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Thermolyses of *tert*-Butyl $\Delta^{1,1'}$-Dicyclohexenylperoxyacetate. Electrocyclic and Other Transformations of a Pentadienyl Radical

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Abstract: Pentadienyl radical precursor, *tert*-butyl $\Delta^{1,1'}$-dicyclohexenylperoxyacetate (**1**), has been synthesized and the products of its thermolysis have been determined at a variety of temperatures. Ambient temperature vacuum thermolysis affords noncyclized trienes and noncyclized *tert*-butyl ethers by disproportionation and recombination of the radical pair, respectively. An almost twofold preference for recombination at the central carbon atom of the pentadienyl system was observed. At 210 °C, thermolysis affords three additional major products, methylated dienes that arise from recombination of the pentadienyl radical with methyl radical. At 210 °C and above, an additional product, a cyclized diene (**9a**) is formed. Its stereochemistry corresponds to that which would result from conrotatory electrocyclic closure of the pentadienyl radical to a cyclopentenyl radical, followed by disproportionation. The presence of the corresponding diene **9b** that would result from disrotatory closure of the pentadienyl radical could not be conclusively established. If present, it accounts for no more than 13% of the cyclized diene mixture. At higher temperatures, products arising from hydrogen abstraction and methyl recombination of the cyclopentenyl radical are observed. Only those products with anti-backbone (conrotatory closure) were observed (by GLC comparison with authentic samples). These results point to at least a highly stereoselective cyclization of the pentadienyl radical and establish that the HOMO of the pentadienyl radical is not the factor controlling the stereochemical course of the cyclization.

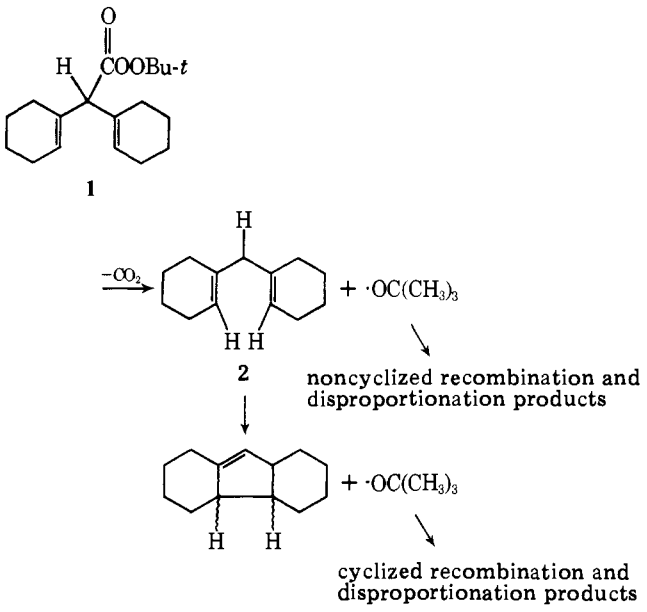
Two little-explored properties of the pentadienyl radical are the regiochemistry of its recombination with other radicals and the stereochemistry of its cyclization. The latter property is particularly interesting because of conflicting theoretical predictions of the simple MO methods, which vary from stereospecific disrotatory cyclization (HOMO symmetry control)[1] to possible nonstereospecificity (state correlation diagrams[2] and the PMO method[3]). Further, more sophisticated calculations[4,5] for the related cyclopropyl radical → allyl radical reaction yield a stereochemical prediction opposite that based upon the HOMO method.

We chose to generate pentadienyl radical (**2**) by thermolysis of perester **1**. The anticipated transformations by which it was hoped to answer the above questions are indicated in Scheme I.

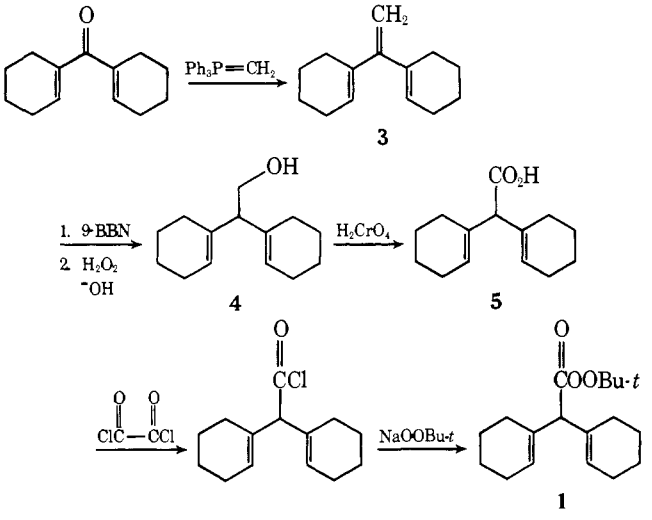
Results and Discussion

Synthesis and Properties of *tert*-Butyl $\Delta^{1,1'}$-Dicyclohexenylperoxyacetate (1). The pentadienyl radical precursor was synthesized by the sequence of reactions indicated in Scheme II. The perester was obtained as a white solid, mp 34–35 °C. It could be stored under nitrogen in a freezer at −20 °C for

Scheme I



Scheme II



months without appreciable decomposition. However, it gradually decomposed at ambient room temperature. The decomposition was accelerated by exposure to sunlight or air.

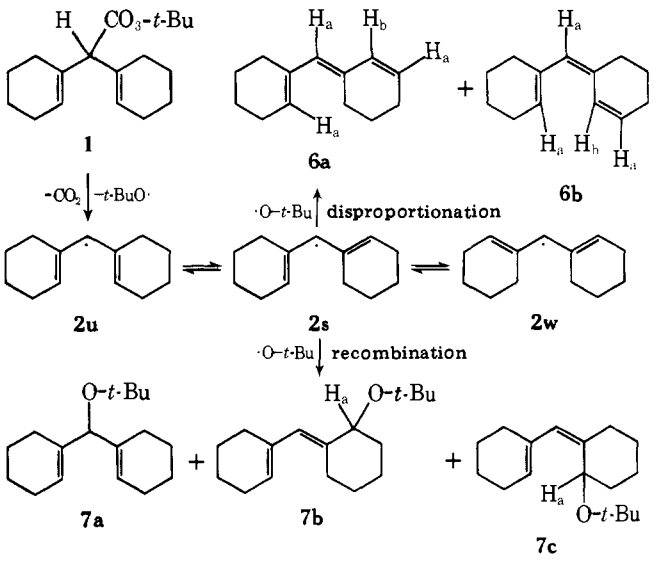
Ambient Temperature Decomposition of 1. Ambient temperature vacuum decomposition proved to be the most successful procedure for decomposing perester **1**. The crystalline, solid **1** was placed in an aluminum foil shielded flask which was evacuated to a vacuum of 0.01 Torr and was connected to a trap that was cooled in dry ice-isopropyl alcohol. No peroxy ester sublimed to the cold trap under these conditions. After 6 days, decomposition of **1** was complete, and only a small amount of residue, presumed to be polyester from induced decomposition,[8] remained. The product mixture, collected in the cold trap, was found by gas-liquid chromatography (GLC) to contain five components, compounds **6a** (8.1%), **6b** (12%), **7a** (28.7%), **7b** (9.5%), and **7c** (21.5%) (Scheme III).

The spectroscopic properties of **6a, 6b, 7a, 7b,** and **7c** are cited in Table I. The trienes **6a** and **6b** possess similar spectroscopic properties. The assignment of their structures was based primarily on the chemical shift of proton H_b, which is easily recognized in the NMR spectrum of each compound. The absorption of H_b in **6b** (centered at δ 6.05) is significantly upfield from the corresponding absorption of **6a** (centered at

Table I. Spectroscopic Properties of the Products of Ambient Temperature Vacuum Decomposition of Perester **1**

Compd	^{1}H NMR ($CDCl_3$, δ)	Uv (hexane, nm) λ_{max} (ϵ_{max})	Ir (cm^{-1}, film)
6a	6.4-6.8 (1 H, br d, J = 10 Hz, H_b), 5.4-6.0 (3 H, m, H_a's), 1.2-2.4 (14 H, m)	273 (17 781) 265 (17 380)	3030, 1640, 1615, 915, 870
6b	5.9-6.2 (1 H, br d, J = 10 Hz, H_b), 5.4-5.9 (3 H, m, H_a's), 2.35-2.65 (2 H, br t, J = 6 Hz), 1.2-2.3 (12 H, m)	273 (23 934) 265 (22 421)	3030, 1635, 1605, 915, 875
7a	5.61 (2 H, m), 4.04 (1 H, br s), 1.3-2.1 (16 H, m), 1.13 (9 H, s)	End absorption	1660, 1380, 1360, 1190, 1050
7b	5.42 (2 H, m), 4.72 (1 H_a, br s), 2.58 (1 H, m), 1.3-2.2 (15 H, m), 1.08 (9 H, s)	232 (9039)	1640, 1380, 1355, 1190, 1060
7c	5.81 (1 H, br s), 5.45 (1 H, m), 3.79 (1 H_a, m), 2.7 (1 H, m), 1.3-2.2 (15 H, m), 1.16 (9 H, s)	234 (11 217)	1640, 1380, 1355, 1190, 1085

Scheme III



δ 6.60). The upfield shift of H_b in **6b** is expected, since it should lie in the shielding cone of the double bond of the cyclohexene ring.

Similarly, structures were assigned to **7b** and **7c** on the basis of the different chemical shifts of the H_a protons in those structures. Thus, in **7c**, H_a appears at δ 3.79, significantly upfield from the corresponding absorption of H_a in **7b** (δ 4.72).

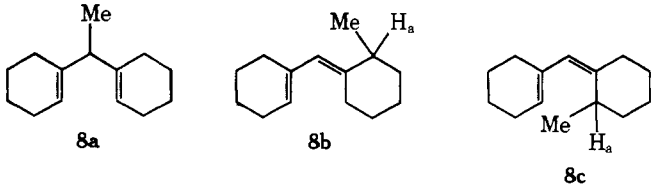
The products cited are those expected to result from disproportionation (trienes) and recombination (*tert*-butyl ethers) of pentadienyl radical **2** with *tert*-butoxyl radical (Scheme III). The pentadienyl radical can be delocalized in U (**2u**), sickle (**2s**), and W (**2w**) conformations. Particular combinations of products can be formed by reaction out of each conformation. Thus, **2u** → **6b** + **7a** + **7b**, **2w** → **6a** + **7a** + **7b**, and **2s** → **6a** + **6b** + **7a**. The only conformation that by itself could account for all the observed products is the **2s** conformation. On the other hand, it is possible that the observed products result from disproportionation and recombination reactions via some combination of all three conformations.

The *tert*-butyl ether distribution (**7a**:**7b** + **7c** = 28.7:31), when statistically corrected for the presence of two terminal carbon atoms and only one central carbon atom, indicates an almost twofold preference for recombination at the central carbon atom. The major factors affecting the position of recombination are the relative spin densities at the carbons and steric effects. Steric effects are difficult to assess, but should not be large in this system, since both the central carbon atom and the terminal carbon atoms are attached to two carbon atoms and one hydrogen atom, and inspection of molecular models reveals no major steric effect. To our knowledge, the relative spin densities have not been measured in a true pentadienyl radical, although they have been reported for the related cyclohexadienyl radical.[9] Molecular orbital calculations utilizing self-consistent Hückel molecular orbitals,[10] which resulted in the best fit with experimental results, predict relative spin densities of 0.34 and 0.54 at the terminal and central carbon atoms, respectively. Thus, the observed preference for attack at the central atom is consistent with the larger calculated spin density at that atom.

The perester **1** was also decomposed at ambient room temperature in degassed hexane. Although only the same five products (**6** and **7**) were observed by GLC, the yield of the five products (ca. 30%) is much lower. Further, the yields of several products were found to decrease with time, reflecting their instability to the reaction conditions, and a viscous film that exhibited a broad carbonyl absorption centered at 1745 cm^{-1} formed on the reaction vessel walls. The latter absorption is characteristic of polyesters formed by induced decomposition[8] of peresters.

Thermolyses at Elevated Temperatures. Although the ambient room temperature vacuum thermolysis of **1** afforded desired information about recombination reactions of the pentadienyl radical, no cyclization was observed. Apparently, the activation barrier to cyclization is sufficiently high that the competing recombination and disproportionation reactions of the pentadienyl radical occur to the exclusion of cyclization under those conditions. To observe cyclization, it is necessary to generate the radical under sufficiently energetic conditions so that cyclization occurs to some extent prior to recombination and disproportionation. Since the products **6** and **7** appeared to be relatively unstable in hexane solution even at room temperature, it was felt that vapor phase thermolysis afforded the best alternative. However, the results of the room temperature vacuum thermolysis indicated that simple sublimation of the perester into a heated tube would not succeed, since the perester would thermolyze prior to entering the heated tube. Thus, the apparatus indicated in Figure 1 was designed and used in all subsequent thermolyses. Samples to be thermolyzed were introduced into the vacuum hot tube as hexane solutions by injection via syringe. Injection into the vacuum served to strip away the solvent and to introduce samples quickly onto the heated glass surface as a fine mist.

At a vacuum of 0.05–0.01 Torr, a temperature of 210 °C or greater was required to cause complete thermolysis of **1** in the hot tube. At 210 °C, three major new products, the noncyclized methylated dienes **8a**, **8b**, and **8c**, are formed. They



8a **8b** **8c**

are the expected products of recombination of methyl radical (from *tert*-butoxyl radical fragmentation) and the pentadienyl radical. At 210 °C, they are produced in the ratio **8a**:**8b**:**8c** = 2.5:1.1:1. Similar ratios were observed at higher temperatures.

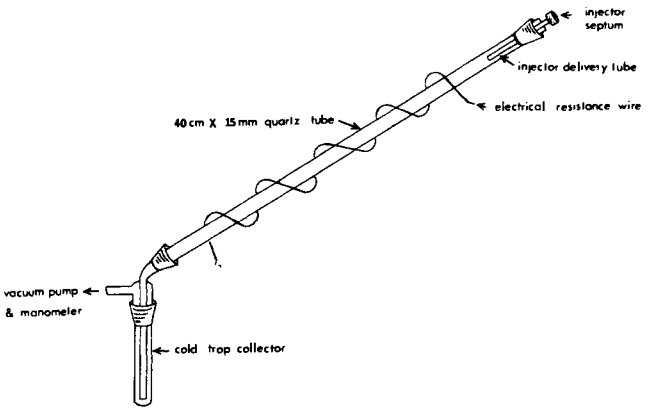


Figure 1. Vacuum thermolysis apparatus.

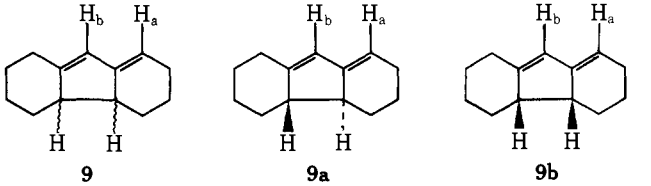
Table II. Spectroscopic Properties of Methylated Dienes **8a**, **8b**, and **8c**

Compd	^1H NMR ($CDCl_3$, δ)	Uv (hexane, nm) λ_{max} (ϵ_{max})	Ir (cm^{-1}, film)
8a	5.43 (2 H, m), 2.52 (1 H, br q, J = 7 Hz), 1.44–2.14 (16 H, m), 1.05 (3 H, d, J = 7 Hz)	End absorption	3040, 1645
8b	5.46 (2 H, m), 3.09 (1 H, m), 1.43–2.20 (16 H, m), 1.09 (3 H, d, J = 8 Hz)	233 (8323)	3020, 1640
8c	5.47 (2 H, m), 2.67 (1 H, m), 1.38–2.20 (16 H, m), 1.01 (3 H, d, J = 7 Hz)	233 (8517)	3020, 1640

The preference for recombination at the central carbon atom is similar to that observed for recombination with *tert*-butoxy radical, although it is somewhat greater.

The spectroscopic properties of **8a**, **8b**, and **8c** are recorded in Table II. The assignment of structures of **8b** and **8c** was based upon the appearance of H_a in **8c** at a higher field (δ 2.67) in the NMR spectrum than the corresponding absorption of H_a in **8b** (δ 3.09). The shift is attributed to shielding by the cyclohexene double bond anisotropy in **8c**, which is not possible in **8b**.

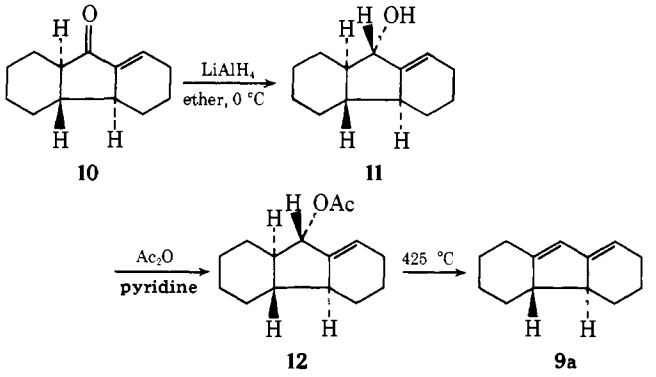
At 210 °C, an additional minor product appears in the GLC trace. Its percentage increased as the temperature of thermolysis was increased. It was isolated and purified by a combination of PLC and preparative GLC and its spectral properties and microanalytical data established it as a conjugated diene of structure **9**, but did not enable a distinction between the anti and syn forms of **9** (**9a** and **9b**, respectively). Thus, both **9a** and **9b** were prepared by unambiguous synthetic routes and



9 **9a** **9b**

their physical properties were compared with those of **9** obtained from thermolysis of perester **1**. The anti diene **9a** was synthesized according to the procedure outlined in Scheme IV. The spectral properties of **11** and **12** did not enable a decision about the relative stereochemistry at the carbon atom bearing the oxygen atom, and inspection of models did not allow a clear decision about which face of the carbonyl group in **10** would

Scheme IV

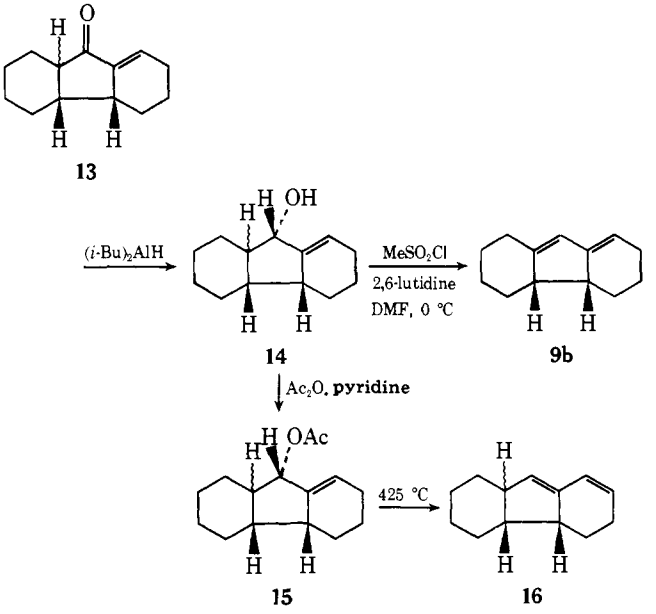


10 11 12 9a

be more susceptible to attack by $LiAlH_4$. The conversion of the acetate to **9a** in reasonable yield supports the structural assignment, but the opposite stereochemistry at the carbon bearing oxygen is possible in **11** and **12**.

The syn diene **9b** was synthesized according to the procedures outlined in Scheme V. Since the major product of thermolysis of the acetate was conjugated diene **16** (28%), with the desired diene **9b** being produced in only about a 9% yield, an alternative approach involving dehydration of the alcohol **14** was attempted and provided the syn diene **9b** in 22% yield, along with some diene **16** (ca. 7% yield).

Scheme V



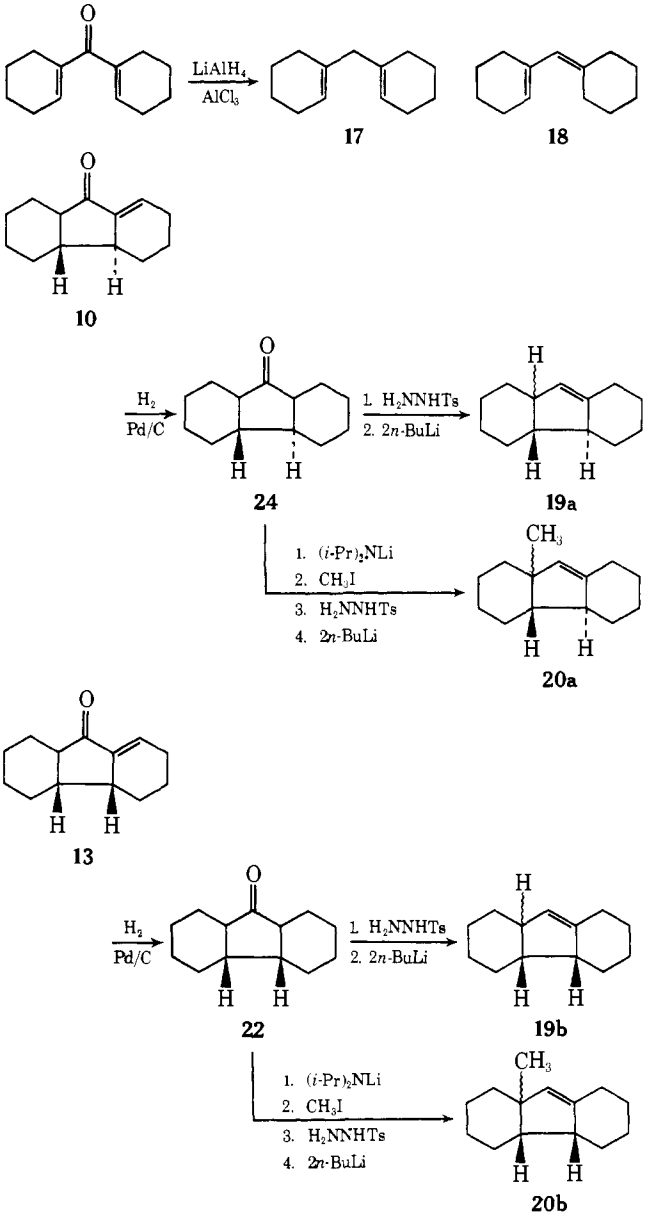
13 14 9b 15 16

The physical and spectral properties of the diene recovered from thermolysis of perester **1** were identical with those of the anti diene **9a** and were clearly different from those of the syn diene **9b**. Accordingly, this new product, which we envision to be formed by cyclization of pentadienyl radical **2** to a cyclopentenyl radical, followed by disproportionation with some other radical in the system, is that which results from conrotatory cyclization of the pentadienyl radical.

With samples of the syn diene **9b** available for comparison purposes, it became possible to search the reaction mixture for its presence. Although no peak corresponding to that of the syn diene could be noted in the GLC trace of thermolyses of **1** at 210, 250, and 275 °C, a peak corresponding to its retention time was observed in pyrolyses at 300 °C and above. Considerable effort was expended to isolate the compound and to determine if it was **9b**. However, the yield of the product was low, and an effective preparative GLC separation of the product could not be achieved. A variety of GLC SCOT columns and conditions (100 ft FFAP, 50 ft SE-30, 50 ft OS-138) were tested in an attempt to separate the peak from that of **9b**, but in no instance was a separation achieved. Thus, the possibility that the peak corresponds to **9b** must be acknowledged. Nonetheless, the product is a minor one, accounting at most for less than 8% of the diene **9** mixture at 300 °C, and 13% of the diene **9** mixture at 350°.

Other Possible Products of Elevated Temperature Thermolyses. Additional compounds for which evidence was sought were: the noncyclized dienes **17** and **18**, which would be formed by hydrogen atom abstraction by the pentadienyl radical; the anti- and syn-cyclized monoalkenes **19a** and **19b**, respectively, which would be formed by hydrogen abstraction by the cyclopentenyl radical; the anti- and syn-methylated cyclized monoalkenes **20a** and **20b**, respectively, which would be formed by recombination of the cyclopentenyl radical with methyl radical. These molecules were prepared according to the routes indicated in Scheme VI.

Scheme VI



17 18 10 24 19a 20a 13 22 19b 20b

Evidence for the presence of these compounds was sought by coinjection of the synthetic products with product mixtures resulting from thermolysis of the perester **1**. In order to establish the presence or absence of these compounds with reasonable certainty, three different SCOT columns (100 ft FFAP, 50 ft SE-30, 50 ft OS-138) and a variety of conditions

Table III. Product Distribution in Vacuum Thermolyses of Perester 1

T, °C	P, Torr	6a	6b	7a	7b	7c	8a	8b	8c	9a	9b	17	18	19a	Total[a]
250	0.03	2.3	4.4	1.8	1.2	1.6	8.3	3.8	3.5	0.2		0.09	0.04		27.2
300	0.01	3.0	3.8	2.4	1.3	2.0	10.3	4.6	4.4	1.0	0.08	0.31	0.25	0.08	33.5
350	0.01	3.3	4.4	4.3	1.3	2.5	9.2	2.7	3.2	2.7	0.39	1.0	1.1	1.2	37.3

[a] All yields cited are in percent of theoretical.

were employed in an effort to effect any possible separations. The lack of peaks in the GLC trace of the thermolysis of **1** corresponding to the syn alkenes **19b** and **20b** established their absence. On the other hand, peaks corresponding to those of the noncyclized dienes **17** and **18** and to the cyclized monoalkenes **19a** and **20a** were observed under all conditions attempted for separation. The latter observation is taken as further evidence for a preferred conrotatory closure of the pentadienyl radical, since the anti monoalkenes are derived from cyclopentenyl radical with an anti backbone, which results from conrotatory closure of the pentadienyl radical.

The thermolysis mixtures were analyzed quantitatively by GLC, using dicyclohexylmethane as an internal standard. The results of the quantitation of thermolyses at 250, 300, and 350 °C are recorded in Table III. A representative GLC trace at 250 °C is shown in Figure 2. At higher temperatures, the product distribution became increasingly complex. Of the identified products, only the methylated alkenes were not analyzed quantitatively, since their peaks were not well resolved from interfering peaks under the GLC conditions used for quantitation.

Control Experiments. A number of control experiments were performed. First, it was established that the syn diene **9b** survives thermolysis at 325 °C. Quantitative analysis by GLC indicated that 75% of the syn diene **9b** was recovered. Also, analysis by GLC of the products of thermolysis of a mixture of syn diene (0.74×10^{-3} M) with **1** (36×10^{-3} M) in hexane at 325 °C established that about 60% of the syn diene survived thermolysis under these conditions.

Second, it was established that the major products of the thermolysis, **6a, 6b, 7a, 7b, 7c, 8a, 8b,** and **8c,** do not yield the anti diene **9a** at the temperature of the thermolyses. Thus, a mixture of the above compounds was isolated from a lower temperature thermolysis and was then subjected to thermolysis conditions at 350 °C. No anti diene was observed and no major changes in the product distribution were noted.

Finally, it was considered possible that the cyclopentadienes **21a, 21b,** and **21c** might be a source of the anti diene **9a.** To check this possibility, the synthesis and isolation of these compounds was attempted (Scheme VII). The major component of the reaction mixture, **21b,** could be isolated by fractional crystallization as a white solid, mp 38.5–40 °C. The other two products could not be isolated in pure form. When gas chromatographic separation of the three products was attempted, significant tailing of the first two peaks into that of the third (corresponding to **21b**) occurred. Further, the first two peaks always appeared in GLC traces of purified **21b.** On this basis, we consider structures **21a** and **21c** likely for the other two peaks (Scheme VII). At the elevated temperatures involved, interconversion of the three products via [1,5] shifts is likely, which would account for the observed GLC behavior. Since **21b** was thermally interconverted with **21a** and **21c,** it was sufficient to examine **21b** under the thermolysis conditions. Thus, **21b** was thermolyzed at 350 °C. *No* anti diene **9a** was observed under those conditions. Further, the cyclopentadiene **21b** was added to a solution of the perester **1** (0.1 mol of **21b**:1.0 mol of **1**), and the resulting mixture was thermolyzed at 350 °C. Under these conditions, no additional anti diene **9a** was formed; in fact, somewhat less **9a** was formed than would have been anticipated if **21b** were absent. Therefore, the cyclopentadienes are not precursors to the anti diene.

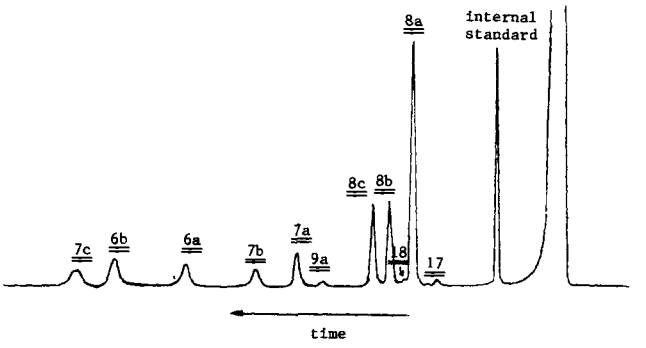
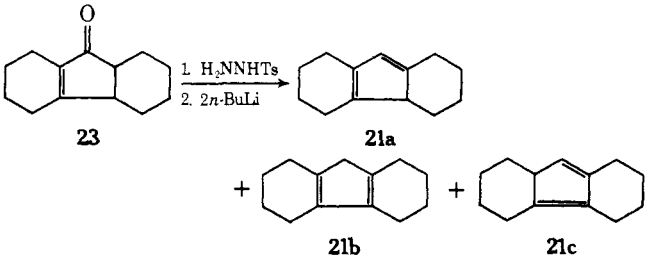


Figure 2. GLC trace of products of thermolysis of perester **1** at 250 °C.

Scheme VII



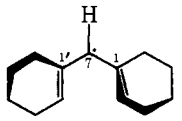
It is felt that our results are best interpreted in terms of the reactions outlined in Scheme I. Namely, thermolysis of the perester **1** produces the pentadienyl radical **2,** which either undergoes recombination and disproportionation (the sole observed pathway at room temperature) or, at higher temperatures, competitively cyclizes to a cyclopentenyl radical, which then undergoes recombination and disproportionation reactions. The increasing yields of cyclized products at higher temperatures are consistent with this view. Unfortunately, by 350 °C the reaction mixture became very complex, with several new products appearing. It is felt that those products arise from isomerization of the primary products. In particular, **7b, 7c, 8b,** and **8c** might well isomerize by [1,5] shifts under those conditions.

The total yield of analyzable products in the vacuum hot tube thermolyses of **1** is not high, even under conditions where no, or very little, cyclization occurs. About 30% of the perester could be accounted for in terms of the products analyzed. It is felt that most of the material is lost through the known[8] induced decomposition of peresters containing α hydrogens. Direct evidence for this pathway in thermal decomposition of **1** was obtained through observation of polyester in the hexane thermolysis of **1.** Also, intermolecular addition of pentadienyl radicals to double bonds of product molecules could lead to products of sufficient size (at least C_{26}) that they would not be observed under the GLC conditions employed.

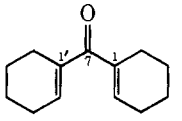
If one assumes that the amount of material loss via the above processes is about the same under conditions where cyclization occurs (the similarity in total yields at 250, 300, and 350 °C suggests this), then the relatively low total yield of cyclized

products does not detract from their significance. Indeed, at 350 °C, over 10% of the analyzed products are cyclized.

The stereochemical analysis of the cyclized products indicates a large predominance of products of anti backbone. These products are those that would result from *conrotatory* closure of the pentadienyl radical. This observation is at variance with the prediction, based upon HOMO arguments and extended Hückel calculations,[1] that conjugated radicals should cyclize in a stereochemical course determined by the symmetry of the HOMO. The stereochemical course of the cyclization is clearly *not* controlled by the symmetry of the HOMO. Remaining is the question of *what* factor in this system controls the observed cyclization mode. One possibility is that electronic factors related to orbital symmetry have a negligible effect, and that steric factors determine the stereochemistry. It is likely that the preferred conformation of the U-shaped pentadienyl radical (**2u**) is one in which the two cyclohexene rings are tilted in opposite directions with respect to the C(1), C(1′), C(7) plane, as indicated. Thus, the x-ray crystallographic structure determination[11] of ketone **25**, which should be hybridized very similarly to **2u**, has established that **25** adopts a "U-shaped"



2u



25

conformation, and that the cyclohexene rings are tilted in opposite directions from the C(1), C(1′), C(7) plane by rotations of 34 and 28° about the C(1), C(7) and C(1′), C(7) bonds. Similar effects are observed in the crystal structures of benzophenone and its derivatives.[12] This conformation of **2u** should favor the conrotatory product, although the magnitude of the steric effect is difficult to assess.

Ketone **25**, despite its preferred conformation (in the solid state) that would favor conrotatory closure, has been shown[6] to cyclize stereospecifically via a disrotatory pathway under photolytic conditions, while under conditions of acid catalysis it cyclized stereospecifically by a conrotatory pathway. Thus, steric effects in the system, which should be very similar to those in **2u**, are insignificant when orbital symmetry control prevails.

Another possible explanation of the observed stereochemical course of the reaction is that orbital symmetry effects are controlling the course of the cyclization, but that molecular orbital analyses more sophisticated than HOMO arguments will be required to elucidate the basis for the observed cyclization mode. To our knowledge, only one other study of the stereochemistry of a free radical electrocyclization, namely that of the ring opening of cyclopropyl radicals to allyl radicals, has been reported.[13] The HOMO prediction in this system is that conrotatory opening should occur. In contrast, more sophisticated molecular orbital calculations (MINDO/2[4] and CNDO/2[5]) predict a strong preference for disrotatory opening. Rüchardt and co-workers obtained results that could be interpreted in terms of favored disrotatory opening, although they could not rigorously exclude a nonstereospecific ring-opening pathway.

Electronically very similar to free radicals are anion radicals, which also have an odd number of electrons in their conjugated system. The electrocyclic ring opening of the anion radicals of *cis*- and *trans*-3,4-diphenylbenzocyclobutene[14] and *cis*- and *trans*-1,2-diphenylphenanthro[*l*]cyclobutene[15] have been studied by Bauld and co-workers. HOMO symmetry arguments predict disrotatory opening in this system, while INDO/MO[14] calculations strongly favor the conrotatory process. In each of the above systems, stereospecific conrotatory ring opening is observed.

Alone among the reports of electrocyclic reactions of open-shell systems proceeding as predicted by HOMO symmetry control is that of the anion radicals of *cis*- and *trans*-bicyclo[6.1.0]nona-2,4,6-triene.[16] However, the possible involvement of dianions in the ring opening in the latter case has been raised.[17]

In conclusion, our results establish that HOMO symmetry control is not operative in the cyclization of pentadienyl radical **2** to a cyclopentenyl radical. It is possible that orbital symmetry related effects are negligible, and steric factors control the stereochemistry of the cyclization. However, the possibility that orbital symmetry related factors are dominant must be considered in light of recent reports of electrocyclizations of open-shell systems from other laboratories. Sophisticated molecular-orbital calculations may enable a choice between the two alternative explanations.

Experimental Section

All melting points were obtained on a Gallenkampf MF 370 capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Beckman IR-8 spectrophotometer. Ultraviolet spectra were obtained on a Varian Techtron 635 spectrophotometer. The 60- and 100-MHz ^{1}H NMR spectra were obtained on Varian T-60 and XL-100 spectrometers, respectively. Preparative gas chromatography was done on a Varian 90-P gas chromatograph. Analytical gas chromatography was done on a Hewlett-Packard 5760 gas chromatograph equipped with a flame-ionization detector. The support coated open tubular (SCOT) columns used were Perkin-Elmer brand. Preparative and thin layer chromatography (PLC and TLC) were done using silica gel $PF_{254+366}$ uv indicating gel. Olefin-free, dry hexane refers to hexane which had been treated with concentrated H_2SO_4 prior to distillation from CaH_2. THF was freshly distilled from $LiAlH_4$. Degassed solvents refer to solvents which had been frozen and thawed several times under a vacuum. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

1,1-Bis(Δ^1-cyclohexenyl)ethylene (3). To a suspension of finely powdered Ph_3PCH_3I (16.36 g, 40.5 mmol) in 450 ml of dry ether maintained under N_2 was added *n*-BuLi (41.7 mmol). The mixture was stirred for 1 h, then $\Delta^{1,1'}$-dicyclohexenyl ketone (5.16 g, 27.2 mmol) in dry hexane (15 ml) was added and the mixture was stirred for 1 h. The mixture was filtered, concentrated, and chromatographed (silica gel, hexane) to give **3** as a slightly yellowed oil (4.29 g, 84%). Distillation at 50 °C (0.05 Torr) gave **3** as a colorless oil: ir (cm^{-1}, film) 1630, 1590, 880, 850; ^{1}H NMR (60 MHz, $CDCl_3$, δ) 5.65 (2 H, m), 4.8 (2 H, s), 1.4–2.3 (16 H, m). Anal. ($C_{14}H_{20}$) C, H.

2,2-Bis(Δ^1-cyclohexenyl)ethanol (4). The procedure followed closely that reported by Knights and Brown.[18] In that manner, the triene **3** (1.1 g, 5.8 mmol) in THF (50 ml) under N_2 was reacted with 9-BBN (5.92 mmol). The adduct was treated with 6 N NaOH (2.5 ml) and 30% H_2O_2 (2 ml) After workup, the crude product was chromatographed (PLC, silica gel, 20% EtOAc/hexane) to give **4** as a slightly yellowed oil that crystallized on standing (0.94 g, 78%). Recrystallization from hexane (−78 °C) gave **4** as a pure white solid, mp 38–39.5 °C: ir (cm^{-1}, KBr) 3280, 1050; ^{1}H NMR (60 MHz, CCl_4, δ) 5.45 (2 H, m), 3.55 (2 H, d, J = 7 Hz), 2.5 (1 H, br t, J = 7 Hz), 1.4–2.2 (17 H, m). Anal. ($C_{14}H_{22}O$) C, H.

$\Delta^{1,1'}$-Dicyclohexenylacetic Acid (5). To alcohol **4** (1 g, 4.85 mmol) in acetone (100 ml) was added Jones reagent[19] (5 ml containing 13.35 mmol of CrO_3) as rapidly as possible (5–10 s), and the resulting mixture was stirred for 5 min. Excess oxidant was quenched with *i*-PrOH. The mixture was concentrated, hexane was added, and the hexane phase was extracted with several portions of water. The hexane solution was then extracted with 10% NaOH (3×, 200 ml total) and the basic extract was cooled (0 °C) and acidified to pH 1 with cold 20% H_2SO_4. The acidified solution was extracted with hexane (3×, 200 ml total) and the hexane extracts were washed with water and dried ($MgSO_4$). Filtration and concentration afforded **5** as a white solid (0.52 g, 49%), mp 112 114 °C. Recrystallization from hexane (−20°) gave **5** as pure white crystals, mp 114–115.5 °C; ir (cm^{-1}, KBr) 3450, 1700, 1125, 1080; ^{1}H NMR (60 MHz, $CDCl_3$, δ) 10.1 (1 H, br s), 5.65 (2 H, m), 3.55 (1 H, br s), 1.4–2.3 (16 H, m). Anal. ($C_{14}H_{20}O_2$) C, H.

***tert*-Butyl $\Delta^{1,1'}$-Dicyclohexenylperoxyacetate (1).** To acid **5** (220 mg, 1 mmol) in benzene (5 ml) under N_2 was added oxalyl chloride

(0.213 ml, 2.5 mmol). The resultant mixture was stirred for 1.5 h. Concentration produced the acid chloride as a viscous oil, to which dry, olefin-free hexane (20 ml) was added. The resultant solution was cooled (0°), stoppered, and shielded from light (Al foil). Finely powdered sodium *tert*-butyl peroxide[20] (280 mg, 2.5 mmol) was added and the mixture was stirred at 0° for 3.5 h. During the remainder of this procedure, special care was taken to shield reaction and work-up vessels from light and to maintain them at as cold a temperature as possible. The reaction mixture was filtered wiith suction through a precooled supercel filter into a dry ice cooled flask (Al foil shielding). The filtrate was washed with hexane (0°). The hexane solution was concentrated (0°). The peroxyacetate **1** was obtained as a white solid (245 mg, 84%), mp 33–34 °C. After recrystallization (hexane, −78 °C), it had mp 34–35 °C: ir (cm^{-1}, CCl_4) 1770, 1380, 1365, 1075, 1060; ^1H NMR (100 MHz, C_6D_6, δ) 5.82 (2 H, m), 3.62 (1 H, br s), 1.7–2.3 (8 H, m), 1.3–1.7 (8 H, m), 1.2 (9 H, s). Analysis was not obtained for **1**.

Isolation of Δ¹-Cyclohexenyl-(*E*)-cyclohex-2-enylidenemethane (6a), Δ¹-Cyclohexenyl-(*Z*)-cyclohex-2-enylidenemethane (6b), Bis(Δ¹-cyclohexenyl)-1,1-dimethylethoxymethane (7a), Δ¹-Cyclohexenyl-(*E*)-2-(1,1-dimethylethoxy)cyclohexylidenemethane (7b), and Δ¹-Cyclohexenyl-(*Z*)-2-(1,1-dimethylethoxy)cyclohexylidenemethane (7c). The trienes **6a** and **6b** and the ethers **7a, 7b,** and **7c** were most easily isolated and purified from mixtures produced by ambient temperature vacuum decomposition of **1**. The reaction mixture was chromatographed by PLC with 2% EtOAc/hexane. This produced two major zones on the PLC plate, which were visualized under the 254-nm uv lamp. The top zone contained the trienes **6a** and **6b.** The second zone contained the ethers **7a, 7b,** and **7c.**

The trienes were obtained as a yellowed oil that contained mainly **6a** and **6b,** and were further separated and purified by preparative GLC on FFAP or Carbowax 20M. Distillation at 90 °C (0.1 Torr) gave both isomers as clear colorless oils that yellowed on exposure to atmosphere. Anal. ($C_{13}H_{18}$) C, H.

The ethers were chromatographed by PLC with 2% EtOAc/hexane. Usually, the PLC plates were developed two or three times to separate the three isomeric ethers. This produced three zones on the plates. The top zone contained **7b** and was visualized under the 254-nm uv lamp. The third zone contained **7c** and was also visualized under the uv lamp. The second zone, which contained the unconjugated ether **7a,** could not be visualized under the uv lamp, but was found in the area between the first and third zones. The ethers were obtained as clear oils in each case which were pure by GLC and TLC examination. Distillation at 110 °C (0.01 Torr) gave all three isomers as colorless oils. Anal. ($C_{17}H_{28}O$) C, H.

Isolation of 1,1-Bis(Δ¹-cyclohexenyl)ethane, (8a), Δ¹-Cyclohexenyl-(*E*)-2-methylcyclohexylidenemethane (8b), Δ¹-Cyclohexenyl-(*Z*)-2-methylcyclohexylidenemethane (8c), and 1,2,4,4aα,4bβ,5,6,7-Octahydro-3*H*-fluorene (9a). The methylated dienes **8a, 8b,** and **8c** and the anti diene **9a** were isolated from mixtures produced by the vacuum hot tube decomposition of **1**. The product mixtures from several experiments were combined and used for their isolation. The combined mixtures were chromatographed by PLC with 2–3% EtOAc/hexane. This produced two major zones on the PLC plates which were visualized under the 254-nm uv lamp. The top zone contained hydrocarbons including **8a, 8b, 8c, 9a, 6a, 6b,** and other minor hydrocarbon components. This allowed separation of the hydrocarbons from the *tert*-butyl ethers (second zone). The hydrocarbon zone was rechromatographed by PLC with dry hexane. This produced two zones of hydrocarbons which were visualized under the uv lamp. The top zone contained the methylated dienes **8a, 8b,** and **8c** along with smaller amounts of the other minor components. The second zone contained mainly the anti diene **9a** and the trienes **6a** and **6b.** The mixture containing **8a, 8b,** and **8c** was separated and purified by preparative GLC (FFAP). Distillation at 35–40 °C (0.05 Torr) gave all three isomers as clear, colorless oils. Anal. ($C_{14}H_{22}$) C, H.

The anti diene **9a** was isolated from the second zone by preparative GLC (FFAP). Distillation at 40 °C (0.05 Torr) afforded anti diene identical in all characteristics (^1H NMR, mass, ir, uv, and GLC retention time) with the synthetic sample.

2,3,4,4aα,4bβ,5,6,7,8,8aα-Decahydro-9*H*-fluoren-9α-ol (11). To a cooled (0 °C) solution of ketone **10**[6] (1.57 g, 8.26 mmol) in ether (100 ml) was slowly added an ethereal solution of $LiAlH_4$ (2.45 mmol in 1 ml). The reaction mixture was stirred at 0 °C for a few minutes, then the reaction was quenched by slow addition of 20% HOAc (30 ml). The usual workup produced **11** as a white solid (1.48 g, 93%), mp 85–88 °C. Recrystallization (0 °C, hexane) gave **11** as pure white crystals, mp 87–89 °C: ir (cm^{-1}, CCl_4) 3620, 1670, 1110; ^1H NMR (60 MHz, CCl_4, δ) 5.75 (1 H, m), 4.35 (1 H, m), 0.8–2.2 (18 H, m). Anal. ($C_{13}H_{20}O$) C, H.

2,3,4,4aα,4bβ,5,6,7,8,8aα-Decahydro-9*H*-fluoren-9α-yl Acetate (12). The alcohol (**11**) (1.48 g, 7.7,mmol), pyridine (20 ml), and Ac_2O (15 ml) were refluxed for 3 h. The usual workup, followed by PLC with 10% EtOAc/hexane, gave **12** as a clear oil (1.65 g, 91%) that solidified at −20 °C. Recrystallization from hexane (−70 °C) gave pure white **12** of mp 57–58.5 °C: ir (cm^{-1}, film) 1735, 1240; ^1H NMR (60 MHz, CCl_4, δ): 5.75 (1 H, m), 5.15 (1 H, br d, J = 7 Hz), 1.95 (3 H, s), 0.8–2.2 (17 H, m). Anal. ($C_{15}H_{22}O_2$) C, H.

1,2,4,4aα,4bβ,5,6,7-Octahydro-3*H*-fluorene (9a). The acetate (**12**) (317 mg, 1.29 mmol) was deposited on Chromosorb W (45/60 mesh, 1.2 g) and was introduced slowly into a hot tube (425 °C) over a 5–10 min period, using a N_2 flow rate of ca. 45 ml/min. Diene **9a** was obtained from the crude product by preparative GLC (Carbowax 20M), which yielded **9a** as a slightly yellowed oil (102 mg, 45%). Distillation at 70 °C (0.05 Torr) gave **9a** as a colorless oil that yellowed on exposure to air: ir (cm^{-1}, film) 3040, 1660, 1615, 890, 860; ^1H NMR (60 MHz, CCl_4, δ) 5.65 (1 H_b, br s), 5.15 (1 H_a, m). 0.75–2.70 (16 H, m); uv (hexane, nm): λ_{max} 248, ϵ_{max} 16 344. Anal. ($C_{13}H_{18}$) C, H.

2,3,4,4aβ,4bβ,5,6,7,8,8a-Decahydro-9*H*-fluoren-9α-ol (14). To a solution of ketone **13**[6] (2 g, 10.5 mmol) in dry benzene (75 ml) at ca. 0° under N_2, was added $(i\text{-Bu})_2AlH$[21] (4 g, 28.2 mmol) in dry benzene (30 ml). The reaction mixture was stirred at ca. 0° for 1 h. Methanol (40 ml) was added slowly and the mixture was concentrated. Ether (100 ml) was added and the mixture was filtered. The aluminum precipitates were washed with ether (200 ml). Concentration led to a viscous oil that was chromatographed by PLC with 20% EtOAc/hexane to give **14** as a slightly yellowed oil (1.4 g, 69%) that crystallized upon standing. Recrystallization (−70 °C, hexane/ether) gave **14** as pure white crystals, mp 48–50 °C: ir (cm^{-1}, CCl_4) 3620, 1670, 1110; ^1H NMR (60 MHz, CCl_4, δ) 5.75 (1 H, m), 4.35 (1 H, m), 0.8–2.2 (18 H, m). Anal. ($C_{13}H_{20}O$) C, H.

2,3,4,4aβ,4bβ,5,6,7,8,8a-Decahydro-9*H*-fluoren-9α-yl Acetate (15). The alcohol **14** (1 g, 5.21 mmol), pyridine (15 ml), and acetic anhydride (10 ml) were heated under reflux for 2.25 h. The mixture was diluted with ether (100 ml), washed with four 100-ml portions of water, and the ether phase was dried over Na_2SO_4. The mixture was filtered, concentrated, and chromatographed by PLC with 10% EtOAc/hexane to yield acetate **15** as a slightly yellow oil (1.15 g, 94%) that solidified on standing. Several recrystallizations (hexane, −70 °C) gave **15** as a white solid, mp 36–37.5 °C: ir (cm^{-1}, CCl_4) 1735, 1240; ^1H NMR (60 MHz, CCl_4, δ): 5.6 (2 H, m), 2.05 (3 H, s), 0.8–2.2 (17 H, m). Anal. ($C_{15}H_{22}O_2$) C, H.

4,4aβ,4bβ,5,6,7,8,8a-Octahydro-3*H*-fluorene (16). The acetate (**15**) (1 g, 4.28 mmol) was deposited on Chromosorb W (45/60 mesh, 4 g) and was introduced slowly into a hot tube (425 °C) under a N_2 flow rate of ca. 45 ml/min. Distillation of the crude product at 85 °C (0.1 Torr) gave a slightly yellowed oil that was purified by GLC (Carbowax 20M) to give **16** as a yellow oil (212 mg, 28%). Distillation at 55 °C (0.01 Torr) gave **16** as a colorless oil that yellowed rapidly upon exposure to air: ir (cm^{-1}, film) 3030, 1625, 860, 815; ^1H NMR (60 MHz, CCl_4, δ) 6.2 (1 H, br d, J = 10 Hz), 5.7 (1 H, m), 5.25 (1 H, br s), 0.6–3.0 (15 H, m); uv (nm, hexane) λ_{max} 243, ϵ_{max} 17 423. Anal. ($C_{13}H_{18}$) C, H. A small amount of **9b** (ca. 9%, impure) was also isolated by this procedure.

1,2,4,4aα,4bα,5,6,7-Octahydro-3*H*-fluorene (9b). Alcohol **14** (103 mg, 0.54 mmol) was dissolved in dry DMF (3 ml) and dry 2,6-lutidine (0.4 ml) at ca. 0°. Methanesulfonyl chloride (0.125 ml), enriched with SO_2 by distillation at atmospheric pressure,[22] was then added. The mixture was stirred at 0° for 2.5 h. Water (1 ml) was added and the mixture was poured into hexane (75 ml). The hexane phase was washed with water, cold 5% H_2SO_4, saturated aqueous $NaHCO_3$, and dried (Na_2SO_4). Filtration and concentration gave a yellow oil that was quickly chromatographed on a short column of Florisil with hexane. Only column effluent containing uv active components was collected. Concentration gave 28 mg of a clear, slightly yellowed oil containing **9b** in ca. 22% of theory and **16** in ca. 7% of theory (GLC). Diene **9b** was isolated by preparative GLC (FFAP). Distillation at 40 °C (0.01 Torr) gave **9b** as a colorless oil that yellowed on exposure to air: ir (cm^{-1}, film) 3040, 1660, 1615, 880, 850; ^1H NMR (60 MHz, C_6D_6, δ) 5.8 (1 H, br s), 5.2 (1 H, m), 0.8–2.8 (16 H, m); uv (nm, hexane) λ_{max} 245, ϵ_{max} 15 624. Anal. ($C_{13}H_{18}$) C, H.

Δ¹,¹'-Dicyclohexenylmethane (17) and Δ¹-Cyclohexenylcyclohex-

ylidenemethane (18). To a cooled (0 °C) solution of $LiAlH_4$ in ether (0.9 M, 1.6 ml, 0.015 mol) under N_2 was added a solution of $\Delta^{1,1'}$-dicyclohexenyl ketone (**25,** 1.0 g, 0.005 mol) in ether (5 ml). The solution was stirred at 0° for 45 min. To this solution was admixed at 0° the complex formed by adding $LiAlH_4$ (0.9 M, 1.6 ml) to $AlCl_3$ (10.3 g, 0.0029 mol). The mixture was stirred at 0° (1½ h) and 25 °C (1½ h). Excess $LiAlH_4$ was destroyed with EtOAc, 20% aqueous H_2SO_4 was added, and the ether layer was washed with aqueous $NaHCO_3$ and H_2O, dried (Na_2SO_4), filtered, and concentrated to leave a light yellow oil (0.93 g). The dienes were isolated by preparative GLC on a poly(ethylene glycol) column. For **17,** ir (cm^{-1}, film) 3050, 1660, 1440, 930, 810; ^1H NMR (60 MHz, $CDCl_3$, δ) 5.33 (2 H, br s), 2.50 (2 H, s), 1.3–2.3 (16 H, m). Anal. ($C_{13}H_{20}$) C, H. For **18,** ir (cm^{-1}, film): 3020, 1640, 1440; ^1H NMR (60 MHz, $CDCl_3$, δ) 5.50 (2 H, br s), 1.8–2.5 (8 H, m), 1.3–1.8 (8 H, m); uv (nm, 95% EtOH) λ_{max} 234, ϵ_{max} 10 300. Anal. ($C_{13}H_{20}$) C, H.

1,2,3,4,5,6,7,8-Octahydro-9*H*-fluorene (21b). A mixture of ketone **23** (201 mg), $TsNHNH_2$ (198 mg), THF (3 ml), and glacial HOAc (3 drops) were heated in a pressure bottle at 95 °C for 5 h. The solution was concentrated and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 phase was washed with aqueous HCl and H_2O, dried ($MgSO_4$), and concentrated. The yellow, oily residue was crystallized from ether to afford the tosyl hydrazone as slightly yellow crystals (151 mg), mp 160–165 °C. To a solution of the tosyl hydrazone (250 mg) in THF (15 ml) under N_2 was added *n*-BuLi (0.75 ml, 2.0 M). After 10 min, MeOH (4 ml) was added. The solution was concentrated and the residue was dissolved in hexane and washed with water. The hexane layer was dried ($MgSO_4$), filtered, and concentrated to afford a dark yellow oil (109 mg) that was chromatographed on Florisil (hexane) to yield a clear oil (82 mg). GLC (FFAP) revealed three peaks in a 1:1:2 ratio. Crystallization of the oil (hexane, −70 °C) produced **21b** (48 mg) as a white solid, mp 39–41 °C: ir (cm^{-1}, CCl_4) 2930, 1640, 1435, 1377, 1270; ^1H NMR (60 MHz, CCl_4, δ): 2.55 (2 H, m), 1.9–2.4 (8 H, m), 1.4–1.9 (8 H, m); uv (nm, hexane) λ_{max} 266, ϵ_{max} 3805. Anal. ($C_{13}H_{18}$) C, H.

1,2,4,4aα,4bβ,5,6,7,8,8a-Decahydro-3*H*-fluorene (19a). Ketone **10** (270 mg)[6] in 95% EtOH (50 ml) was hydrogenated over 5% Pd/C (300 mg). The usual workup yielded an oil from which, after PLC (10% EtOAc/hexane), ketone **24** was obtained as a white solid (260 mg), mp 66–67 °C after recrystallization from hexane or EtOH: ir (cm^{-1}, CCl_4) 2930, 1735, 2860, 1440, 1200; ^1H NMR (60 MHz, CCl_4, δ) 0.7–2.3 (all H's). Anal. ($C_{13}H_{20}O$) C, H.

Ketone **24** (600 mg), $TsNHNH_2$ (700 mg), and glacial HOAc (2 drops) in THF (15 ml) were refluxed (12 h), and the solution was concentrated to yield a slightly yellowed solid that was washed with ether to give the tosyl hydrazone as a white solid (550 mg), mp 160–165 °C. To a solution of the tosyl hydrazone (300 mg) in THF (15 ml) under N_2 was added *n*-BuLi (1.6 ml, 2.15 N). Gas was evolved and the solution became dark red. The solution was stirred (2 h), then MeOH was added until the solution became clear. The solution was concentrated and the residue was dissolved in ether (25 ml). The ether phase was washed with water, dried ($MgSO_4$), filtered, and concentrated to leave a yellow oil that was chromatographed (PLC, silica gel, hexane) to yield **19a** as a clear oil (100 mg). The oil was further purified by distillation (40 °C (0.01 Torr)). Analytical GLC (FFAP) revealed two peaks in a 1:3 ratio: ir (cm^{-1}, CCl_4) 3030, 2920, 2850, 1650, 1460, 1278, 820; ^1H NMR (60 MHz, CCl_4, δ) 5.22 (1 H, br s), 0.5–2.5 (19 H, m). Anal. ($C_{13}H_{20}$) C, H.

1,2,4,4aβ,4bβ,5,6,7,8,8a-Decahydro-3*H*-fluorene (19b). Ketone **13** (500 mg)[6] was hydrogenated according to the procedure described for ketone **10.** Saturated ketone **22** was obtained as a liquid or semisolid: ir (cm^{-1}, film) 2940, 1733, 2860, 1440, 1095; ^1H NMR (60 MHz, CCl_4, δ) 0.5–2.6 (all H's). Anal. ($C_{13}H_{20}O$) C, H.

Ketone **22** (1.0 g), $TsNHNH_2$ (1.10 g), and glacial HOAc (2 drops) in THF (25 ml) were refluxed (24 h) and the solution was concentrated. The solid residue was washed with Et_2O to give the tosyl hydrazone as a white solid (1.10 g), mp 144–149 °C dec.

By the same procedure described for **19a,** the tosyl hydrazone (500 mg) was converted into **19b,** which was purified by PLC (silica gel, hexane) and distillation (60–70 °C (7 Torr)). Analytical GLC (FFAP) of **19b** thus obtained (100 mg) revealed two peaks in a 1:4 ratio: ir (cm^{-1}, film): 2925, 2855, 1443, 800, 810; ^1H NMR (60 MHz, CCl_4, δ) 5.05 (1 H, br s), 0.6–2.9 (19 H, m). Anal. ($C_{13}H_{20}$) C, H.

1,2,4,4aα,4bβ,5,6,7,8-Nonahydro-8a-methyl-3*H*-fluorene (20a). To a solution of diisopropylamine (0.42 ml) in dry THF (15 ml) under argon at ca. −40 °C was added *n*-BuLi (1.5 ml, 2.0 M). After 10 min, ketone **24** (570 mg) was added rapidly. The solution was warmed to room temperature, then MeI (0.34 ml) was added rapidly. The mixture was stirred (10 min), the solvents were removed under reduced pressure, and the residue was washed with hexane and water. The hexane layer was washed with aqueous HCl and water, dried (Na_2SO_4), filtered, and concentrated. The oily residue (570 mg) was purified by distillation and PLC (silica gel, 5% EtOAc/hexane), which separated monomethylated and dimethylated ketones from **24.** This mixture (180 mg), THF (5 ml), $TsNHNH_2$ (180 mg), and glacial HOAc (2 drops) were heated at 95 °C for 5 h in a pressure bottle. The solution was concentrated and the residue was purified by PLC (silica gel, 10% EtOAc/hexane). The tosyl hydrazone thus obtained (155 mg) was converted to **20a** without further purification. Thus, to a solution of the tosyl hydrazone (63 mg) in dry THF (10 ml) under N_2 was added *n*-BuLi (0.17 ml, 2.0 M). The mixture was stirred (15 min), water was added, the THF was removed, and hexane was added. The hexane phase was extracted with H_2O and aqueous NH_4Cl, dried (Na_2SO_4), filtered, and concentrated. The oily residue was purified by PLC (silica gel, hexane). The methylated alkene (**20a,** 20 mg) was found in a zone that appeared light green under visualization with uv light. GLC analysis (FFAP) revealed two peaks, in a 1:4 ratio: ir (cm^{-1}, film) 3022, 2930, 2858, 1627, 1440, 1363, 820, 805; ^1H NMR (60 MHz, CCl_4, δ): 5.30 (1 H, br s), 0.6–2.6 (18 H, m), 0.75 (3 H, s). Anal. ($C_{14}H_{22}$) C, H.

1,2,4,4aβ,4bβ,5,6,7,8-Nonahydro-8a-methyl-3*H*-fluorene (20b). The procedure followed in detail that described for **20a.** Ketone **22** (694 mg) was converted to its enolate with $(i\text{-}Pr)_2NH$ (0.56 ml) and *n*-BuLi (1.99 ml) and methylated with CH_3I (0.45 ml). The crude ketone mixtures (265 mg), $TsNHNH_2$ (265 mg), and glacial HOAc (2 drops) in THF were heated at 90 °C for 19 h. The tosyl hydrazone (73 mg, mp 155–158 °C) of the monomethylated ketone was isolated by PLC (silica gel, 15% EtOAc/hexane). The tosyl hydrazone (57 mg) was converted to **20b** by treatment with *n*-BuLi (0.167 ml, 2 M) in THF (10 ml). PLC (silica gel, hexane) yielded **20b** (12 mg) as an oil. GLC analysis (FFAP) revealed two peaks in a ratio of 10:1: ir (cm^{-1}, film): 3020, 2930, 2855, 1640, 1440, 1365, 820; ^1H NMR (60 MHz, CCl_4, δ) 5.0 (1 H, br s), 0.6–2.8 (18 H, m), 0.91 (3 H, s). Anal. ($C_{14}H_{22}$) C, H.

Vacuum Thermolysis Conditions and Quantitation Procedure. The data in Table III were obtained in the following manner. Injections (four 50-μl) of **1** (0.108 M in hexane) were made onto the heated tube. Between injections, the vacuum was allowed to recover to 0.05–0.01 Torr. The products were collected in a trap (−70 °C). To them was added dicyclohexylmethane (1.04×10^{-6} mol) as an internal standard. The mixture was diluted to a volume of 1 ml with hexane and was analyzed by GLC (FFAP). The detector response to each cited component relative to that of the internal standard was measured and used, along with the relative peak areas, in the calculation of yields.

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Rate Constants for Some Electrophilic Reactions of Benzyl, Benzhydryl, and Trityl Cations in Solution[1]

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Abstract: Absolute rate constants have been determined by the pulse radiolysis technique for several electrophilic reactions of the benzyl, the benzhydryl, and the trityl cation in 1,2-dichloroethane solution. The rate constants for the reactions of these carbonium ions with chloride ion, with bromide ion, and with iodide ion are all very nearly the same, namely 6×10^{10} M^{-1} s^{-1} at 24 °C. The values very likely represent the diffusion controlled limit for the ion combination reactions. The rate constants for the reactions with triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine range from 2.0×10^9 to 7×10^6 M^{-1} s^{-1} at 24 °C. With increasing phenyl substitution, the decreasing trend in the magnitude of the rate constant is consistent with the combined electronic and steric effects. With increasing size of the amine, the decrease in the value of the rate constant seems to indicate that the steric effect predominates. The values of the rate constants for reactions of benzyl and of benzhydryl cation with methanol, ethanol, and 2-propanol indicate the following. The rate constant is higher for reaction with the alcohol dimer in solution than with alcohol monomer. The rate constants for reaction with alcohol monomer have values of 1×10^8 M^{-1} s^{-1} or lower.

We have shown in a recent report[2] that reactive arylcarbenium ions can be formed in solution and observed on a submicrosecond time scale by the pulse radiolysis method.[3] With this fast reaction method, the absolute reactivity of these carbonium[4] ions may be determined for a variety of their reactions. The optical absorption spectrum of the benzyl cation, which had not been observed by other methods, was thus determined,[2] and absolute rate constants for a few commonly known types of reactions were obtained.

These investigations have now been extended to a systematic determination of the rate constants, in 1,2-dichloroethane solution, of several electrophilic reactions of three arylcarbenium ions, namely benzyl cation, $C_6H_5CH_2^+$, benzhydryl cation, $(C_6H_5)_2CH^+$, and trityl cation, $(C_6H_5)_3C^+$. The nucleophiles for which the reactivity was determined are halide ions, tertiary aliphatic amines, and some aliphatic alcohols. Rate constants ranging from 7×10^6 to 8×10^{10} M^{-1} s^{-1} at 24 °C were obtained.

Experimental Section

As in our earlier studies,[5] the source of the electron pulse was a Varian V-7715A electron linear accelerator delivering 3–4 MeV electrons in pulses ranging from 20 to 1500 ns duration. Pulse current was about 300 mA for pulse duration of 100 to 1500 ns and about 600 mA for pulse duration of 80 ns or less. Electron pulses ranging from 40 to 800 ns were used in this work. Transient absorption spectra were determined using an RCA 1P28 or RCA 7200 photomultiplier as detector. The time resolution of the detection system was about 5 ns with the 1P28, so that it was feasible to observe the kinetics on a submicrosecond time scale. A Bausch and Lomb grating monochromator, type 33-86-25, *f*/3.5, with a grating having a dispersion factor of 7.4 nm/mm was used. Exit slit widths were always 0.4 mm or less, resulting in a band-pass of 3 nm or less. Appropriate Corning filters were used to eliminate second-order components from the analyzing light beam.

Our standard 20-mm reaction cells, equipped with high-purity silica windows, were used in all experiments with, for the most part, a double pass of the analyzing light beam. A full description of the optical arrangement and the electronic detection system has been provided.[3b,5] All the data were accumulated at 24 ± 1 °C.

The solvent used exclusively was 1,2-dichloroethane (1,2-DCE), reagent grade, from Matheson Coleman and Bell. It was purified by a scheme detailed elsewhere.[6] Just prior to each experiment, the desired quantity of 1,2-DCE was distilled in vacuo into the reaction cells from a storage bulb, and the amount distilled was determined by weight difference.

A variety of compounds was used as carbonium ion precursors: dibenzylmercury from Alfa Inorganics; bromodiphenylmethane, technical grade, from Chemical Samples Co.; chlorodiphenylmethane, technical grade, from Chemical Samples Co.; triphenylmethanol from Aldrich Chemical; and triphenylmethyl bromide from J. T. Baker and Co. Dibenzylmercury was recrystallized from absolute ethanol and stored in the dark until used. Chlorodiphenylmethane was purified by a series of fractional freezing cycles, followed by treatment with activated charcoal. It was then dried with barium oxide and stored in a closed vessel until used. In some experiments involving bromodiphenylmethane, the compound was used as obtained. Otherwise it was purified by vacuum sublimation, which resulted in only a slight increase in the lifetime of the benzhydryl cation in the DCE solution. Triphenylmethanol was recrystallized from absolute ethanol, the filtrate being treated with activated charcoal. Triphenylmethyl bromide was recrystallized from DCE.

Additionally, the following compounds were used as reactants in determining absolute rate constants: tetraethylammonium bromide and tetraethylammonium iodide from ICN-K&K Laboratories, triethylamine from J. T. Baker Chemical Co., tri-*n*-propylamine from two sources, Aldrich Chemical Co. or ICN-K&K Laboratories, tri-*n*-butylamine from Matheson Coleman and Bell as well as from ICN-K&K, methanol from Eastman, ethanol from U.S.I., and 2-propanol from Matheson Coleman and Bell.

The quaternary ammonium salts were used as obtained. The triethylamine was purified by distillation under argon into lithium alu-