N,N-Diisopropyl-2-trimethylsilylpropanoamide: isolated yield, 34%; bp (0.05 Torr) 60–61 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (m, 2 H), 2.4 (q, 1 H, J = 5 Hz), 1.6 (d, 3 H, J = 5 Hz), 1.4 (m, 12 H), 0.10 (s, 9 H).

1-Trimethylsiloxy-1-diisopropylaminopropene: isolated by preparative GLC; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (q, 1 H, J = 6 Hz), 2.6 (m, 2 H), 1.5 (d, 3 H), 1.4 (m, 12 H), 0.23 (s, 9 H).

O-Silylated derivative of 1-methyl-2-piperidine (5): isolated yield, 25%; bp (3 Torr) 80–85 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.9 (t, 1 H, J = 4 Hz), 3.0 (m, 2 H), 2.7 (s, 3 H), 2.0 (m, 4 H), 0.14 (s, 9 H).

C-Silylated derivative of 1-methyl-2-piperidone (6): isolated yield, 40%; bp (4 Torr) 98–100 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.4 (m, 2 H), 3.1 (s, 3 H), 2.5 (m, 1 H), 2.0 (m, 4 H), 0.08 (s, 9 H).

1-*tert*-Butyldimethylsiloxy-1-dimethylaminoethene: isolated by preparative GLC; ^{1}H NMR (CCl_4, internal Me_4Si) δ 2.77 (m, 2 H), 2.43 (s, 6 H), 0.87 (s, 9 H), 0.13 (s, 6 H); IR (CCl_4) 1640 cm^{-1} (C=C).

N,N-Dimethyl-2-*tert*-butyldimethylsilylacetamide: isolated yield (THF solvent), 60%; bp (0.6 Torr) 88–90 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 2.93 (s, 3 H), 2.83 (s, 3 H), 1.83 (s, 2 H), 0.93 (s, 9 H), 0.07 (s, 6 H); IR (CCl_4) 1630 cm^{-1} (C=O).

1-*tert*-Butyldimethylsiloxy-1-dimethylaminopropene: isolated yield, 90%; bp (0.6 Torr) 58 °C; ^{1}H NMR (CCl_4, internal Me_4Si) δ 3.50 (q, 1 H), 2.37 (s, 6 H), 1.43 (d, 3 H), 0.97 (s, 9 H), 0.13 (s, 6 H); IR (CCl_4) 1665 cm^{-1} (C=C).

Hydrolysis of Silylated Derivatives of Amides. *N,N*-Dimethyltrimethylsilylacetamide (**4**), 10 mmol, was dissolved in 10 mL of THF in a round-bottom flask under a nitrogen atmosphere. Acetic acid (5 mL, 2 M) was injected and the solution was stirred for 15 min in a 25 °C water bath. At the end of this time, the solution was saturated with anhydrous K_2CO_3 and analyzed by GLC. The recovery of **4** was 99% (9.9 mmol). A similar experiment using 5 mL of 2 M hydrochloric acid in place of acetic acid gave a 17% yield of **4** (1.7 mmol), together with a 83% yield of *N,N*-dimethylacetamide (8.3 mmol) after 5 min of stirring and a 100% yield (10 mmol) of *N,N*-dimethylacetamide after 15 min. Similar procedures were used with other silylated derivatives.

Thermolysis of 4. A 50-mL round-bottom flask equipped with septum inlet and reflux condenser was flushed with nitrogen and 5.4 mL (15 mmol) of **4** was injected. The compound was heated to 160 °C for 1 h. At the end of this time, GLC analysis showed traces of **4** (<1 mmol), together with a component of longer retention time. Vacuum distillation gave 1.0 g (5 mmol) of **11**: bp (0.1 Torr) 60–65 °C; ^{1}H NMR spectrum (CCl_4, internal Me_4Si) δ 4.1 (m, 2 H), 3.0 (s, 2 H), 2.9 (s, 3 H), 2.8 (s, 3 H), 0.21 (s, 9 H).

Acknowledgment. We thank the National Science Foundation for partial support of this work.

Registry No.—**3**, 23138-90-1; **4**, 23184-28-3; **5**, 64728-08-1; **6**, 64728-09-2; 1-trimethylsiloxy-1-dimethylaminopropene, 64728-10-5; *N,N*-dimethyl-2-trimethylsilylpropanoamide, 64728-11-6; 1-trimethylsilyloxy-1-dimethylamino-1-butene, 64728-12-7; *N,N*-diethyl-2-trimethylsilylpropanoamide, 64728-13-8; *N,N*-diisopropyl-2-trimethylsilylpropanoamide, 64728-14-9; 1-trimethylsiloxy-1-diisopropylaminopropene, 64728-15-0; 1-*tert*-butyldimethylsiloxy-1-dimethylaminoethene, 64728-16-1; *N,N*-dimethyl-2-*tert*-butyldimethylsilylacetamide, 64728-17-2; 1-*tert*-butyldimethylsiloxy-1-dimethylaminopropene, 64728-18-3; *N,N*-dimethylacetamide, 127-19-5; lithio *N,N*-dimethylacetamide, 55259-70-6; *N,N*-dimethylpropanoamide, 758-96-3; lithio *N,N*-dimethylpropanoamide, 58079-54-2; *N,N*-dimethylbutyramide, 760-79-2; lithio *N,N*-dimethylbutyramide, 55259-71-7; *N,N*-diethylacetamide, 685-91-6; lithio *N,N*-diethylacetamide, 62702-96-9; *N,N*-diisopropylpropanoamide, 1113-75-3; lithio *N,N*-diisopropylpropanoamide, 64728-06-9; *N*-methyl-2-piperidone, 931-20-4; lithio *N*-methyl-2-piperidone, 64728-05-8; TMCS, 75-77-4; TBCS, 18162-48-6; lithium diisopropylamide, 4111-54-0.

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Mass Spectral Fragmentation of Substituted Pentaphenylcyclopentadienols

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The mass spectral decomposition pathway for a series of pentaphenylcyclopentadienols substituted in the para position of the 1- or 3- and 4-phenyl rings has been observed to consist of a continuum of two superimposed pathways with the choice of the major decomposition mode being determined by the electron-donating or -withdrawing ability of the substituents. Attempts to establish a linear-free-energy relationship for the mass spectral decomposition of the 1-para-substituted phenylcarbinols were unsuccessful, whereas similar attempts with the 3- and 4-para-substituted phenylcarbinols were successful.

The mass spectral fragmentations of tetracyclone, tetraarylquinones, and tetraphenylthiophene dioxides have been extensively studied by Bursey et al.[1-5] who has also published extensively on the use of fluorine as a "dead label" in the decomposition of pentaphenylcyclopentadienols.[1,3,5] The most interesting aspect of their work is the mass spectral production and decomposition of the parent and fluorosubstituted tetraphenyltetrahedrane radical cations from the decomposition of 1,2,3,4,5-pentaphenylcyclopentadien-2,4-ol-1 (**1**, R = H) and its *p*-fluoro derivatives.[5]

Since a large number of mono- and disubstituted pentaphenylcyclopentadienols have been prepared in our laboratories for a kinetic study of the electronic effects involved in a [1,5]-sigmatropic phenyl shift in such systems,[6-8] it became of interest to study the mass spectral fragmentations[9] of the complete family of 1-(para-substituted phenyl)-2,3,4,5-te-

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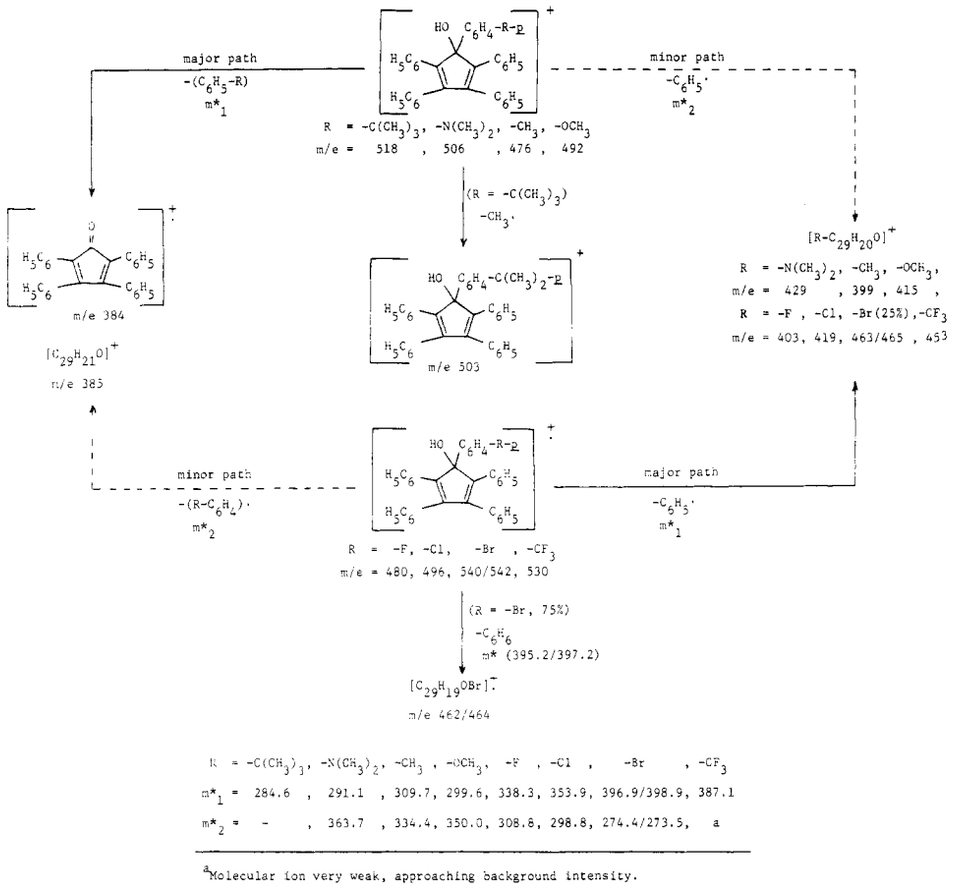
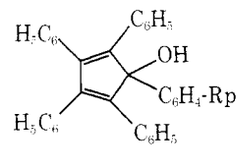


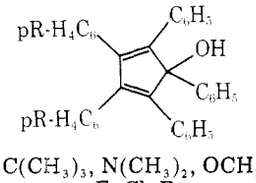
[a] Molecular ion very weak, approaching background intensity.

Figure 1. Mass spectral decomposition pathways of 1-(para-substituted phenyl)-2,3,4,5-tetraphenylcyclopentadien-2,4-ols-1.

traphenylcyclopentadien-2,4-ols-1 (**1**), and bis[3- and 4-(para-substituted phenyl)]-2,5-diphenylcyclopentadien-2,4-ols-1 (**2**) shown below. Of the substituted carbinols shown



1, R = $C(CH_3)_3$, $N(CH_3)_2$, OCH_3, CH_3, H, F, Cl, Br, CF_3



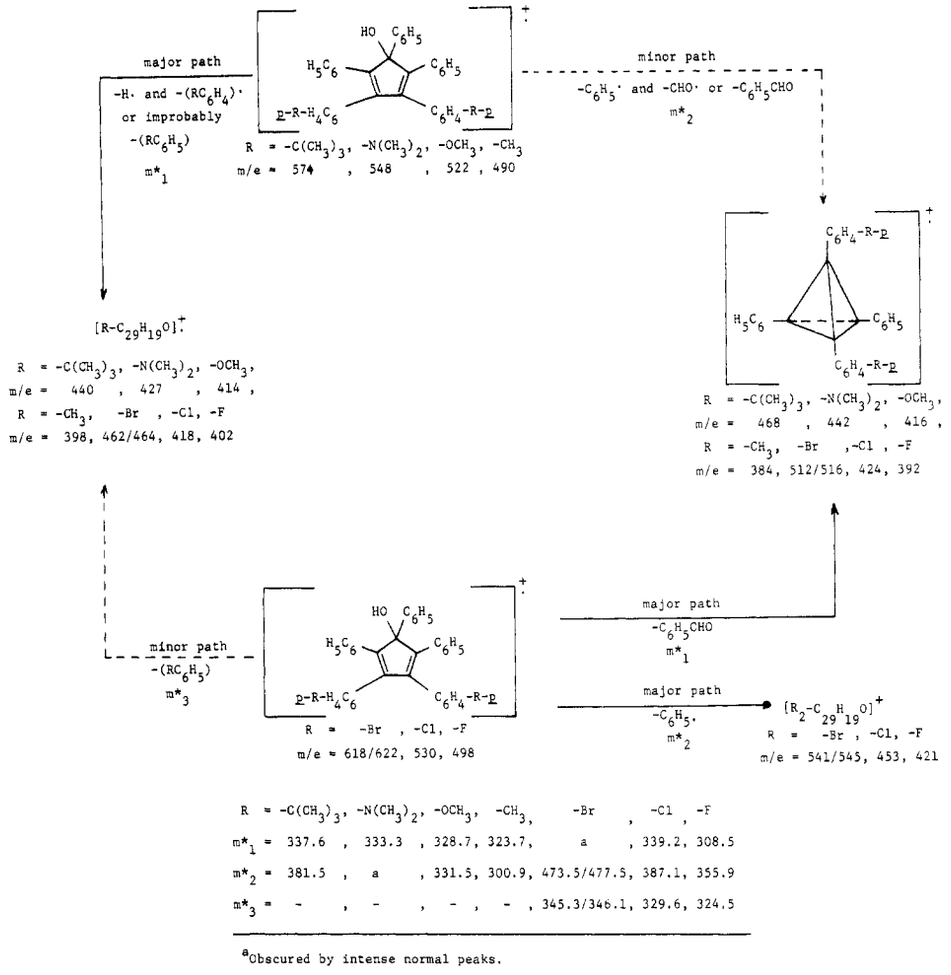
2, R = $C(CH_3)_3$, $N(CH_3)_2$, OCH_3, CH_3, F, Cl, Br

only two have been studied previously by Bursey et al.,[5] **1**, R = H and F, and in our hands both showed similar initial decomposition patterns as previously reported.[5]

The substituent effect we have observed for the initial decomposition of carbinols **1** causes a continuum of two superimposed decomposition paths. At one extreme of the continuum is the decomposition pathway observed for **1** (R = $C(CH_3)_3$). By critical investigation of the peak intensities and prominent metastable ion peaks it was established that the initial breakdown for this carbinol consisted of loss of CH_3·, or the loss of $C_6H_5C(CH_3)_3$ (metastable ion at 284.6) (Figure 1).

Investigation of carbinols **1** (R = $N(CH_3)_2$, OCH_3, or CH_3) was expected to show a similar decomposition pathway, consisting of the loss of C_6H_5R. This was indeed observed as the major decomposition pathway; however, a minor decomposition pathway consisting of the loss of C_6H_5· was also observed (Figure 1). This minor decomposition pathway is observed to become the major decomposition pathway as the substituents are changed from strongly electron donating to weakly electron donating to weakly electron withdrawing to strongly electron withdrawing. Thus, observation of the mass spectral decomposition of carbinols **1** (R = F, Cl, or CF_3) shows the major decomposition pathway to consist of loss of C_6H_5·. With the aid of metastable ions it can be seen that with these substituents the minor pathway appears to be decomposition in the "normal" manner, i.e., loss of RC_6H_4· (Figure 1). In the case of carbinol **1** (R = Br) however, although the minor decomposition pathway is exactly as described above, and approximately 25% of the parent molecular ion decomposes via the major pathway already discussed for the other electron-withdrawing substituents, the majority (~75%) of the parent ion decomposes via a different major decomposition pathway consisting of the loss of C_6H_6·. To establish if this new major decomposition pathway was unique for carbinol **1** (R = Br) alone, the *p*-iodo analogue (**1**, R = I) was investigated and, although it is not illustrated on Figure 1, this carbinol also decomposed via the two major pathways reported for carbinol **1** (R = Br) but in a 10 to 90% ratio, respectively. Possibly the differences in electronegativity between F, Cl, Br, and I can account for this difference in the ratio of the initial major decomposition pathways.

Observation of the mass spectral decomposition of carbinols **2** again shows that the substituents do play a significant role in the choice of which route in the decomposition continuum the molecule will follow. With electron-donating substituents, the major decomposition pathway is observed to be loss of one *p*-RC_6H_4 group, most likely via a stepwise loss of H· and RC_6H_4· instead of a concerted loss of *p*-RC_6H_5 (Figure 2).



[a] Obscured by intense normal peaks.

Figure 2. Mass spectral decomposition pathways of bis[3- and 4-(para-substituted phenyl)]-2,5-diphenylcyclopentadien-2,4-ols-1.

The minor decomposition pathway observed for these compounds (**2**, R = $C(CH_3)_3$, $N(CH_3)_2$, OCH_3, and CH_3) again consisted of loss of the units C_6H_5· and CHO· sequentially or loss of the entire C_6H_5CHO unit, to produce the monosubstituted tetraphenyltetrahedrane cation radical.

Also represented in Figure 2 are the major and minor decomposition pathways for the carbinols **2** (R = Br, Cl, and F) containing electron-withdrawing substituents. It can be seen that in these cases the major and minor decomposition pathways observed for carbinols **2** containing electron-donating substituents have now become reversed. It is also interesting to note that in varying degrees and with all substituents, loss of one of the monosubstituted phenyl units is observed even though this unit is structurally removed from the carbinol center in the molecule.

Although Bursey et al.[5] have described the major decomposition pattern of the *p*-fluoro-substituted carbinols they studied as a "stepwise loss of the elements aryl and CHO·" and we have observed this stepwise loss with the para-halo carbinols **2**, it does not appear that this sequence represents the major decomposition pathway for either the fluoro-, bromo-, or chloro-substituted carbinols **2** (R = F, Br, or Cl) because of the greater intensities observed for both the ions corresponding to $P\text{-}C_6H_4X$ and the metastable ions at 324.5, 345.7, or 329.6, respectively, which are consistent with the loss of C_6H_4X from the parent ions **2** (R = F, Br, or Cl). It also appears that this loss of C_6H_4F from the parent ion of **2** (R = F) may have occurred in the *p*-fluoro-substituted carbinol studied by Bursey et al.[5] and may be the reason that they were unable to unequivocally establish T_d symmetry for the di(*p*-fluoro)-substituted tetraphenyltetrahedrane radical cation they observed.

In view of the results obtained with both classes of carbinols **1** and **2**, it appears that in every case the major fragmentation pathway involves the loss of the most electron-donating aromatic group, either as Ar·, or as Ar· and H·, or possibly as ArH. Thus, given a choice between the loss of RC_6H_4 (R = $C(CH_3)_3$, $N(CH_3)_2$, OCH_3, or CH_3) or C_6H_5·, carbinols **1** and **2** fragment by loss of RC_6H_4 (Figures 1 and 2), but given a choice between the loss of RC_6H_4 (R = F, Cl, Br, or CF_3) or C_6H_5·, the same carbinols fragment by loss of C_6H_5· preferentially (Figures 1 and 2).

In addition to the partial hydrogen and phenyl scrambling observed to occur in the respective molecular ions of all of the mono- and disubstituted carbinols **1** and **2** studied before fragmentation, it was observed that the intensity ratios of the normal peaks for these carbinols were independent of both the ionization voltage used (down to values very near the appearance potentials) and the temperature of the probe (80–240 °C). The most startling observation about the mass spectral fragmentation of these carbinols was made with the aid of high-resolution mass spectrometry[10] which shows that oxygen is lost $(M - 16)^+$· to the extent of 10–15% from the parent ions of all the carbinols studied.

Although attempts to establish a free-energy relationship[11-14] and a Hammett plot for the carbinols **1** proved unsuccessful using any of the common fragmentation routes in the initial portion of the decomposition of these alcohols, attempts to establish such a relationship with the carbinols **2** was successful. Thus, using the relationship shown below, a

Chart I

R	Mp (°C) and lit. ref or Anal.
H	175–176[18]
$C(CH_3)_3$	103–104; Calcd for $C_{39}H_{34}O$: C, 90.31; H, 6.61. Found: C, 90.13; H, 6.72
$N(CH_3)_2$	229–230 (lit.[19] 248–249)
OCH_3	201–202 (lit.[20,21] 203)
CH_3	192–192.5 (lit.[22] 188–189, 199–200)
F	183.5–184.5 (lit.[5] 180–182)
Cl	211–212; Calcd for $C_{35}H_{25}OCl$: C, 84.58; H, 5.07; Cl, 7.13. Found. C, 84.64; H, 5.01; Cl, 7.10
Br	217–219; Calcd for $C_{35}H_{25}OBr$: C, 77.64; H, 4.65; Br, 14.75. Found: C, 77.62; H, 4.57; Br, 14.73
CF_3	210–211; Calcd for $C_{36}H_{25}OF_3$: C, 81.49; H, 4.75; F, 10.74. Found: C, 81.40; H, 4.77; F, 10.69

Chart II

R	b	Mp (°C) and lit. ref or Anal. for carbinols 2
$C(CH_3)_3$	a	218–219; Calcd for $C_{43}H_{42}O$: C, 89.85; H, 7.36. Found: C, 89.56; H, 7.22
$N(CH_3)_2$	17, 18, 23	225–226 (lit. 270–271,[17] 252,[19] 225–226[23])
OCH_3	24, 25, 26	195–196; Calcd for $C_{37}H_{30}O_3$: C, 85.03; H, 5.79. Found: C, 84.82; H, 5.98
CH_3	24, 25, 26	207–208; Calcd for $C_{37}H_{30}O$: C, 90.58; H, 6.16. Found: C, 90.27; H, 6.32
F	1	163–164; Calcd for $C_{35}H_{24}OF_2$: C, 84.32; H, 4.85; F, 7.62. Found: C, 84.19; H, 5.12; F, 7.55
Cl	26, 27	159–160; Calcd for $C_{35}H_{24}OCl_2$: C, 79.10; H, 4.55; Cl, 13.34. Found: C, 79.08; H, 4.58; Cl, 13.35
Br	16, 24, 25	190–191 (lit.[16] 195)

[a] New compound, preparation of benzil, cyclone, and carbinol given below. [b] Reference to substituted cyclone starting material.

plot of log Z/Z_0 vs. σ_p[15] for the carbinols **2** afforded a straight-line relationship with ρ calculated to be -2.84 using a linear least-squares program (Figure 3).

$$Z = \frac{[(p\text{-}RC_6H_4)(C_6H_5)_3C_5O]^+\cdot}{[(p\text{-}RC_6H_4)_2(C_6H_5)_3C_5OH]^+\cdot}$$

The negative ρ obtained indicates that the mass spectral decomposition of these carbinols is assisted by electron donation at the reaction site, or at the 3 and 4 position of the cyclopentadiene ring. Also, as the substituent R becomes less electron donating this decomposition pathway decreases in importance. This approach holds for the carbinols **2** where R = $N(CH_3)_2$, OCH_3, Br, Cl and F but not where R = $C(CH_3)_3$ or CH_3, since with these substituents there is considerable loss of CH_3. However, if a plot of log Z/Z_0 vs. σ_p is made for carbinol **2** when R = CH_3 and where Z_0 is the parent molecular ion minus a CH_3 (m/e 475), and Z equals the parent minus $C_6H_5CH_3$, a point on the existing straight line is obtained. Application of this approach to carbinol **2** where R = $C(CH_3)_3$ and where Z_0 = [P − CH_3] and Z = [P − [$C_6H_5C(CH_3)_3$]] affords similar results.

Experimental Section

General. Mass spectra for all compounds were obtained on both an Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer and a modified Varian MAT 112 double focusing mass spectrometer connected to a SpectroSystem 101 MS Varian Mat (620/1-100) computer system equipped with a Tektronix storage oscilloscope to provide hard copies of spectra. With both instruments the carbinols were introduced into the ionization chamber maintained at 175 °C using a direct inlet probe and spectra were recorded at 75 eV, with an ionizing current of 80 μA. Low-voltage spectra on both instruments were recorded with a filment current of 2.0 and 2.4 μA. With the Hitachi Perkin-Elmer RMU-7 double focusing mass spectrometer, mass assignments were based upon high boiling perfluorokerosene as an internal standard.

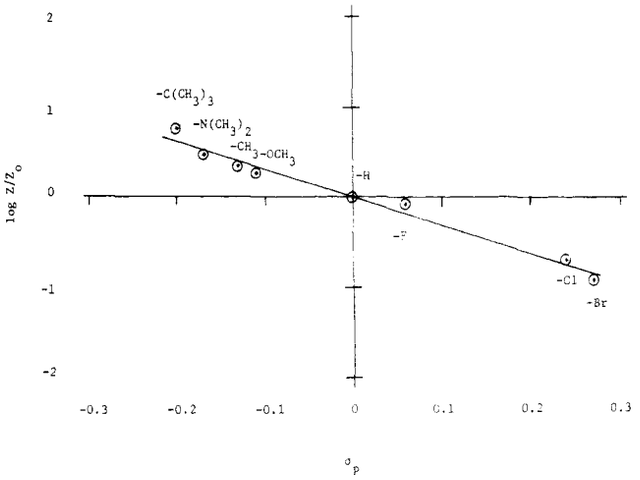


Figure 3. Hammett plot of log Z/Z_0 vs. σ_p for carbinols **2**.

Preparation of Carbinols 1. These carbinols were prepared in the normal manner[16,17] by Grignard addition of the appropriately para-substituted phenylmagnesium bromide to tetracyclone (Chart I).

Preparation of Carbinols 2. These carbinols were prepared by Grignard addition of phenylmagnesium bromide to the appropriate 3- and 4-(para-substituted phenyl)-2,5-diphenylcyclopentadien-2,4-ones-1. Listed in Chart II are the literature reference to the appropriately substituted tetracyclones as well as the melting points and analyses for the new carbinols.

4,4′-Di(*tert*-butyl)benzil. *p*-(*tert*-Butyl)bromobenzene (K & K, Labs) was converted to *p*-(*tert*-butyl)benzaldehyde according to the literature procedure.[28] Treatment of 243 g (1.5 mol) of *p*-(*tert*-butyl)benzaldehyde dissolved in 300 mL of 95% ethanol with 30 g (0.46 mol) of potassium cyanide dissolved in 150 mL of water all contained in a 1-L three-necked, round-bottomed flask equipped with a mechanical stirrer and a reflux condenser produced a red oil after 3.5 h of refluxing. Cooling with stirring overnight afforded 74.2 g (0.23 mol, 30%) of the corresponding benzoin which was oxidized as obtained without further purification using the Weiss and Appel[29] procedure to give 64.0 g (0.20 mol, 88%) of 4,4′-di(*tert*-butyl)benzil, mp 104–104.5 °C (lit.[30] 104–104.5 °C).

3,4-Bis[*p*-(*tert*-butyl)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1. This compound was prepared by Fieser's method[31] from 4,4′-di(*tert*-butyl)benzil and 1,3-diphenylpropanone in 90% yield, mp 251–252 °C. Anal. Calcd for $C_{37}H_{36}O$: C, 89.52; H, 7.29. Found: C, 89.72; H, 7.37.

3,4-Bis[*p*-(*tert*-butyl)phenyl]-1,2,5-triphenylcyclopentadien-2,4-ol-1. Into a 500 mL, three-necked, round-bottomed flask equipped with a magnetic stirrer and a reflux condenser is placed 9.9 g (0.02 mol) of the above cyclone dissolved in 100 mL of anhydrous benzene. To this solution is added dropwise an ether solution of phenylmagnesium bromide prepared from 1.96 g (0.08 g-atom) of magnesium, 13.4 g (0.08 mol) of bromobenzene, and 50 mL of anhydrous ether. After the addition is completed and the reaction subsides, the resulting mixture is refluxed for 2 h, cooled in an ice bath, and hydrolyzed with 100 mL of 10% ammonium chloride solution and the organic layer was separated, washed twice with water, and dried over anhydrous magnesium sulfate. The organic solution is filtered and concentrated to about 30 mL and 200 mL of petroleum ether (bp 30–60 °C) was added to afford the crude alcohol. Recrystallization from benzene–ethanol (95%) afforded 11.4 g (0.0198 mol, 99%) of carbinol.

Acknowledgment. The authors wish to extend their sincere appreciation to Professor Burnaby Munson and Mr. Charles W. Polley for performing the high-resolution mass spectrometry and to Professor David G. I. Kingston for his comments during the reading of this manuscript.

Registry No.—**1** (R = $C(CH_3)_3$), 64706-17-8; **1** (R = $N(CH_3)_2$), 752-09-0; **1** (R = OCH_3), 64706-18-9; **1** (R = CH_3), 64706-19-0; **1** (R

= F), 24523-58-8; 1 (R = Cl), 15946-43-7; 1 (R = Br), 19057-23-9; 1 (R = CF_3), 64706-20-3; 2 (R = $C(CH_3)_3$), 64706-21-4; 2 (R = $N(CH_3)_2$), 916-86-9; 2 (R = OCH_3), 64706-22-5; 2 (R = CH_3), 19059-95-1; 2 (R = F), 64706-23-6; 2 (R = Cl), 22926-90-5; 2 (R = Br), 56549-00-9; 2 (R = H), 2137-74-8; phenyl bromide, 108-86-1; 3,4-bis[*p*-(*tert*-butyl)-phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 64706-24-7; 3,4-bis[*p*-(dimethylamino)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 751-71-3; 3,4-bis[*p*-(dimethoxy)phenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 668-29-1; 3,4-bis[*p*-methylphenyl]2,5-diphenylcyclopentadien-2,4-one-1, 38305-61-2; 3,4-bis[*p*-fluorophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 56805-29-9; 3,4-bis[*p*-chlorophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 38268-08-5; 3,4-bis[*p*-bromophenyl]-2,5-diphenylcyclopentadien-2,4-one-1, 38268-11-0; 2,3,4,5-tetraphenylcyclopentadien-2,4-one-1, 479-33-4.

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(10) We thank Professor Burnaby Munson and Mr. Charles Polley for performing these experiments for us.
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Synthesis and Absolute Configuration of (−)-D_{2d}-Bisnoradamantan-2-one (Tricyclo[3.3.0.0^{3,7}]octan-2-one)[1]

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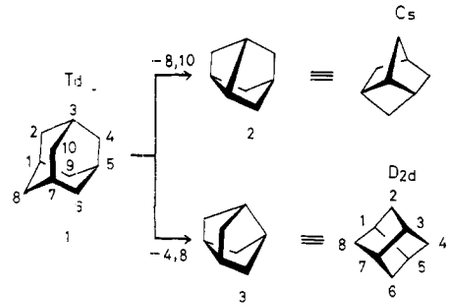
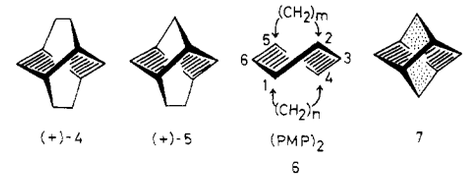
(−)-Tricyclo[3.3.0.0^{3,7}]octane-2-carboxylic acid (**23**) was converted into (−)-D_{2d}-bisnoradamantan-2-one (**9**), whose circular dichroism spectrum indicated the 1*R*,3*R*,5*R*,7*R* absolute configuration.

Although the high symmetry (T_d) inherent to the adamantane molecule (**1**) requires stereochemical equivalence among all of the six methylene groups, sets of two methylene groups can be classified into two different categories: the sets made of two methylene groups not situated on the same C_2 axis (e.g., 8–10) and the sets made of two methylene groups situated on the same C_2 axis (e.g., 4–8). Simultaneous removal of the two methylene groups (e.g., 8–10) belonging to the former category gives tricyclo[3.2.1.0^{3,6}]octane (**2**)[2] with C_s symmetry. On the other hand, simultaneous removal of the two methylene groups (e.g., 4–8) classified in the latter category will afford tricyclo[3.3.0.0^{3,7}]octane (**3**),[3] which belongs to the D_{2d} point group and which, for convenience, shall be referred to as D_{2d}-bisnoradamantane in this paper.



In D_{2d}-bisnoradamantane (**3**), one can discern a D_2 twist-boat cyclohexane moiety which is specified by hatching. We have been interested in syntheses and chiroptical properties of high-symmetry chiral (gyrochiral[4]) cage-shaped molecules, and preparations of (+)-twistane (**4**)[5] having D_2 symmetry and (+)-twist-brendane (**5**)[6] having C_2 symmetry, both with known absolute configurations, that have been reported from our laboratory.



In these molecules, the $(PMP)_2$ chiral twist-boat conformation of the cyclohexane ring is frozen by means of two short bridges, $(CH_2)_m$ and $(CH_2)_n$, spanning over the C-1 and C-4 as well as C-2 and C-5 carbon atoms as shown in structure **6**. D_{2d}-Bisnoradamantane corresponds to **6** with $m = n = 1$, and the molecular model (**7**) of this compound shows that the molecule consists of two enantiomeric D_2 twist-boat cyclohexane species (the hatched and the dotted ones indicated in formula **7**) fused together as shown in **7**. This molecular geometry results in two sets of homotopic methylene groups

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