolved in ether. The organic layer was dried (magnesium sulfate) and the solvent was partially evaporated in vacuo. Addition of petroleum ether (bp 60–70°) gave a crystalline precipitate which, after recrystallization from petroleum ether (bp 80–110°), gave 335 mg (86%) of colorless crystals: mp 171–172°; ir 3630, 3570 cm^{-1}; NMR 7.73–7.18 (m, 10), 5.12 (s, 1), 2.43 (br s, 1), 1.35 ppm (s, 18).

Anal. Calcd for $C_{27}H_{30}O_2$ (386.54): C, 83.90; H, 7.82. Found: C, 83.74; H, 7.69.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-methoxyfluorene (11b). Sodium methoxide (540 mg, 10 mmol) was added to a stirred suspension of **3** (368 mg, 1 mmol) in dimethyl sulfoxide (25 ml) under nitrogen. The mixture was kept for 15 min at 80°, then diluted with water (200 ml) and neutralized with acetic acid. The precipitate thus formed was recrystallized twice from aqueous ethanol (75%) to give 342 mg (85%) of colorless to pale yellow crystals: mp 141–142°; ir 3630 cm^{-1}; NMR 7.75–7.20 (m, 10), 5.07 (s, 1), 2.95 (s, 3), 1.34 ppm (s, 18).

Anal. Calcd for $C_{28}H_{32}O_2$ (400.57): C, 83.96; H, 8.05. Found: C, 83.74; H, 7.97.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-cyanofluorene (11c). Sodium cyanide (735 mg, 15 mmol) and **3** (1.11 g, 3 mmol) in dimethyl sulfoxide (50 ml) were stirred for 15 min at 80° under nitrogen. The resulting green solution was slowly diluted with water (200 ml) to give a colorless, crystalline precipitate which was recrystallized from aqueous ethanol: yield 1.10 g (92%); mp 181–182°; ir 3595, 2240 cm^{-1}; NMR 7.85–7.15 (m, 8), 7.08 (s, 2), 5.20 (s, 1), 1.32 ppm (s, 18).

Anal. Calcd for $C_{28}H_{29}NO$ (395.55): C, 85.02; H, 7.39. Found: C, 84.77; H, 7.40.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-[(methylsulfonyl)methyl]fluorene (11d). Potassium *tert*-butoxide (560 mg, 5 mmol) was added to a stirred suspension of **3** (1.11 g, 3 mmol) and dimethyl sulfone (942 mg, 10 mmol) in dimethyl sulfoxide (50 ml). The stirred reaction mixture was kept under nitrogen for 5 min at 70°. Dilution with ice–water and neutralization with acetic acid gave a crystalline precipitate. Recrystallization from ethanol in the presence of charcoal gave 1.05 g (75%) of colorless crystals: mp 218–219°; ir 3625, 1310, 1125 cm^{-1}; NMR 7.89–7.67 (m; 2), 7.62–7.18 (m, 6). 7.02 (s, 2), 5.15 (s, 1), 4.30 (s, 2), 2.00 (s, 3), 1.32 ppm (s, 18).

Anal. Calcd for $C_{29}H_{34}O_3S$ (462.66): C, 75.29; H, 7.41. Found: C, 75.10; H, 7.51.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(9″-fluorenyl)fluorene (11e). Potassium *tert*-butoxide (460 mg, 4 mmol) was added to a solution of **3** (1.11 g, 3 mmol) and fluorene (670 mg, 4 mmol) in dimethylformamide (50 ml). The mixture was stirred for 30 min at 90° under nitrogen. Addition of ice gave a crystalline precipitate which was recrystallized by dissolving in warm acetone and adding aqueous ethanol (75%): yield 1.30 g (81%) of colorless crystals, mp 204–205°; ir 3620 cm^{-1}; NMR 7.66–6.66 (m, 16), 6.18 (br, s, 1), 6.05 (br s, 1), 5.33 (br s, 1), 5.15 (s, 1, exchangeable with D_2O), 1.40 ppm (s, 18).

Anal. Calcd for $C_{40}H_{38}O$ (534.74): C, 89.85; H, 7.16. Found: C, 89.56; H, 7.29.

3,5-Di-*tert*-butyl-4-hydroxy-4-phenyl-1-(9-fluorenylidene)-2,5-cyclohexadiene (12). Phenyllithium (6 ml, 2 M in benzene–ether, 70:30) was added to a stirred suspension of **3** (1.11 g, 3 mmol) in benzene (20 ml) under nitrogen. The mixture was kept for 1 hr at room temperature under nitrogen and the solvent was partially evaporated in vacuo. Slow dilution with methanol gave a yellow, crystalline precipitate which was recrystallized by dissolving in hot methylene chloride and adding methanol: yield 0.93 g (69%) of yellow crystals, mp 205–206°; ir 3570, 1640 cm^{-1}; NMR 8.08–7.08 (m, 15), 2.05 (s, 1), 1.18 ppm (s, 18); uv (methanol) λ ($\epsilon \times 10^{-3}$) 233 (34.3), 251 (42.0), 265 (sh, 21.2), 275 (sh, 16.7), 390 nm (36.6).

Anal. Calcd for $C_{33}H_{34}O$ (446.63): C, 88.74; H, 7.67. Found: C, 88.33; H, 7.58.

9-[(3′,5′-Di-*tert*-butyl-4′-phenyl)phenyl]-9-methoxyfluorene (13). Concentrated hydrochloric acid (0.2 ml) was added to a solution of **12** (150 mg, 0.34 mmol) in chloroform (5 ml) and methanol (10 ml). The reaction mixture was refluxed for 30 min and the resulting pale yellow solution was concentrated by partial evaporation of solvent in vacuo, giving a colorless precipitate. It was recrystallized by dissolving in hot methanol and adding water: yield 150 mg (96%); mp 174–175°; NMR 7.75–7.20 (m, 15), 2.16 (s, 3), 0.95 ppm (s, 18).

Anal. Calcd for $C_{34}H_{36}O$ (460.66): C, 88.65; H, 7.88. Found: C, 88.43; H, 7.74.

9-[(3′,5′-Di-*tert*-butyl)-4′-phenyl]fluorene (14). Concentrated hydrochloric acid was added dropwise to a refluxing mixture of **12** (200 mg, 0.45 mmol) and zinc powder (2 g) in dioxane (25 ml) until the solution was colorless. The mixture was filtered and the filtrate was concentrated (to ca. 5 ml) by vacuum evaporation of solvent. Addition of methanol and water gave a crystalline precipitate which was recrystallized by dissolving in ether and adding methanol to give 155 mg (80%) of colorless crystals: mp 173–174°; NMR 7.87–7.70 (m, 2), 7.66–7.22 (m, 13), 5.10 (br s, 1), 0.98 ppm (s, 18).

Anal. Calcd for $C_{33}H_{34}$ (430.63): C, 92.04; H, 7.96. Found: C, 91.70; H, 7.90.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(*N*-isopropylamino)fluorene (15a). A suspension of **3** (555 mg, 1.5 mmol) in isopropylamine (20 ml) was stirred under nitrogen for 30 min at room temperature. The resulting yellow solution was concentrated to 5 ml by vacuum evaporation. Dropwise addition of water to the stirred mixture gave a pale yellow crystalline precipitate which was recrystallized by dissolving in isopropylamine and dropwise addition of water: yield 535 mg (87%) of colorless to pale yellow crystals, mp 133–134°; ir 3625 cm^{-1}; NMR 7.76–7.20 (m, 10), 5.03 (br s, 1), 2.43 (m, 1), 1.85 (br s, 1), 1.35 (s, 18), 0.75 ppm (d, J = 6 Hz, 6).

Anal. Calcd for $C_{30}H_{37}NO$ (427.64): C, 84.26; H, 8.72. Found: C, 83.96; H, 8.65.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(*N*-cyclohexylamino)fluorene (15b). **3** (555 mg, 1.5 mmol) was dissolved in warm cyclohexylamine (15 ml). Upon cooling to room temperature, the red solution turned pale orange colored. Careful dilution with water gave a crystalline precipitate which was recrystallized by dissolving in warm cyclohexylamine and adding water: yield 440 mg (63%) of colorless to pale yellow crystals, mp 172–174°; ir 3625 cm^{-1}; NMR 7.72–7.19 (m, 10), 5.00 (br s, 1), 2.30–0.80 ppm (br m containing a sharp peak at 1.33, 30).

Anal. Calcd for $C_{31}H_{37}NO_2$ (455.64): C, 81.72; H, 8.19. Found: C, 81.83; H, 8.24.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(*N*-morpholino)fluorene (15c). **3** (555 mg, 1.5 mmol) in morpholine (15 ml) was stirred for 30 min at 50–60° under nitrogen. Careful dilution with water gave a crystalline precipitate which was recrystallized by dissolving in warm morpholine and dropwise addition of water: yield 675 mg (99%) of colorless crystals, mp 230–231°; ir 3630

cm^{-1}; NMR 7.76–7.29 (m, 10), 5.10 (br s, 1), 3.67 (m, 4), 2.35 (m, 4), 1.35 ppm (s, 18).

Anal. Calcd for $C_{31}H_{37}NO_2$ (455.64): C, 81.72; H, 8.19. Found: C, 81.83; H, 8.24.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-9-(*N*-pyrrolidino)fluorene (15d). **3** (1.11 g, 3 mmol) was dissolved in pyrrolidine (30 ml) at room temperature under nitrogen. After 10 min, excess pyrrolidine was removed by vacuum evaporation, giving a yellowish crystalline residue. Recrystallization by dissolving in benzene and adding ethanol gave 1.21 g (91%) of pale yellow crystals: mp 219–221°; ir 3620 cm^{-1}; NMR 7.72–7.15 (m, 10), 5.00 (br s, 1), 2.40 (m, 4), 1.60 (m, 4), 1.35 ppm (s, 18).

Anal. Calcd for $C_{31}H_{37}NO$ (439.65): C, 84.69; H, 8.48. Found: C, 84.52; H, 8.45.

9-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)fluorene (16). A suspension of **3** (3.68 g, 10 mmol) and zinc powder (3 g) in concentrated acetic acid (150 ml) was refluxed for 45 min under nitrogen. The reaction mixture was filtered and the filtrate was diluted with water (200 ml) to give a colorless, crystalline precipitate. Recrystallization from ethanol gave 3.53 g (95%): mp 177–178°; ir 3615 cm^{-1}; NMR 7.89–7.70 (m, 2), 7.54–7.21 (m, 6), 6.95 (s, 2), 5.05 (s, 1, exchangeable with D_2O), 5.00 (br s, 1), 1.36 ppm (s, 18).

Anal. Calcd for $C_{27}H_{30}O$ (370.51): C, 87.52; H, 8.16. Found: C, 87.44; H, 8.15.

9,9′-Bis(3″,5″-di-*tert*-butyl-4″-hydroxyphenyl)-9,9′-bifluorenyl (18a). A suspension of **3** (1.12 g, 3.04 mmol) in ethyl acetate (140 ml) was hydrogenated over 10% platinum on charcoal, H_2 uptake 45 ml (at 20°, 745 mm; 1.55 mmol). Vacuum evaporation of solvent from the essentially colorless solution obtained after removal of catalyst gave a precipitate which was filtered off after addition of petroleum ether (bp 60–70°). Several washings with *n*-pentane left a pale yellow product, yield 795 mg (71%), mp 175–195° dec. Attempts to recrystallize the crude product (under nitrogen) resulted in considerable loss of material: NMR 7.68–6.54 (m, 20), 5.10 (s, 2), 1.30 ppm (s, 36).

9,9′-Bis(4″-acetoxy-3″,5″-di-*tert*-butylphenyl)-9,9′-bifluorenyl (18b). A. By Acetylation of 18a. **18a** (300 mg, 0.4 mmol) was added under stirring to a 2 *M* solution of acetic anhydride in ethyl acetate–$HClO_4$[26] (10 ml). The mixture was stirred for 30 min at room temperature and then diluted with ethanol (20 ml). Concentration by vacuum evaporation of solvent to a volume of 5 ml followed by addition of methanol (10 ml) and some drops of water gave a crystalline precipitate. Recrystallization from ethanol gave 260 mg (78%) of colorless crystals: mp 203–206° dec; ir 1762 cm^{-1}; NMR 7.60–6.50 (m, 20), 2.33 (s, 6), 1.18 ppm (s, 36).

Anal. Calcd for $C_{58}H_{62}O_4$ (823.14): C, 84.63; H, 7.59. Found: C, 84.31; H, 7.66.

B. From Reaction between Phenylmagnesium Bromide and 3. Ten milliliters of a phenylmagnesium bromide solution prepared from 1.10 g of magnesium turnings and bromobenzene (5 ml) in ether (50 ml) was added dropwise to a stirred suspension of **3** (1.11 g, 3 mmol) in ether (25 ml) under nitrogen. The light green suspension thus obtained was stirred for 20 min under nitrogen at room temperature and was then hydrolyzed with a saturated ammonium chloride solution under nitrogen blanketing and the organic layer was dried (magnesium sulfate) under nitrogen. Addition of petroleum ether (bp 60–70°) and evaporation of diethyl ether in vacuo gave a colorless to pale yellow precipitate which was removed by filtration. The crude product was acetylated with 50 ml of acetylating agent[26] as described under A. Vacuum evaporation of solvent to ca. 5 ml gave a colorless precipitate. It was recrystallized from ether–ethanol to give 630 mg (51%), mp 203–207°.

From the original petroleum ether filtrate of the Grignard reaction, 70 mg (30%) of diphenyl, mp 69–70° (no depression upon admixture of authentic material), was isolated by vacuum sublimation (0.1 mm) at room temperature.

C. From 9-(4′-Acetoxy-3′,5′-di-*tert*-butylphenyl)-9-bromofluorene (20) and Zinc Powder. A solution of **20** (200 mg, 0.4 mmol) in anhydrous benzene (15 ml) was shaken under nitrogen with zinc powder (2 g). After 1 hr, the reaction mixture was filtered, the inorganic material was washed with benzene, and the solvent was partially evaporated in vacuo. Addition of ethanol gave a colorless, crystalline precipitate, yield 127 mg (77%), mp 204–207° dec. The identity of the products obtained by procedures A–C was confirmed by NMR.

9-(4′-Acetoxy-3′,5′-di-*tert*-butylphenyl)fluorene (19). Compound **16** (500 mg, 1.35 mmol) was added to a stirred acetic anhydride solution in ethyl acetate–$HClO_4$[26] (20 ml). Addition of ethanol (30 ml) after 30 min followed by vacuum evaporation of solvents gave a colorless, crystalline precipitate which was washed with water. Recrystallization from boiling ethanol gave **19** (500 mg, 90%): mp 166–167°; ir 1760 cm^{-1}; NMR 7.90–7.70 (m, 2), 7.50–7.21 (m, 6), 7.08 (s, 2), 5.05 (br s, 1), 2.32 (s, 3), 1.25 (s, 18).

Anal. Calcd for $C_{29}H_{32}O_2$ (412.58): C, 84.42; H, 7.82. Found: C, 84.22; H, 7.82.

9-(4′-Acetoxy-3′,5′-di-*tert*-butylphenyl)-9-bromofluorene (20). A mixture of **19** (825 mg, 2 mmol), *N*-bromosuccinimide (400 mg, 2.2 mmol), and dibenzoyl peroxide (10 mg) in carbon tetrachloride (25 ml) was refluxed for 1 hr. Succinimide was filtered off and washed with carbon tetrachloride. Vacuum evaporation of solvent from the combined filtrates gave a solid residue which was dissolved in boiling petroleum ether (bp 80–110°) and filtered through Celite. The clear solution thus obtained was concentrated by vacuum evaporation of solvent, giving a crystalline precipitate. Recrystallization from *n*-hexane gave 660 mg (67%) of colorless crystals: mp 178–180°; ir 1760 cm^{-1}; NMR 7.77–7.23 (m, 10), 2.30 (s, 3), 1.28 ppm (s, 18).

Anal. Calcd for $C_{29}H_{31}BrO_2$ (491.47): C, 70.87; H, 6.36. Found: C, 70.59; H, 6.22.

9,9′-Bis(4″-acetoxy-3″,5″-di-*tert*-butylphenyl)-9,9′-bifluorenyl Peroxide (21). A stream of oxygen was passed into a solution of **18b** (150 mg, 0.182 mmol) in refluxing benzene (50 ml). After 1 hr about 90% of the benzene was removed by vacuum evaporation. Addition of ethanol (50 ml) followed by further vacuum evaporation of solvent gave a colorless, crystalline precipitate which was recrystallized by dissolving in methylene chloride and adding methanol to give 140 mg (90%) (after drying under vacuum at 100° for 2 hr): mp 209–211°; ir 1760 cm^{-1}; NMR 7.75–7.15 (m, 16), 6.93 (s, 4), 2.23 (s, 6), 1.07 ppm (s, 36).

Anal. Calcd for $C_{58}H_{62}O_6$ (855.14): C, 81.47; H, 7.31. Found: C, 81.13; H, 7.26.

ESR Measurements. The ESR spectrum (Figure 2) was obtained at 98° by using a degassed solution of dimer **18b** in xylene which had been distilled from sodium. The kinetic experiment was performed in anisole solution by measuring the signal intensity *S* as function of the temperature between 75 and 120°. The ΔH of the equilibrium between **17b** and **18b** was obtained from a plot of ln *S* vs. T^{-1} using the least-squares method.

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Registry No.—**2b,** 13131-76-5; **3,** 57196-25-5; **4a,** 128-39-2; **4b,** 576-26-1; **4c,** 2219-82-1; **4d,** 2432-11-3; **4e,** 96-76-4; **4f,** 91-10-1; **4g,** 100-66-3; **5a,** 57196-26-6; **5b,** 57196-27-7; **5c,** 57196-28-8; **5d,** 57196-29-9; **5e,** 57196-30-2; **5f,** 57196-31-3; **5g,** 57196-32-4; **6,** 57196-33-5; **7,** 57196-34-6; **8,** 57196-35-7; **9,** 57196-36-8; **10a,** 13145-53-4; **10b,** 57196-37-9; **11a,** 57196-38-0; **11b,** 57196-39-1; **11c,** 57196-40-4; **11d,** 57196-41-5; **11e,** 57196-42-6; **12,** 57196-43-7; **13,** 57196-44-8; **14,** 57196-45-9; **15a,** 57196-46-0; **15b,** 57196-47-1; **15c,** 57196-48-2; **15d,** 57196-49-3; **16,** 57196-50-6; **18a,** 57196-51-7; **18b,** 57196-52-8; **19,** 57196-53-9; **20,** 57196-54-0; **21,** 57196-55-1; 2,6-di-*tert*-butyl-1,4-benzoquinone, 719-22-2; fluorenylidenetriphenylphosphorane, 4756-25-6; acetic anhydride, 108-24-7; 9-bromofluorene, 1940-57-4; 2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 84-58-2; methanol, 67-56-1; potassium hydroxide, 1310-58-3; sodium methoxide, 124-41-4; sodium cyanide, 143-33-9; dimethyl sulfone, 67-71-0; fluorene, 86-73-7; phenyllithium, 591-51-5; isopropylamine, 75-31-0; cyclohexylamine, 108-91-8; morpholine, 110-91-8; pyrrolidine, 123-75-1; phenylbromide, 108-86-1; *N*-bromosuccinimide, 128-05-8.

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Reaction of Substituted Malachite Green Cations with Cyanide Ion

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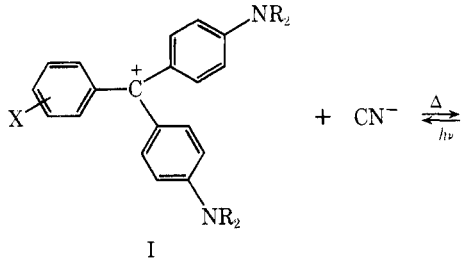
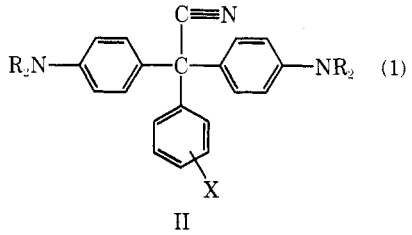
The reaction rate constants and the activation parameters for the reaction of cyanide ion with a variety of substituted triarylmethane carbocations have been measured in dimethyl sulfoxide (Me_2SO) containing 8% water by volume. The reaction is second order overall and first order with respect to each reactant. The nucleophilicity system parameter ($N_+ = 8.1$) indicates a nucleophilic system much like that found in pure Me_2SO. The slope of the Hammett plot ($\rho = 0.647$) and the large negative "salt effect" closely resemble the results found for reactions of these carbocations in water, indicating a similar transition state structure and mechanism.

The reaction of the stable triarylmethyl cations (i.e., primarily dye cations) with a variety of nucleophiles in a number of solvents has been studied extensively.[1] The reaction of the cyanide nucleophile with this class of dye carbocation (I) has been shown to be a kinetically straightforward anion–cation recombination, which can be easily followed by spectrophotometry at low concentrations because of the very high extinction coefficients of the cations (ϵ 10^5 M^{-1}). The relatively slow reaction to form the covalent triarylmethane leuconitrile (II) has been treated as a nucleophilic attack involving an ion pair at the transition state.[2] More recently it has been considered as a reaction involving the reorganization of the solvent structure around a one solvent separated ion pair,[3] as a critical factor at the transition state.

The present work will examine the reactions of cyanide ion with a variety of substituted triarylmethane cations (eq 1) in dimethyl sulfoxide containing 8% water by volume, in



I



II (1)

order to measure the activation parameters of these reactions and to determine further applicability of the linear free energy relationship to a series of triarylmethanes[4] carrying a larger number of substituents than the series studied by previous investigators.

Results

The reactions of the carbonium ions with cyanide ions in dimethyl sulfoxide (Me_2SO) containing 8% water were studied by irradiating a solution containing the leuconitrile of the dye and potassium cyanide. The irradiation, which was carried out in a spectrophotometer, produced the desired dye cation in concentration of ca. 10^{-6} *M*. The reaction kinetics with excess cyanide (ca. 10^{-5}–10^{-3} *M*) are pseudo-first-order with respect to the dye, to at least 90% completion. The plots of the pseudo-first-order rate constants (k_{ps}) are linear in all cases with respect to the cyanide ion concentration over a wide range (20–500 ×), Figure 1. As would be expected, all the carbonium ions were found to follow excellent second-order kinetics in their reactions with cyanide ion.

Certain salts have been shown to cause retardation of the pseudo-first-order rates of this reaction, as shown by an inverse relation between k_{ps} and salt concentration.[2,5] Although we also found that some salts have a strong retarding effect on the rate (vide infra), potassium cyanide did not display such as effect, nor did it cause side reactions.

An 8% aqueous Me_2SO resolution containing potassium cyanide, even at the low concentrations used in the kinetic studies, will contain hydroxyl ions formed by the hydrolysis of the salt. The concentration of these ions was measured using apparatus similar to that described by Ritchie and Unschold.[6] The hydroxide ion concentration in this solvent was found to be similar to the calculated concentrations assuming a mixture of solvents. Over the range of potassium cyanide concentrations studied, the hydroxyl ion concentration is smaller than that of the cyanide ion by as much