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On the Neophyl-like Rearrangement of 2-(9-Anthryl)ethyl Radicals

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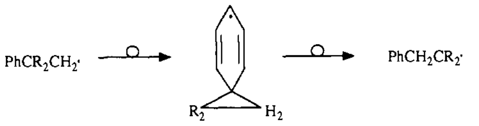
Abstract: The 1,2 migration of the aryl group in deuterated 2-(9-anthryl)ethyl and 2-[9-(10-phenylanthryl)]ethyl radicals has been studied by product analyses with the use of the competing reaction $ArCH_2CD_2^{\bullet} + Bu_3SnH$. The rearrangement was so fast that equimolecular mixtures of the unrearranged ($ArCH_2CD_2H$) and rearranged ($ArCD_2CH_3$) hydrocarbons were obtained even in the presence of a large excess of Bu_3SnH (ca. 1 M). The lower limit for the rate constant of the intramolecular process, k_r, could be estimated as 5×10^7 s^{-1}. Ab initio MO computations, performed on the 2-phenylethyl radical, chosen as the simplest model for 2-arylethyls, showed that the aryl migration may occur either through the intermediacy of the spirocyclopropanecyclohexadienyl radical or via a three-membered transition state having geometrical and electronic properties different from those of the potential cyclic intermediate. The spectroscopic and chemical results are consistent with the rearrangement taking place via the intermediacy of spirocyclopropane radicals, which, as both thermochemical calculations and experimental evidence indicate, are characterized by a considerable thermodynamic stability. In fact, the spiro radicals could be easily observed by EPR spectroscopy when generated by hydrogen abstraction from the corresponding cyclic hydrocarbons, and the kinetics of their decay could be studied. The diamagnetic dimer of the 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl radical was also isolated, and its structure determined by X-ray crystallographic analysis. The same cyclized radicals were detected when producing the two arylethyl radicals within the EPR cavity. Chemical generation of the 2-(9-anthryl)ethyl radical in the presence of low concentrations of hydrogen donors led to the isolation of remarkable amounts of the dimer of its cyclic structural isomer. These results provide evidence that the 2-anthrylethyl radical and the phenyl-substituted analogue may exist in either of the two rapidly equilibrating open-chain and cyclized forms and react preferentially in one of them depending on the experimental conditions.

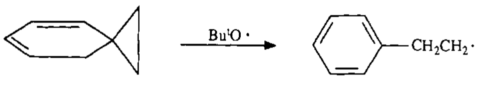
The neophyl (**1**; R = Me) rearrangement[1] as well as other 1,2-aryl shifts in 2-arylethyl radicals are thought to proceed via a spirocycloalkanecyclohexadienyl intermediate or transition state[2] (eq 1).



(1)

1 **2** **3**

Many attempts have been made to detect spiro radicals of structure **2** by EPR, all of them without success.[3] Recently, radical **2** (R = H) was generated by Ingold and co-workers[4] by hydrogen abstraction with *tert*-butoxyl radicals from spiro[2,5]-octa-4,6-diene (**4**, eq 2). Although only the spectrum of the



(2)

4 **5**

ring-opened 2-phenylethyl (**5**) was observed by EPR even at temperatures as low as 100 K, the spiro radical **2** (R = H) could be identified by optical methods by means of its absorption and fluorescence at wavelengths of ca. 560 nm, which are characteristic of cyclohexadienyl radicals. In contrast with the behavior of the relatively long-lived cyclohexadienyl, the signals from **2** (R = H) decayed in the nanosecond time scale following first-order kinetics. Of course, the detection of a spiro[cyclopropanecyclohexadien]yl radical does not prove, as has been emphasized by the same authors,[4] that such species is a genuine intermediate in reaction 1.

In a subsequent ^{13}C CIDNP study of ring-substituted 2-phenylethyl radicals, Olah et al.[5] reported that the observed ^{13}C polarizations were not consistent with their cyclization to the spiro radical **2** (R = H). However, Griller has pointed out that if evidence for cyclization is to be obtained from polarization transfer, then ring closure would have to take place before relaxation of the nuclear spin states of the radical.[6] Since it is known that the rate constant for the rearrangement of 2-phenylethyl is several orders of magnitude lower than this,[4,7] the absence of polarization is entirely to be expected even if **2** is a true intermediate in reaction 1.

The results of these investigations lead to the conclusion that the very short life time of the spiro[cyclopropanecyclohexadien]yl radical together with the sluggishness of reaction 1 for R = Ph, make extremely difficult or perhaps impossible to test experimentally whether or not this radical is an intermediate in the reaction coordinate for the migration of the phenyl group.

It is worth pointing out that two examples have been recently reported in which the intramolecular migration of unsaturated groups takes place without the intervention of the cyclic intermediate arising by ring closure of the primary radicals. These are the 1,2-migration of the acyloxy group in β-(acyloxy)ethyl radicals[8] and the allylic rearrangement of hydroperoxides.[9] Saebo

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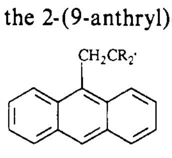
Table I. EPR Spectral Parameters for the Spirocyclopropane Radicals **8a–e** (Hyperfine Splitting Constants in gauss)

radical	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	a_{other}	g	T/K	solvent[a]
8a	3.47	1.19	4.14	1.19	12.95 (H9)	2.0026	298	BB
8b	3.39	1.13	3.97	1.13	0.59 (4 H) 0.32 (1 H)	2.0026	230	BB
8c	3.52	1.16	3.91	1.16		2.0028	298	BB
8d	3.49	1.15	3.95	1.15		2.0028	373	$HSiPh_3$
8e	3.47	1.14	3.91	1.14		2.0027	373	$HGePh_3$

[a] BB = *tert*-butylbenzene.

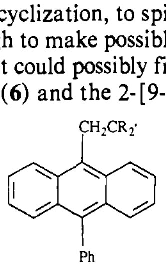
et al. have actually performed reasonably accurate MO computations to examine the mechanism of 1,2-acyloxy migration in the β-(formyloxy)ethyl radical.[10] They showed that the calculated transition structure resembles a loose complex between ethylenic and formyloxy fragments. The 1,2-dioxolanyl radical, i.e., the cyclic putative intermediate, although having an energy comparable with that of the complex (ca. 23 kcal/mol above the unrearranged radical), can only be reached by crossing an energy barrier as large as 53 kcal/mol.

In an attempt to bring a contribution to the solution of the problem of the intermediacy of spirocyclopropane radicals in the rearrangement of 2-arylethyls, we searched other substrates that would be expected to rearrange faster than 2-phenylethyl and that would also lead, upon cyclization, to spiro radicals characterized by lifetimes long enough to make possible their detection by EPR. Suitable candidates that could possibly fit these requirements were the 2-(9-anthryl)ethyl (**6**) and the 2-[9-(10-phenylanthryl)]ethyl (**7**) radicals; in fact, both thermodynamic considerations and the analogy with the related rearrangement of the 2-(9-anthryl)ethyl cation[11] suggested that the spiro intermediate, if formed, should be of comparable stability with the unrearranged radical and that the 1,2 shift of the anthryl group should be considerably faster than that of the phenyl group.



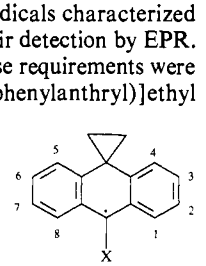
6a; R=H

6b; R=D



7a; R=H

7b; R=D



8a; X=H

8b; X=Ph

8c; X=OSiEt$_3$

8d; X=OSiPh$_3$

8e; X=OGePh$_3$

We report here a spectroscopic (EPR) and chemical investigation on the behavior of these two radicals and of the deuterated analogues **6b** and **7b** and on that of variously substituted 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl radicals (**8a–e**) produced from suitable precursors. SCF MO calculations on the rearrangement reaction of the model radicals $PhCH_2CH_2^{\bullet}$ have also been performed to explore the possible reaction pathways and the nature of the transition states.

Results

Endothermicity of the Cyclization Reactions. The 2-(9-anthryl)ethyl cation gives, much more easily than the corresponding 2-phenylethyl cation, the nonclassical bridged ion, which is liable to direct observation by NMR in appropriate experimental conditions.[11] By analogy, it was conceivable that 2-(9-anthryl)ethyl radicals would also cyclize intramolecularly to spiro radicals more easily than 2-phenylethyls. This expectation was supported by thermochemical estimates based on group additivity principles[12] and on bond dissociation energy values determined for related systems. The reported estimates of the endothermicity of the ring-closure reaction **1** → **2** (R = Me) are in the range ca. 11[13] to ca. 21 kcal/mol,[14] the magnitude depending essentially on the value chosen for the C–H bond strength in cyclohexadiene, i.e., 73 ± 5 kcal/mol.[15] A more accurate determination of the latter bond strength as 73 ± 2 kcal/mol has been recently reported by Griller et al. by using a photoacoustic technique.[16] If one calculates the endothermicity for the formation of the spiro intermediate **2** using this value together with the more recent data for the strength of primary C–H bonds (ca. 100 kcal/mol),[17] enthalpies of reaction of 15.6 for R = H, and 14.1 kcal/mol for R = Me are obtained.[18]

By repeating the calculations in the assumption that in radicals **1** and **2** (R = H) the phenyl ring is replaced by a 9-anthryl group[18] and using the bond dissociation energy $D[C_{14}H_{11}\text{–}H] = 75.3$ kcal/mol reported for 9,10-dihydroanthracene,[15] one derives the heat of reaction for the formation of the spiro radical as only 0.2 kcal/mol. The 2-(9-anthryl)ethyl radical (**6a**) and the related 2-[9-(10-phenylanthryl)]ethyl (**7a**) are therefore expected to be very useful systems to investigate the mechanistic implications, especially with regard to the possible participation of a spiro intermediate, in the rearrangement reaction of 2-arylethyl radicals.

Thermochemistry, of course, provides approximate values of the endothermicity of the cyclization reaction but not of the activation energy. Since however the reverse reaction, i.e., ring opening, is reputed to be very fast, the assumption is often made that the activation energy of ring closure is approximated by its endothermicity. This might lead to large misestimates since, even for the highly transient spiro[cyclopropanecyclohexadien]yl radical **2** (R = H), the activation energy for ring opening has been reported to be 2.8 kcal/mol.[4] To obtain reliable values of the activation energies for aryl migration, the endothermicities for ring closure should be increased by the barriers to ring opening, which in most cases are unknown.

Open-Chain Radicals. Radicals **6a,b** and **7a,b** were generated either by reacting the parent bromides **9a,b** and **10a,b** with tributyltin radicals or by thermal or photolytic decomposition of β-(9-anthryl)propanoyl *m*-chlorobenzoyl peroxide (**11**), *tert*-butyl β-(9-anthryl)perpropanoate (**12**), β-[9-(10-phenylanthryl)]propanoyl *m*-chlorobenzoyl peroxide (**13**), and *tert*-butyl β-[9-(10-phenylanthryl)]perpropanoate (**14**).

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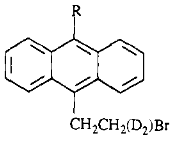
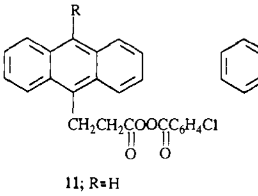
[18] $\Delta H_f°$ were calculated by using group values and ring strains listed in Table A1 of ref 12. Missing group values were extrapolated either as $[C\text{–}(C_d)_2(C)_2] = [C\text{–}(C)_4] + [C\text{–}(C_d)_2(H)_2] - [C\text{–}(C)_2(H)_2] = 1.14$ kcal/mol[14] and $[C\text{–}(C_B)_2(C)_2] = [C\text{–}(C)_4] + [C\text{–}(C_B)_2(H)_2)] - [C\text{–}(C)_2(H)_2] = 0.31$ kcal/mol (the value of $[C\text{–}(C_B)_2(H)_2] = -5.12$ kcal/mol was determined from the $\Delta H_f°$ of formation of 9,10-dihydroanthracene given in ref 15) or as $[C\text{–}(C_d)_2(C)_2] = [C\text{–}(C)_4] + 2\{[C\text{–}(C_d)(C)_3] - [C\text{–}(C)_4]\} = 2.86$ kcal/mol and $[C\text{–}(C_B)_2(C)_2] = [C\text{–}(C)_4] + 2\{[C\text{–}(C_B)(C)_3] - [C\text{–}(C)_4]\} = 5.12$ kcal/mol. We have taken the averages of the values obtained with the two procedures, i.e., 2.0 and 2.71 kcal/mol, respectively.



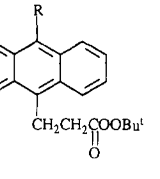
9a,b; R=H

10a,b; R=Ph



11; R=H

13; R=Ph



12; R=H

14; R=Ph

To determine the rate constants for the rearrangement of **6b** and **7b**, their bromide precursors were let to react with tributyltin hydride in degassed benzene solutions at 343 K in the presence of bis(isopropyl peroxydicarbonate) as thermal initiator (eq 3–8).[19]

$$(i\text{-PrOC(O)O})_2 \rightarrow 2i\text{-PrOC(O)O}^\bullet \qquad (3)$$

$$i\text{-PrOC(O)O}^\bullet + \text{Bu}_3\text{SnH} \rightarrow i\text{-ProOC(O)OH} + \text{Bu}_3\text{Sn}^\bullet \qquad (4)$$

$$\text{Bu}_3\text{Sn}^\bullet + \text{ArCH}_2\text{CD}_2\text{Br} \rightarrow \text{Bu}_3\text{SnBr} + \text{ArCH}_2\text{CD}_2^\bullet \qquad (5)$$

$$\text{ArCH}_2\text{CD}_2^\bullet \overset{k_r}{\rightleftharpoons} \text{ArCD}_2\text{CH}_2^\bullet \qquad (6)$$

$$\text{ArCH}_2\text{CD}_2^\bullet + \text{Bu}_3\text{SnH} \xrightarrow{k_H} \text{ArCH}_2\text{CD}_2\text{H} + \text{Bu}_3\text{Sn}^\bullet \qquad (7)$$

$$\text{ArCD}_2\text{CH}_2^\bullet + \text{Bu}_3\text{SnH} \xrightarrow{k_H} \text{ArCD}_2\text{CH}_3 + \text{Bu}_3\text{Sn}^\bullet \qquad (8)$$

When the reaction was complete, the arylethanes were separated by column chromatography and analyzed by NMR and mass spectrometry[20] to determine the ratio of the two deuterated hydrocarbons $\text{ArCH}_2\text{CD}_2\text{H}$ and ArCD_2CH_3. In no case were products arising from ring closure of **6b** and **7b** detected.

The kinetic expressions describing reactions 6–8 are

$$\text{d}[\text{ArCD}_2\text{CH}_2^\bullet]/\text{d}t = k_r[\text{ArCH}_2\text{CD}_2^\bullet] - (k_r + k_H[\text{Bu}_3\text{SnH}])[\text{ArCD}_2\text{CH}_2^\bullet] \qquad (9)$$

$$\text{d}[\text{ArCH}_2\text{CD}_2\text{H}]/\text{d}t = k_H[\text{ArCH}_2\text{CD}_2^\bullet][\text{Bu}_3\text{SnH}] \qquad (10)$$

$$\text{d}[\text{ArCD}_2\text{CH}_3]/\text{d}t = k_H[\text{ArCD}_2\text{CH}_2^\bullet][\text{Bu}_3\text{SnH}] \qquad (11)$$

Since the reactions were carried out in the presence of an excess of Bu_3SnH, eq 9–11 can be easily solved within the steady-state approximation to give

$$[\text{ArCH}_2\text{CD}_2\text{H}]/[\text{ArCD}_2\text{CH}_3] = 1 + (k_H/k_r)[\text{Bu}_3\text{SnH}] \qquad (12)$$

The rate constant k_H at 343 K is calculated as 5.23×10^6 M^{-1} s^{-1} from the Arrhenius expression $\log (k_H/\text{M}^{-1}\ \text{s}^{-1}) = (9.07 \pm 0.24) - (3.69 \pm 0.32)/2.303RT$ obtained by Chatgilialoglu et al.[21] in a kinetic study of the hydrogen abstraction reaction from Bu_3SnH by primary alkyl radicals, $\text{RCH}_2^\bullet$. The Bu_3SnH concentrations used in the competitive kinetic experiments were 0.79 M for **6b** and 0.61 M for **7b**. In both cases equimolecular amounts of $\text{ArCH}_2\text{CD}_2\text{H}$ and ArCD_2CH_3 were obtained. By assuming a limiting error of 4% for the measured ratio of the two isotopically labeled compounds, the rate constants for the rearrangement of both **6b** and **7b** at 343 K is derived as $k_r > 5 \times 10^7\ \text{s}^{-1}$.

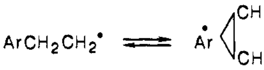
This value, not unexpectedly, is exceptionally large when compared to those for the analogous rearrangements of 2-phenylethyl (**1**, R = H)[2a] $k_r^{298} < 0.01\ \text{s}^{-1}$ and neophyl (**1**, R = Me)[14] $k_r^{298} = 7.6 \times 10^2\ \text{s}^{-1}$ and is of the right order of magnitude to be determined by dynamic EPR studies.

We therefore attempted to generate radical **6a** within the cavity of an EPR spectrometer either by reacting 2-(9-anthryl)ethyl bromide (**9a**) with $\text{Bu}_3\text{Sn}^\bullet$ radicals photolytically produced from hexabutylditin or by direct photolysis of the peroxide **11** or of the perester **12**. With the first two compounds no EPR signals were detected in the temperature range 193–383 K, this being likely due to their very low solubility. On the other hand, when a toluene solution of the more soluble peroxide **12** was photolyzed at 173 K, a complex spectrum approximately 33 G wide was detected, instead of the expected exchange-broadened five-line spectrum due to **6a**. The EPR spectral parameters were, within experimental error, identical with those of the cyclic 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl (**8a**) radical (see the following section). Attempts to reveal by EPR radical **7a** produced either by bromine abstraction from **10a** with photolytically generated $\text{Bu}_3\text{Sn}^\bullet$ radicals or by direct photolysis of the perester **14** also failed. Instead, a fairly complicated spectrum due to a persistent paramagnetic species that could be identified as the 9,10-dihydro-9-phenyl-10-spiro[cyclopropaneanthracen]-9-yl radical (**8b**) gradually grew up under continuous photolysis below 273 K. It is therefore concluded that both the 2-arylethyl radicals **6a** and **7a** may, at least partially, undergo ring closure to give **8a** and **8b**.

Since we could not get direct spectroscopic evidence of the existence of the open-chain radicals, we attempted the trapping of one of them (**6a**) by using 2-methyl-2-nitrosopropane (N*t*B) as scavenger. Thermal decomposition of the perester **12** inside the EPR cavity at 378 K in deoxygenated toluene in the presence of the spin trap (0.12 M) led to the appearance of strong signals due to a radical species whose spectral parameters ($a_N = 15.32$, $a_H(2\text{H}) = 9.67$, $a_H(2\text{H}) = 0.72$ G, $g = 2.0060$) were those expected for the 2-(9-anthryl)ethyl adduct to N*t*B, $\text{C}_{14}\text{H}_9\text{CH}_2\text{CH}_2(t\text{-Bu})\text{N–O}^\bullet$. Upon decomposing the perester **12** at room or lower temperature photolytically, the superimposed EPR spectra of $t\text{-Bu}_2\text{N-O}^\bullet$ and of $t\text{-BuO}(t\text{-Bu})\text{N–O}^\bullet$, resulting from the trapping of *tert*-butoxyl radicals arising from **12** were detected. Under these conditions the nitroxide adduct, $\text{C}_{14}\text{H}_9\text{CH}_2\text{CH}_2(t\text{-Bu})\text{N–O}^\bullet$, was no longer observable because of its photolability.

The EPR results can be rationalized as follows. The failure to detect the arylethyl radicals by EPR in the absence of hydrogen donors can be due only to the fact that the radical lifetime is shorter than ca. 10^{-4} s due to unimolecular decay. The detection of the 2-(9-anthryl)ethyl adduct to N*t*B also suggests that the decay rate constant of **6a** is lower or, at most, comparable with $k_T[\text{N}t\text{B}]$, where k_T is the rate constant for the spin trapping of a primary alkyl radical by N*t*B ($1.7 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$ at 378 K),[22] i.e., $2 \times 10^6\ \text{s}^{-1}$.

This has the following implications with regard to the mechanism of rearrangement. If the intramolecular aryl migration is concerted, and therefore the observed radicals **8a** and **8b** are formed in a concurrent minor reaction, both **6a** and **7a** should undergo, besides rearrangement and self-combination or disproportionation, some other unimolecular reaction occurring with a rate constant k in the range $10^4 < k < 10^6\ \text{s}^{-1}$. On the other hand, if the rearrangement takes place via a spiro intermediate, radicals **6a** and **7a** should be in equilibrium with their cyclic structural isomers **8a** and **8b** (eq 13) and the equilibrium should be largely shifted to the right, i.e., $k_{13} = k_r \gg k_{-13}$.



$$\text{ArCH}_2\text{CH}_2^\bullet \rightleftharpoons \overset{\bullet}{\text{Ar}}\langle^{\text{CH}_2}_{\text{CH}_2} \qquad (13)$$

Spirocyclopropane Radicals. To investigate the properties of the 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl radical (**8a**), a deoxygenated *tert*-butylbenzene solution of the parent hydrocarbon **18** and of di-*tert*-butyl peroxide was photolyzed within the EPR cavity. At room temperature a weak, but nevertheless interpretable, spectrum was observed which was assigned to radical **8a** on the basis of the similarity of the hyperfine splitting constants with those of the 9,10-dihydroanthracen-9-yl radical[23] (see Table I). With respect to the latter, the spectrum of **8a** differed for the absence of the two methylene proton splitting and for a larger line width ($\Delta H_{pp} = 0.22$ G) conceivably due to unresolved coupling of the unpaired electron with the four cyclopropane ring protons. Radical **8a** is characterized by a considerable thermodynamic

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(19) Chateauneuf, J.; Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 6727–6731.

(20) $\text{ArCH}_2\text{CD}_2\text{H}$ and ArCD_2CH_3 can be easily distinguished from their mass spectra since they give rise to very intense peaks due to dibenzotropilium ions differing by two mass units.

(21) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

(22) Schmidt, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2493–2500.

(23) Bohme, V. R.; Jesse, G. V. *Chem. Phys. Lett.* **1969**, *3*, 329–332.

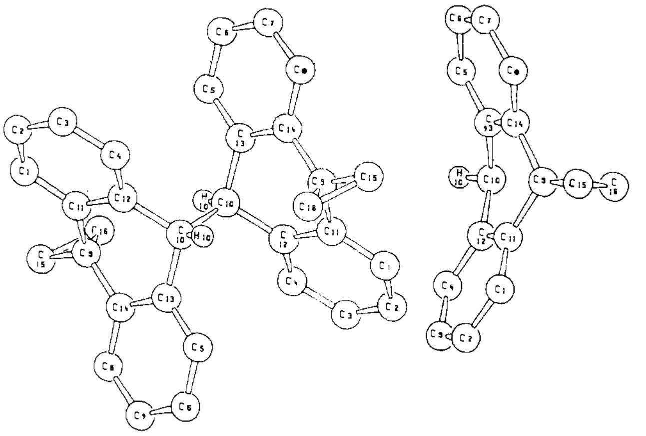
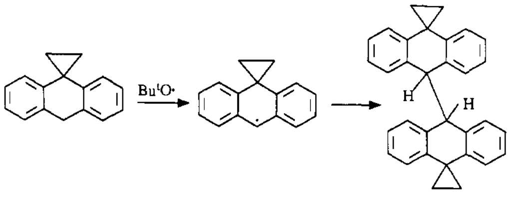


Figure 1. Left: structure of the dimeric compound **19** determined from a single-crystal X-ray analysis. Right: a view of a monomeric unit showing the conformation of the central ring.

stability since its spectrum was observable up to 413 K. Continuous irradiation was, however, essential for the detection of the radical, and when the light was cut off, the spectrum immediately disappeared. We could then study the radical decay by EPR; at 298 K the decay curves followed second-order kinetics with a diffusion-controlled rate constant $2k_t = (4.5 \pm 1.2) \times 10^9$ M^{-1} s^{-1}. Sample tubes irradiated for long periods, when taken out of the EPR cavity, showed at the bottom the presence of a white precipitate. To establish the chemical nature of this compound, the reaction was repeated on a preparative scale by thermally decomposing bis(isopropyl peroxydicarbonate) in a benzene solution containing the hydrocarbon **18** under nitrogen at 343 K. The products recovered were anthraquinone (6% yield), 9-ethylanthracene (10%), and a major compound (80%) that showed NMR and mass spectra consistent with the head-to-head dimer **19** of radical **8a**. This structure was confirmed by X-ray diffractometric analysis as shown in Figure 1.

The dimer has a center of symmetry along the C_{10}–$C_{10'}$ bond, and the two monomeric units adopt a conformation folded around the C_9–C_{10} axis with a dihedral angle between the benzene rings of 138.5°. Atoms C_9 and C_{10} are found to be 0.43 and 0.48 Å, respectively, out of the plane through C_{11}, C_{12}, C_{13}, and C_{14}. Bond distances and bond angles involving the atoms of the central rings are collected in Table II. All values fall within the range measured in similar "butterfly" compounds variously substituted at carbons C_9 and C_{10}.[24]

Thus, both the kinetic results and the structural data indicate that, in the absence of hydrogen donors, the spirocyclopropane radical **8a** essentially decays by self-combination to afford the dimer **19** (eq 14) and that opening of the cyclopropane ring does take place only to a minor extent.



(14)

18 8a 19

The stability of this class of radicals was also confirmed by the behavior of **8d** and **8e** produced by addition of photochemically generated triphenylsilyl or triphenylgermyl radicals to cyclopropaneanthrone at 373 K in a melt of the silane (or germane) and $(t\text{-BuO})_2$, which showed a remarkable persistence at such high temperatures. Radicals **8d** and **8e** were characterized by larger peak-to-peak line widths ($\Delta H_{pp} = 0.25$ G), smaller *g* factors, and greater hyperfine splitting constants than the adducts of $Ph_3Si^\bullet$ and $Ph_3Ge^\bullet$ to 9,10-anthraquinone,[25] as should be expected for the assigned structures.

Table II. Relevant Bond Distances (angstroms) and Bond Angles (degrees) of Compound **19**

C_9–C_{11}	1.499 (3)	C_{10}–C_{12}	1.511 (3)
C_9–C_{14}	1.507 (3)	C_{10}–C_{13}	1.505 (3)
C_9–C_{15}	1.503 (3)	C_{11}–C_{12}	1.401 (3)
C_9–C_{16}	1.539 (3)	C_{13}–C_{14}	1.397 (3)
C_{10}–$C_{10'}$	1.575 (4)	C_{15}–C_{16}	1.499 (4)
$\angle C_{11}$–C_9–C_{14}	112.8 (2)	$\angle C_{10'}$–C_{10}–H_{10}	106.2 (2)
$\angle C_{11}$–C_9–C_{15}	119.9 (2)	$\angle C_{12}$–C_{10}–C_{13}	110.1 (2)
$\angle C_{11}$–C_9–C_{16}	117.6 (2)	$\angle H_{10}$–C_{10}–C_{12}	109.8 (2)
$\angle C_{14}$–C_9–C_{15}	119.8 (2)	$\angle H_{10}$–C_{10}–C_{13}	108.4 (2)
$\angle C_{14}$–C_9–C_{16}	117.5 (2)	$\angle C_9$–C_{11}–C_{12}	118.0 (2)
$\angle C_{15}$–C_9–C_{16}	59.0 (2)	$\angle C_{10}$–C_{12}–C_{11}	118.6 (2)
$\angle C_{10'}$–C_{10}–C_{12}	110.8 (2)	$\angle C_{10}$–C_{13}–C_{14}	119.4 (2)
$\angle C_{10'}$–C_{10}–C_{13}	111.5 (2)	$\angle C_9$–C_{14}–C_{13}	117.4 (2)

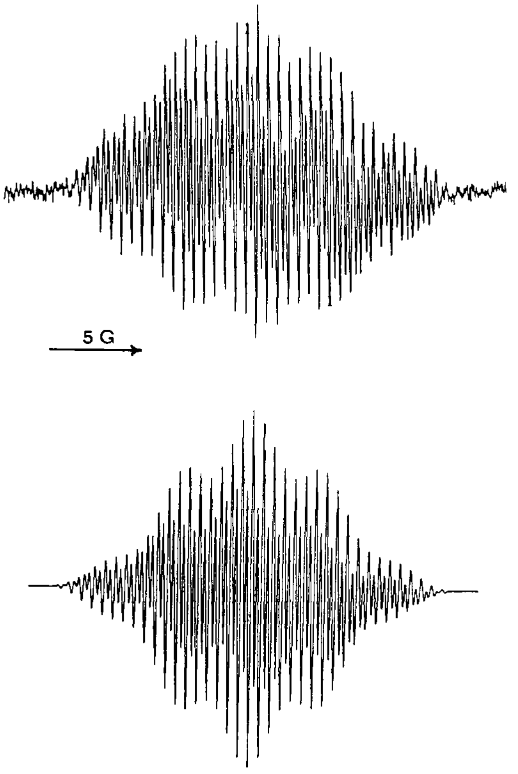


Figure 2. Experimental (top) and computer-simulated EPR spectrum of the 9,10-dihydro-9-phenyl-10-spiro[cyclopropaneanthracen]-9-yl radical (**8b**).

Low temperature was instead required to record well-resolved spectra of the 9,10-dihydro-9-phenyl-10-spiro[cyclopropaneanthracen]-9-yl radical (**8b**) obtained by hydrogen abstraction from the corresponding hydrocarbon. As shown in Figure 2, the EPR spectrum was fairly complicated because of the additional coupling of the unpaired electron with the phenyl protons, and its interpretation could be accomplished only by computer simulation. However, also in this case the hyperfine splitting constants (see Table I) left little doubt concerning the assigned structure. Radical **8b** was much more persistent than **8a** and at 230 K decayed following second-order kinetics with a rate constant $2k_t$ of $(2.3 \pm 0.3) \times 10^3$ M^{-1} s^{-1}. To establish the fate of radical **8b**, the same reaction was carried out on a preparative scale but without success since only tars were obtained.

From these experiments it is concluded that 9,10-dihydro-10-spiro[cyclopropaneanthracen]-9-yl radical (**8a**) and the phenyl-substituted analogue **8b** are by far more stable than their open-chain counterparts **6a** and **7a**. Therefore, if rearrangement of the latter radicals proceeds via the spirocyclopropane intermediates,

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[24] Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Acta Crystallogr.* **1986**, *B42*, 181–187.

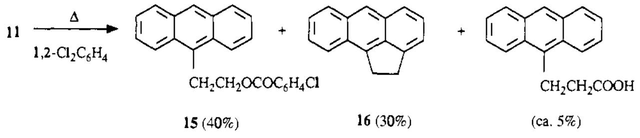
[25] Alberti, A.; Hudson, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1098.

the generation of **6a** and **7a** in the presence of a small amount or, better, in the absence of hydrogen donors should lead to the isolation of the same products obtained from radicals **8a,b**.

Product Studies. The reaction of the bromide **9a** with tributyltin hydride was repeated in refluxing benzene with AIBN as thermal initiator by using mixtures approximately stoichiometric of the bromide and of Bu_3SnH (ca. 0.01 M). Chromatographic separation of the reaction products afforded the dimer **19** in a 25% yield together with 9-ethylanthracene (70%). In a second experiment, in which a benzene solution of Bu_3SnH and AIBN were added dropwise to the solution of the bromide, 9-ethylanthracene (68%) and compound **19** (23%) were again obtained.

The amount of the isolated dimer **19** is quite remarkable in view of the fact that these experiments were performed in the presence of Bu_3SnH, which would easily intercept radical **6a** to give 9-ethylanthracene. This provides strong evidence that **6a** and **8a** are rapidly equilibrating species and therefore that the latter one is a true intermediate in the rearrangement of **6a**.

Since the formation of the dimer **19** is expected to be even more favored if generating radical **6a** in the absence of a hydrogen donor such as tributyltin hydride, the diacyl peroxides **11** and **13** were thermally decomposed in boiling 1,2-dichlorobenzene. The two main products isolated from the decomposition of **11** (eq 15) were the ester **15**, resulting from in cage recombination of the *m*-chlorobenzoyloxyl and 2-(9-anthryl)ethyl radicals, and aceanthracene (**16**).

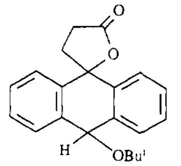


15 (40%) 16 (30%) (ca. 5%)

+ trichlorobiphenyls + *m*-ClC_6H_4COOH (10%) (15)

Similarly, substantial amounts of phenyl substituted aceanthracene were obtained in the thermal decomposition of the diacyl peroxide **13** in boiling 1,2-dichlorobenzene.

In two additional experiments chlorobenzene solutions of the peresters **12** and **14** were accurately degassed, sealed under vacuum, and decomposed at 403 K. Analysis of the product mixtures gave the following results: from the decomposition of **12** we obtained *tert*-butyl 2-(9-anthryl)ethyl ether (45%), 9-ethylanthracene (4%), 9-vinylanthracene (10%), aceanthracene (2%), ca. 1% of compound **19**, and 10% of 9,10-dihydro-9-*tert*-butoxy-10-[γ-(spirobutyro-γ-lactone)]anthracene (**17**). The latter, presumably resulting from the induced decomposition of the peroxide, was identified by spectroscopic and X-ray diffractometric analyses which will be reported in a forthcoming paper. Other products that could not be characterized were also present. Similarly, the decomposition of **14** afforded *tert*-butyl 2-[9-(10-phenylanthryl)]ethyl ether (40%), 9-ethyl-10-phenylanthracene (5%), 9-vinyl-10-phenylanthracene (8%), and 20% of an unidentified product having general formula $C_{23}H_{18}O_2$. The perester **12** was also decomposed in boiling benzene, that is, at a substantially lower temperature (353 K) than in the previous experiments. The products recovered were the same as in chlorobenzene with some difference in the yields, i.e., *tert*-butyl 2-(9-anthryl)ethyl ether (30%), compound **17** (25%), 9-ethylanthracene (2%), 9-vinylanthracene (6%), trace amounts of aceanthracene, and of **19**.



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Although the decomposition of **11** and **13** and that of **12** and **14** followed somewhat different reaction paths, it is evident that in no case are we in the presence of a clean fragmentation to give the radicals of interest, since the major part of the reaction products comes from in-cage recombination or induced decomposition of the peroxides. Products arising from self-combination, disproportionation, or intramolecular cyclization of the 2-arylethyl radicals were recovered only to a small percent. Nevertheless, it is noteworthy that some amount of the dimer **19** was obtained in the decomposition of **12** in both boiling benzene and chlorobenzene. The formation of aceanthracene or of its phenyl-substituted analogue is somewhat puzzling, and we prefer not to speculate on this point.

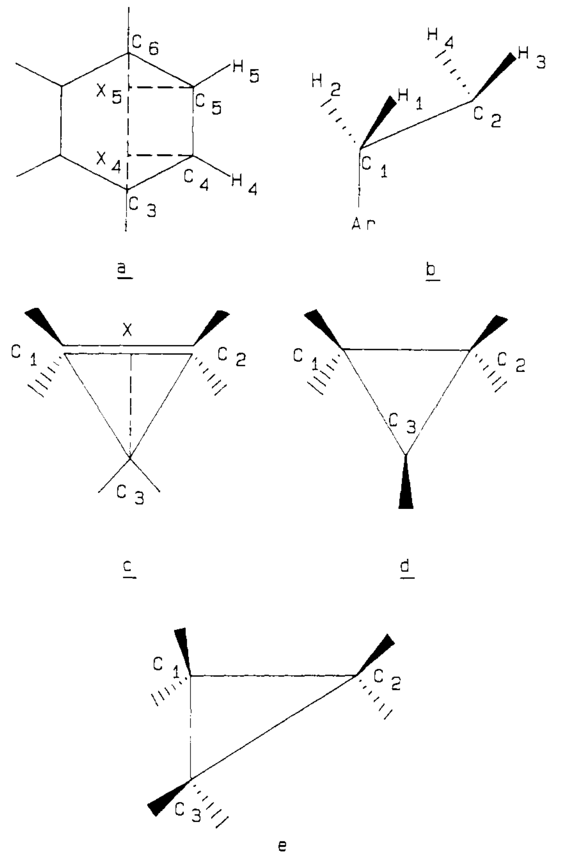

Figure 3. Atomic indexes and geometries for (a) the aryl group and (b–e) the 2-arylethyl radicals.

Table III. MO Configurations and Symmetry Classifications for the C_{2v} Symmetric Structure c of a 2-Arylethyl Radical

	sym	MO config
$CH_2{=}CH_2Ar^{\bullet}$	A	$...\pi^2\sigma$
$CH_2{=}CH_2^{\bullet+}Ar^-$	A	$...\pi\sigma^2$
$CH_2{=}CH_2^{\bullet-}Ar^+$	B	$...\pi^2\pi^*$

Theoretical Study of the Mechanism of Rearrangement

In this section we use MO theory to investigate the possible mechanisms for the 1,2-aryl migration. The 2-phenylethyl radical (**1**, R = H) is the simplest molecular model for this reaction, and the results of actual computations on this system will be used to illustrate our arguments.

The symmetric structure c in Figure 3 is a convenient geometry to start the search of the reaction transition state and intermediates. At this geometry, the molecule can be regarded as an open-shell aryl radical interacting with a closed-shell ethylene molecule. To describe the chemical bonds between the two fragments, the charge-transfer configurations, $CH_2{=}CH_2^{\bullet-}Ar^+$ and $CH_2{=}CH_2^{\bullet+}Ar^-$, should be considered together with the ground electronic configuration, $CH_2{=}CH_2Ar^{\bullet}$. These configurations can easily be written by using the molecular orbitals (MO) of the two fragments and classified as shown in Table III, for the C_{2v} symmetric structure c.

From this simple analysis one recognizes the existence of two different electronic configurations and states of the radical at this

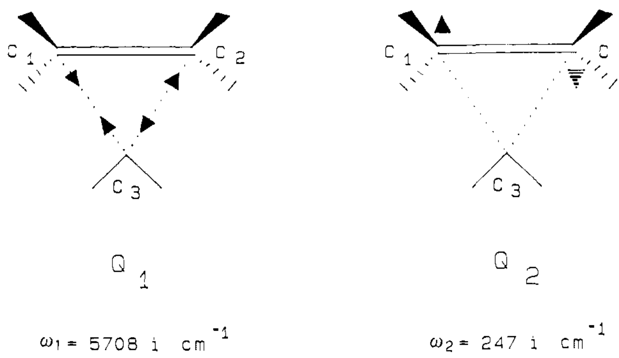

Figure 4. Vibrational modes Q_1, Q_2 and imaginary frequencies for structure c in the B electronic state.

geometry. The equilibrium geometries of the two states computed by using STO-3G orbitals[26] and the RHF method are given in Table IV (column c).

The large interfragment equilibrium distance for one of the states (A) is indicative of a loosely bound complex. The computed C_1–C_2 ethyl bond distance, being a typical double-bond length, suggests a small contribution from the charge-transfer configuration $CH_2{=}CH_2^{\bullet+}Ar^{-}$. In the B state, the C_1–C_2 bond distance is larger due to the breaking of the double bond and to the formation of the cyclic radical structure.

We next performed the harmonic analysis of the potential energy surfaces at the two equilibrium geometries and evaluated the IR frequencies for the two states. This was done by analytical methods and efficient computer programs.[27] Among the set of vibrational frequencies in the B state, two imaginary frequencies were obtained for the asymmetric ring closing/opening mode Q_1 (5708i cm^{-1}; see Figure 4) and for the torsion mode Q_2 (247i cm^{-1}). In the A state, only the Q_1 mode has a low imaginary frequency corresponding to dissociation of the radical complex. Since these frequencies correspond to negative curvatures of the potential energy surface, the two geometries are classified as second-order (B state) and first-order (A state) saddle points, respectively, on the corresponding energy surfaces.

From the local behavior of the potential energy surface and the expression of the normal modes, we infer the global profile of the surfaces along the two coordinates. By disregarding the rotational isomerism of the ethyl group about the C_1–Ar and C_1–C_2 axes, the eclipsed conformer of **1** (R = H) is for both states the limit structural form for large displacements of the Q_1 coordinate. We have therefore evaluated the energy and the geometry of the open radical structure (b), with the results shown in Table IV. The low value of the curvature of the A energy surface along Q_2 at the c geometry suggests that the energy of the state is almost insensitive to torsion (see also the energy values in Table V) and that the internal rotation about the C_2 axis is nearly free in this state. On the contrary the negative curvature of the B surface along Q_2 and the periodic character of this coordinate indicate the presence of one or multiple minima at twisted geometries.

By geometry optimization of the B state under reduced C_2 symmetry constraints, a single minimum was found corresponding to the cyclohexadienyl radical form (d). The computed bond lengths and angles reported in Table IV (column d) show that the main variations with respect to the untwisted structure are in the ring geometry and in some of the aryl internal coordinates. Only real vibrational frequencies have been computed for this radical, proving that this geometry corresponds to a minimum on the B potential energy surface.

Table IV. Internal Coordinates for the Molecular Structures in Figure 3 Computed with STO-3G Orbitals and the RHF Method[a]

fragment		state, geometry			
		A = B, b	A, c	B, c	B, d
phenyl	C_3–X_4	0.7131	0.6487	0.7678	0.8177
	X_4–C_4	1.1954	1.2167	1.1876	1.2442
	X_4–X_5	1.3857	1.3902	1.3865	1.3249
	X_5–C_5	1.1968	1.2051	1.1888	1.2515
	X_5–C_6	0.6987	0.6893	0.7063	0.7439
	C_6–H_6	1.0822	1.0820	1.0827	1.0806
	C_5–H_5	1.0828	1.0834	1.0825	1.0829
	C_4–H_4	1.0817	1.0824	1.0815	1.0832
	$\angle H_5$–C_5–C_4	119.74	119.87	119.06	120.52
	$\angle H_4$–C_4–C_3	119.73	121.54	119.90	116.49
ethyl (cyclic structures)	X–Ar		3.8755	1.6744	1.3245
	C_1–C_2		1.3060	1.4748	1.4970
	H_1–C_1		1.0820	1.0801	1.0808
	$\angle H_1$–C_1–C_2		122.17	118.67	118.27
	$\angle H_1$–C_1–X–Ar		89.99	105.04	107.73
ethyl (open structures)	C_1–Ar	1.5413			
	C_1–C_2	1.5186			
	C_2–H_3	1.0808			
	C_1–H_1	1.0908			
	$\angle H_3$–C_2–C_1	118.29			
	$\angle C_2$–C_1–Ar	115.69			
	$\angle H_1$–C_1–Ar	108.30			
	$\angle H_3$–C_2–C_1–Ar	105.76			
	$\angle H_1$–C_1–C_3–H_4	122.55			

[a] C_{2v} constraints assumed for the aryl group at all geometries. Bond lengths in angstroms and angles in degrees.

Table V. Energies (kcal/mol) of the Molecular Structures in Figure 3 Computed with the RHF, UHF, and UHF + MP2 Methods

geometry	state	RHF	UHF	UHF + MP2
a	A + B	0	0	0
c	A	62	67	53
c	B	117	84	136
d	A		65	
d	B	22	-8	32

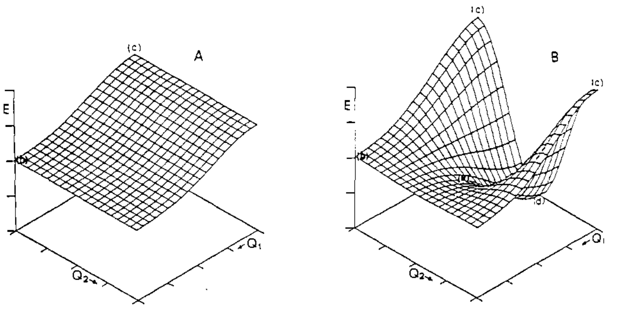

Figure 5. Qualitative shape of the B and A potential energy (E) surfaces in the Q_1, Q_2 "plane".

The computed energy values more than the geometries are expected to be affected by the quality and method of computation and do not provide an unambiguous estimate of the relative energy of the B state at geometries c and d. One may notice large fluctuations in these energy values (see Table V), which are essentially due to the artifacts of the UHF description of the cyclic radical structure due to spin contamination effects.[28] Moreover, large orbital expansions are likely to be required for an accurate estimate of the relative energy of the A and B states, as found for the corresponding states of the parent ethylene molecule (ground and first excited $\pi\pi^*$ states).[29]

Despite these limitations our results are useful for a qualitative picture of the two energy surfaces in the Q_1 and Q_2 coordinates as shown in Figure 5. The curvature of the B surface at geometry c and the relative energies of the state at geometries b and c imply the existence of saddle points in this section of the surface. Rather than attempting a direct numerical determination of these highly

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(26) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(27) Amos, R. D. The Cambridge Analytical Derivatives Publication CCP 1/84/4, SERC, Daresbury Laboratory, Daresbury, Warrington, O WA4 4ad, 1984.

(28) Hehre, W. J. *J. Am. Chem. Soc.* **1973**, *95*, 2643.

(29) For a discussion on this point see: Murchie, L. E.; Davidson, E. R. *J. Chem. Phys.* **1977**, *66*, 2963.

asymmetric structures, their existence can be easily proved by the following simplified arguments.

If expanding the potential energy for the B state at c geometry, the strong anharmonic behavior along the Q_2 coordinate requires the addition of anharmonic components to the harmonic terms of the potential. The lowest order term in both coordinates, which is allowed by symmetry, is of the type $k_{1122}Q_1^2Q_2^2$, where k_{1122} is a positive constant. This leads to the following expression of the potential:

$$V = \tfrac{1}{2}k_{11}Q_1^2 + \tfrac{1}{2}k_{22}Q_2^2 + \tfrac{1}{6}k_{1122}(Q_1Q_2)^2 + \ldots \qquad (k_{11},k_{22} < 0;\ k_{1122} > 0) \quad (16)$$

The stationary conditions for a general geometry where the coordinates Q_1 and Q_2 have been simultaneously displaced from the reference geometry c, imply the vanishing of all intramolecular forces. In particular:

$$\partial V/\partial Q_1 = \partial V/\partial Q_2 = 0 \quad (17)$$

In agreement with the symmetry of the reference geometry c, four stationary points are obtained, for $Q_2 = \pm(-3k_{11}/k_{1122})^{1/2}$ and $Q_1 = \pm(-3k_{22}/k_{1122})^{1/2}$, which are easily shown to be saddle points. To this purpose, the harmonic force constants are evaluated at the stationary points, giving

$$\partial^2 V/\partial Q_1\partial Q_1 = \partial^2 V/\partial Q_2\partial Q_2 = 0$$

$$\frac{\partial^2 V}{\partial Q_1\partial Q_2} = \pm 2(k_{11}k_{22}/k_{1122})^{1/2} \neq 0 \quad (18)$$

From eq 18 the two normal frequencies are evaluated, giving one real and one imaginary frequency as required for saddle points. Given the values computed for the two negative force constants k_{11} and k_{22}, the displacement of the Q_1 coordinate from the reference value (geometry c) is expected to be much smaller compared to Q_2, implying a strongly twisted slightly asymmetric cyclic radical structure (structure e in Figure 3). A number of examples have been reported in the literature that support our analysis; see for example ref 30.

The main conclusion we draw from the present analysis is the identification of two possible coordinates for the aryl migration: one involving both coordinates proceeding through the intermediate cyclic structure d; the other involving mainly the ring mode coordinate Q_1 with formation of a loose complex c. In reality, as soon as the Q_1 coordinate changes from the reference value (c geometry), the distinction between A and B symmetries loses its significance due to the loss of the molecular symmetry and the interaction of the two diabatic surfaces should be taken into account. In the following section we keep the A and B notation simply as an identification label for the two surfaces.

Discussion

The results accumulated during the present investigation demonstrate that the 2-(9-anthryl)ethyl (**6**) and 2-[9-(10-phenyl)anthryl]ethyl (**7**) radicals and their cyclized counterparts, i.e., the spirocyclopropane radicals **8a** and **8b**, are rapidly equilibrating species characterized by very different reactivities. The former ones, besides giving radical–radical reactions, can easily abstract hydrogens from hydrogen donors, while the latter essentially decay by self-combination. Thus, when the 2-arylethyl radicals were produced in the presence of a large excess of tributyltin hydride, the only isolated products were the corresponding ethylarenes while, with low concentrations of the tin hydride, substantial amounts of the dimer of the spirocyclopropane radical were recovered. Disappointingly, all the potential radical precursors (diacyl peroxides and peresters) that might allow the generation of the open-chain radicals in the absence of hydrogen donors, and thus the formation of larger amounts of spirocyclopropane dimers, did not give rise to clean fragmentation processes leading to the desired arylethyl radicals.

Kinetic results obtained by the competing reaction method indicate that the ring-closure reaction of **6** and **7** is very fast, $k_{13} > 5 \times 10^7$ s^{-1}, in agreement with thermochemical calculations showing that the open-chain and the cyclized radicals should have comparable stabilities. The rate constant for the reverse reaction of ring opening could not be determined; however, the EPR detection of only the cyclic radicals when generating the 2-arylethyls by photolysis of the peresters **12** and **14**, suggests that k_{-13} should be at least 2 orders of magnitude smaller than k_{13}.

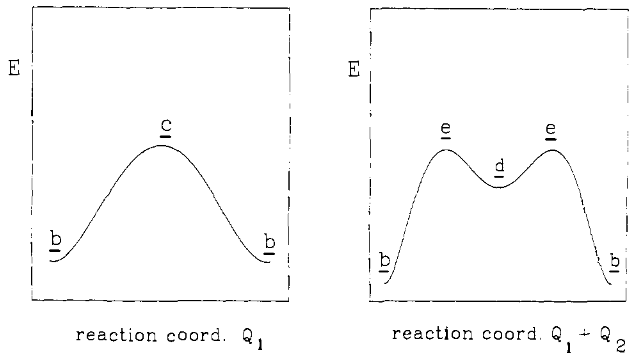

Figure 6. Reaction coordinate and potential energy profile for nonintersecting (left) and intersecting (right) A and B potential energy surfaces.

It is therefore concluded that the spirocyclopropane radicals **8a** and **8b** are involved as intermediates in the neophyl-like rearrangement of 2-(9-anthryl)ethyl (**6**) and 2-[9-(10-phenyl)-anthryl]ethyl (**7**) radicals. The rearrangement rate constant k_r, which, in the present experimental conditions where the large excess of Bu_3SnH prevents the intermediate spiro radicals from reaching a sufficiently high concentration to decay bimolecularly, is coincident with the ring-closure rate constant k_{13}, is much larger than in any other neophyl-like rearrangement so far investigated.

These results can be rationalized by using the qualitative picture given in Figure 6 for the A and B potential energy surfaces. Two limit situations can be envisaged: in the first case, corresponding to the intersection of the A and B energy surfaces, the adiabatic interaction prevents the crossing of the two surfaces, producing the reaction energy profile shown in the right panel of Figure 6. The reaction coordinate involves both the Q_1 and Q_2 coordinates with formation of the intermediate cyclic radical (structure d). This includes the case where structure d is lower in energy than the reactant (b). The saddle would then be removed from the B surface with spontaneous evolution of the reaction from b to d. The results of our computations, as well as those of ref 28 and 31, suggest that the cyclic radicals arising from intramolecular homolytic addition to unsaturated bonds lie on a minimum of the B potential energy surface. This type of mechanism is entirely consistent with our experimental results which demonstrate that the 1,2-aryl shift in radicals **6** and **7** does proceed through a spirocyclopropane radical intermediate. The large rate constant for ring closure, k_{13}, also suggests a small activation energy to the intermediate formation.

The second possibility corresponds to the A surface lying below the B surface, with the aryl migration occurring on the A potential energy surface, Q_1 being the reaction coordinate (see left panel in Figure 6). Along this coordinate, the C–aryl bond is weakened but not dissociated due to the formation of the intermolecular complex c.[30] Although this mechanism is disfavored in the 2-phenylethyl radical by a large activation energy (see Table V), its contribution to the intramolecular migration of other unsaturated groups cannot be ruled out and, as already pointed out in the introduction, it has been invoked for the radical rearrangements studied in ref 8 and 9.

Experimental Section

General Procedures. Melting points were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM 360L instrument, using tetramethylsilane

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as an internal standard. Mass spectra were performed with a VG 7070E double-focusing spectrometer by electron impact with a beam energy of 70 eV, unless otherwise stated. Chromatographic separations were carried out on silica gel column (ICN Silica 63-200 60A), using light petroleum (40–70 °C)/diethyl ether gradient as eluant.

EPR Experiments. Radicals were generated by photolyzing with light, from a 1-kW high-pressure mercury lamp, nitrogen-purged benzene, *tert*-butylbenzene, or toluene solutions of the appropriate precursors. The temperature of the sample was controlled with standard devices and measured with a chromel–alumel thermocouple. EPR spectra were recorded on a Bruker ER-200 spectrometer. Kinetic experiments were performed by accumulating the decay traces of the EPR signals with an ASPECT 2000 dedicated computer. The initial radical concentrations were determined by double integration of the EPR spectra and by comparison with the signal from a standard benzene solution of DPPH.

X-ray Analysis. $C_{32}H_{26}$, $M = 410.56$, orthorhombic, space group *Pbca*, $a = 18.157$ (3), $b = 6.361$ (3), $c = 19.490$ (3) Å, $V = 2251$ Å^3, $Z = 4$, $D_c = 1.21$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 0.34 cm^{-1}, $F_{000} = 872.0$.

Intensity data were collected by a CAD4 diffractometer using $\omega/2\vartheta$ scan; range $2.5° < \vartheta < 25°$. Of 1766 independent reflections, 643 having $I < 2.5\sigma(I)$ were considered unobserved. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centered reflections $8° < \vartheta < 14°$. The structure was solved by direct methods and refined anisotropically by full-matrix least-squares analysis using the SHELX program packages.[32,33] The H atoms were calculated geometrically when they were not found in the Fourier difference syntheses but not refined. The final R was 0.040. Maximum $\Delta/\sigma = 0.007$. Final difference Fourier map excursions 0.51 to −0.35 e Å^{-3}.

Materials. *tert*-Butyl β-(9-anthryl)perpropanoate[34] (**12**) and bis(isopropyl peroxydicarbonate)[35] (DPDC) were synthesized according to the literature; DPDC was stored and used as a 1 M benzene solution.

tert-Butyl hydroperoxide (Merck) was purified by distillation;[34] tri-*n*-butyltin hydride (Aldrich Chemie), *m*-chloroperbenzoic acid (Fluka), *N*,*N*-dicyclohexylcarbodiimide (C. Erba), and 1,1′-carbonyldiimidazole (Aldrich Chemie) were used without any purification.

(1,1-$^2H_2$)-2-(9-Anthryl)ethanol. To a stirred suspension of lithium aluminum deuteride (1.26 g, 30 mmol) in dry diethyl ether (100 mL), a solution of methyl 9-anthrylacetate[36] (3.75 g, 15 mmol) in dry diethyl ether (30 mL) was added dropwise at room temperature under a nitrogen atmosphere, and the mixture was allowed to react for 3 h. The reaction was then cautiously hydrolyzed with water and acidified with hydrochloric acid; the organic layer was washed with water (2 × 50 mL) and dried over magnesium sulfate. The solvent was removed under vacuum, and the residue recrystallized from light petroleum/benzene (1:1, v/v) to give the title compound (2.70 g, 80% yield), mp 106–7 °C (lit.[37] mp 106.5–7.5 °C for the corresponding protic ethanol); ^{1}H NMR(CDCl$_3$) δ 1.57 (s, 1 H, OH), 3.80 (br s, 2 H, CH_2–CD_2), 7.22–8.35 (m, 9 H, H_{arom}); mass spectrum, *m/e* (rel intens) 224 (M$^+$, 36), 191 (100), 189 (25). HRMS calcd for $C_{16}H_{12}D_2O$: 224.11702. Found: 224.11659.

2-(9-Anthryl)ethyl Bromide (9a). To a solution of 2-(9-anthryl)ethanol[37] (4.44 g, 20 mmol) in dry benzene (100 mL), phosphorus tribromide (2.71 g, 10 mmol) was added slowly. After the addition was complete, the reaction was refluxed until the starting ethanol disappeared (ca. 1 h). The mixture was cooled and poured into ice–water and then extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed twice with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed to give 2-(9-anthryl)ethyl bromide (4.3 g, 76% yield), which was recrystallized from light petroleum, mp 105–6 °C; ^{1}H NMR (CDCl$_3$) δ 3.20–4.13 (m, 4 H, CH_2–CH_2), 7.00–8.20 (m, 9 H, H_{arom}); mass spectrum, *m/e* (rel intens) 286 (M$^+$ + 2, 43), 284 (M$^+$, 43), 205 (24), 204 (18), 203 (20), 202 (19), 191 (100), 176 (10). HRMS calcd for $C_{16}H_{13}Br$: 284.02006. Found: 284.01957.

(1,1-$^2H_2$)-2-(9-Anthryl)ethyl Bromide (9b). Following the procedure used for the previous protic bromide, from (1,1-$^2H_2$)-2-(9-anthryl)ethanol (4.48 g, 20 mmol) and phosphorus tribromide (2.71 g, 10 mmol), **9b** was obtained (4.3 g, 75% yield), mp 105–6 °C (from light petroleum); ^{1}H NMR (CDCl$_3$) δ 3.97 (s, 2 H, CH_2), 7.10–8.25 (m, 9 H, H_{arom}); mass spectrum, *m/e* (rel intens) 288 (M$^+$ + 2, 47), 286 (M$^+$, 47), 207 (27), 206 (20), 205 (20), 204 (19), 191 (100), 176 (10). HRMS calcd for $C_{16}H_{11}D_2Br$: 286.03261. Found: 286.03211.

9-(10-Phenylanthryl)acetonitrile. According to the procedure of Ciganek,[38] to a stirred solution of 9-(10-phenylanthryl)methyl chloride[39] (26 g, 86 mmol) in dimethyl sulfoxide (150 mL) maintained at 60 °C, a solution of potassium cyanide (9 g, 138 mmol) in water (20 mL) was added during 30 min. Stirring at 60 °C was continued for 1 h. After the mixture was allowed to stand at room temperature overnight, water (400 mL) was added, and the precipitate was washed with water (2 × 100 mL) and dried in a desiccator under vacuum. After two recrystallizations from light petroleum/benzene (7:3, v/v), the title compound was obtained (19 g, 78% yield), mp 163–5 °C (from benzene); ^{1}H NMR (CDCl$_3$) δ 4.52 (s, 2 H, CH$_2$), 7.10–7.75 (m, 11 H, H_{arom}), 7.97–8.23 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 293 (M$^+$, 100), 292 (10), 253 (16), 252 (20), 216 (10). HRMS calcd for $C_{22}H_{15}N$: 293.12045. Found: 293.12003.

9-(10-Phenylanthryl)acetic Acid. A mixture of 9-(10-phenylanthryl)acetonitrile (19 g, 65 mmol) and sodium hydroxide (8.15 g, 204 mmol) in Cellosolve (60 mL) was heated under reflux for 3 h. After cooling, the solution was diluted with water (250 mL) and acidified with hydrochloric acid. The crude product was collected on a sintered glass funnel, washed with water, and dissolved in boiling solution of sodium carbonate (13.8 g, 130 mmol) in water (500 mL). The mixture was cooled to 60 °C and filtered; the filtrate was cooled and acidified to give the title compound, which was filtered and recrystallized from benzene (14 g, 70% yield), mp 232–3 °C; ^{1}H NMR (CDCl$_3$) δ 4.57 (s, 2 H, CH_2), 7.10–8.30 (m, 14 H, H_{arom} and OH); mass spectrum, *m/e* (rel intens) 312 (M$^+$, 29), 311 (35), 267 (100), 265 (26), 252 (26). HRMS calcd for $C_{22}H_{16}O_2$: 312.11503. Found: 312.11452.

Methyl 9-(10-Phenylanthryl)acetate. In a round-bottomed flask provided with a Soxhlet apparatus containing dry sodium sulfate, 9-(10-phenylanthryl)acetic acid (6.24 g, 20 mmol), methanol (150 mL), and concentrated sulfuric acid (1 mL) were heated under reflux for 24 h. After removing most of the methanol, the residue was dissolved in chloroform and washed with water (2 × 100 mL), 5% sodium carbonate solution (4 × 100 mL), and water again (2 × 100 mL); the organic phase was dried over magnesium sulfate; the solvent was removed in vacuo, and the residue recrystallized from light petroleum/benzene (1:1, v/v) to give the methyl acetate (5.9 g, 90% yield), mp 160–2 °C; ^{1}H NMR (CDCl$_3$) δ 3.60 (s, 3 H, CH_3), 4.60 (s, 2 H, CH_2), 7.05–7.73 (m, 11 H, H_{arom}), 8.03–8.40 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 326 (M$^+$, 68), 267 (100), 265 (31), 252 (30). HRMS calcd for $C_{23}H_{18}O_2$: 326.13068. Found: 326.12998.

2-[9-(10-Phenylanthryl)]ethanol. To a stirred suspension of lithium aluminum hydride (0.114 g, 3.0 mmol) in dry diethyl ether (10 mL), a solution of methyl 9-(10-phenylanthryl)acetate (0.98 g, 3.0 mmol) in dry diethyl ether (20 mL) was added dropwise at room temperature; the mixture was allowed to react for 4 h and then cautiously hydrolyzed first with water and then with hydrochloric acid. The organic layer was washed with water (2 × 20 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure to give the crude ethanol, which was recrystallized from benzene (0.82 g, 92% yield), mp 141–3 °C; ^{1}H NMR (CDCl$_3$) δ 1.97 (s, 1 H, OH), 3.60–4.25 (m, 4 H, CH_2–CH_2), 7.00–7.73 (m, 11 H, H_{arom}), 8.03–8.60 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 298 (M$^+$, 51), 267 (100), 265 (29), 252 (30). HRMS calcd for $C_{22}H_{18}O$: 298.13576. Found: 298.13523.

2-[9-(10-Phenylanthryl)](1,1-$^2H_2$)ethanol. Following the procedure described for the protic ethanol, starting from methyl 9-(10-phenylanthryl)acetate (4.89 g, 15 mmol) and lithium aluminum deuteride (0.63 g, 15 mmol) the title compound was obtained (4.25 g, 94% yield), mp 141–3 °C (from benzene); ^{1}H NMR (CDCl$_3$) δ 1.83 (s, 1 H, OH), 3.87 (s, 2 H, CH_2), 6.97–7.73 (m, 11 H, H_{arom}), 8.10–8.43 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 300 (M$^+$, 55), 267 (100), 265 (26), 252 (28). HRMS calcd for $C_{22}H_{16}D_2O$: 300.14832. Found: 300.14802.

2-[9-(10-Phenylanthryl)]ethyl Bromide (10a). To a solution of 2-[9-(10-phenylanthryl)]ethanol (0.35 g, 1.2 mmol) in dry benzene (10 mL), phosphorus tribromide (0.16 g, 0.6 mmol) was added, and the mixture was refluxed for 1 h. After cooling, the solution was poured into ice–water and then extracted with diethyl ether (3 × 25 mL). The organic layers were washed with water (2 × 25 mL) and dried over magnesium sulfate. The solvent was removed under vacuum, and the residue was chromatographed to give the title bromide (0.30 g, 70% yield), mp 159–61 °C (from light petroleum/benzene 7:3, v/v); ^{1}H NMR (CDCl$_3$) δ 3.43–4.40 (m, 4 H, CH_2–CH_2), 6.93–7.77 (m, 11 H, H_{arom}), 7.97–8.33 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 362 (M$^+$ +

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2, 43), 360 (M^+, 43), 281 (21), 267 (100), 265 (18), 252 (30). HRMS Calcd for $C_{22}H_{17}Br$: 360.05136. found: 360.05178.

2-[9-(10-Phenylanthryl)](1,1-$^2H_2$)ethyl Bromide (10b). According to the procedure described above, from 2-[9-(10-phenylanthryl)(1,1-$^2H_2$)-ethanol (4.5 g, 15 mmol) and phosphorous tribromide (2.03 g, 7.5 mmol) **10b** was obtained (3.9 g, 72% yield), mp 159–61 °C (from light petroleum/benzene 7:3, v/v); ^1H NMR ($CDCl_3$) δ 4.13 (s, 2 H, CH_2), 6.93–7.77 (m, 11 H, H_{arom}), 7.97–8.33 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 364 ($M^+ + 2$, 59), 362 (M^+, 59), 283 (21), 267 (100), 265 (15), 252 (26). HRMS calcd for $C_{22}H_{15}D_2Br$: 362.06391. Found: 362.06452.

β-(9-Anthryl)propanoyl-*m*-chlorobenzoyl Peroxide (11). According to the procedure of Greene and Kazan,[40] to a cold, stirred solution of dicyclohexylcarbodiimide (1.3 g, 6.3 mmol) in diethyl ether (15 mL) was added, in one portion, a solution of β-(9-anthryl)propanoic acid[41] (1.57 g, 6.3 mmol) and *m*-chloroperbenzoic acid (1.08 g, 6.3 mmol) in diethyl ether (45 mL) and methylene chloride (45 mL). The resulting mixture was stirred in an ice bath for 16 h and then filtered on a sintered glass funnel; the remaining urea was slurried with cold methylene chloride (2 × 25 mL). An equal volume of cold diethyl ether was added to the filtrate which was washed with cold saturated ammonium sulfate solution (3 × 25 mL), cold 10% sodium carbonate solution (2 × 25 mL), and cold saturated sodium chloride solution (2 × 25 mL). The organic phase was dried over magnesium sulfate, and the solvent removed under reduced pressure. The residue was rapidly chromatographed, and the collected solid was recrystallized by adding light petroleum to a methylene chloride solution of the peroxide, which separated in yellowish crystals (1.65 g, 65% yield), mp 197–200 °C (dec); ^1H NMR ($CDCl_3$) δ 2.17–2.92 (m, 4 H, CH_2–CH_2), 7.05–7.70 (m, 11 H, H_{arom}), 8.02–8.33 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 406 ($M^+ + 2$, 14), 404 (M^+, 38), 265 (8), 248 (24), 206 (34), 193 (48), 165 (16), 158 (2), 156 (6), 141 (37), 139 (100), 113 (6), 111 (17). HRMS calcd for $C_{24}H_{17}ClO_4$: 404.08154. Found: 404.08241.

Diethyl [9-(10-Phenylanthryl)]methylmalonate. To a solution of sodium ethoxide (5.15 g, 75.7 mmol) in absolute ethanol (200 mL), diethyl malonate (12.12 g, 75.7 mmol) was added. The solvent was removed under reduced pressure, and the residue was suspended in dry benzene (300 mL) under mechanical stirring. A solution of 9-(10-phenylanthryl)methyl chloride[39] (22.90 g, 75.7 mmol) in dry benzene (150 mL) was added dropwise, and the reaction refluxed for 2 h. After cooling, the mixture was washed with water (2 × 100 mL) in a separatory funnel. The organic phase was dried over magnesium sulfate, the solvent was removed under vacuum, and the residue recrystallized from light petroleum to afford the substituted diethyl malonate (29 g, 90% yield), mp 88–90 °C; ^1H NMR ($CDCl_3$) δ 1.03 (t, 6 H, $2CH_3$), 3.73–4.47 (m, 7 H, CH_2–CH and 2 $COOCH_2CH_3$), 6.97–7.73 (m, 11 H, H_{arom}), 8.08–8.43 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 426 (M^+, 66), 279 (26), 267 (100), 265 (14), 252 (22). HRMS calcd for $C_{28}H_{26}O_4$: 426.18311. Found: 426.18231.

[9-(10-Phenylanthryl)]methylmalonic Acid. In a round-bottomed flask, ethanol (100 mL), diethyl [9-(10-phenylanthryl)]methylmalonate (29 g, 68 mmol), and a solution of sodium hydroxide (16.33 g, 408 mmol) in ethanol (400 mL) were placed under mechanical stirring and refluxed for 1 h. The volume was then reduced to 100 mL by removing the ethanol under reduced pressure. After cooling, the separated sodium salt was collected on a sintered glass funnel, washed with diethyl ether (3 × 50 mL), and then suspended in water (200 mL); by addition of hydrochloric acid, a yellow-brownish solid precipitated that was filtered and dried in a desiccator under vacuum. The crude acid was dissolved in diethyl ether and reprecipitated by addition of light petroleum (21.5 g, 85% yield), mp 187–9 °C; ^1H NMR (CD_3–CO–CD_3) δ 3.75–4.47 (m, 3 H, CH_2–CH), 6.97–8.57 (m, 15 H, H_{arom} and 2 $COOH$); mass spectrum *m/e* (30 eV, rel intens) 370 (M^+, 2), 326 (93), 280 (11), 267 (100), 265 (18), 252 (23). Anal. Calcd for $C_{24}H_{18}O_4$: C, 77.82; H, 4.90. Found: C, 77.97; H, 4.94.

β-[9-(10-Phenylanthryl)]propanoic Acid. A round-bottomed flask containing [9-(10-phenylanthryl)]methylmalonic acid (19.5 g, 53 mmol) was placed in an oil bath at 220 °C for 30 min. After cooling, the residue was refluxed with 5% sodium carbonate solution (500 mL) for 1 h. The mixture was cooled to 60 °C and filtered; the filtrate, cooled at room temperature, was cautiously acidified with hydrochloric acid. The crude product was collected on a sintered glass funnel and recrystallized by addition of light petroleum to a dioxane solution of the acid (15.5 g, 90% yield), mp 219–21 °C; ^1H NMR ($CDCl_3$) δ 2.70–3.12 (m, 2 H, CH_2–COOH) 3.83–4.26 (m, 2 H, Ar–CH_2), 7.07–7.77 (m, 11 H, H_{arom}), 8.10–8.43 (m, 2 H, H_{arom}), 9.13 (br s, 1 H, COOH); mass spectrum, *m/e* (rel intens) 326 (M^+, 84), 267 (100) 265 (21), 252 (28). HRMS calcd for $C_{23}H_{18}O_2$: 326.13068. Found: 326.13015.

β-[9-(10-Phenylanthryl)]propanoyl *m*-Chlorobenzoyl Peroxide (13). Following the procedure described for the peroxide **11**, starting from β-[9-(10-phenylanthryl)]propanoic acid (2.05 g, 6.3 mmol), **13** was obtained (1.8 g, 60% yield), mp 211–3 °C (dec); ^1H NMR ($CDCl_3$) δ 1.76–2.85 (m, 4 H, CH_2–CH_2), 7.00–8.03 (m, 17 H, H_{arom}); mass spectrum, *m/e* (rel intens) 482 ($M^+ + 2$, 13), 480 (M^+, 37), 325 (14), 280 (21), 267 (100), 265 (16), 252 (23), 158 (6), 156 (18), 141 (7), 139 (21), 113 (4), 111 (12). HRMS calcd for $C_{30}H_{21}ClO_4$: 480.11284. Found: 480.11367.

***tert*-Butyl β-[9-(10-Phenylanthryl)]perpropanoate (14).** According to the procedure of Singer and Kong,[42] 1,1′-carbonyldiimidazole (2.43 g, 15 mmol) was dissolved in dry tetrahydrofuran (30 mL) under magnetic stirring in a nitrogen atmosphere at room temperature; the solid β-[9-(10-phenylanthryl)]propanoic acid (4.89 g, 15 mmol) was added at once; 1 h later, the mixture was cooled at 0–5 °C in an ice bath, and a solution of *tert*-butyl hydroperoxide (3 g, 33.33 mmol) in light petroleum (45 mL) was added dropwise. After 4 h, water and diethyl ether were added; the organic layer was separated, washed twice with cold water, and dried over magnesium sulfate. The solvent was carefully removed under vacuum at 0–10 °C, and the oily residue was dissolved in as little quantity of light petroleum as possible; by cooling this solution at −30 °C, the perester **14** was recovered as yellowish crystals (3.95 g, 65% yield), mp 117–9 °C; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H, $C(CH_3)_3$), 2.58–3.00 (m, 2 H, CH_2–COO), 3.80–4.21 (m, 2 H, Ar–CH_2), 7.02–7.70 (m, 11 H, H_{arom}), 8.07–8.35 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 398 (M^+, 1), 354 (25), 325 (5), 280 (23), 267 (100), 265 (27), 252 (37). Anal. Calcd for $C_{27}H_{26}O_3$: C, 81.38; H, 6.58. Found: C, 81.86; H, 6.55.

9,10-Dihydro-9-spiro[cyclopropaneanthracene] (18). According to the procedure of Nystrom[43] (method 1), to a stirred suspension of lithium aluminum hydride (0.76 g, 20 mmol) in dry diethyl ether (50 mL), a solution of 9-spiro[cyclopropaneanthracen-10-one][44] (4.40 g, 20 mmol) in dry diethyl ether (200 mL) was added dropwise at a rate such as to produce gentle reflux. After 30 min, the addition of a solution of aluminum trichloride (2.67 g, 20 mmol) in dry diethyl ether (20 mL) was made. One-half hour later, water (10 mL) and 6 N sulfuric acid (10 mL) were added. The clear solution was transferred to a separatory funnel and, after removing the ether phase, the aqueous layer was extracted with diethyl ether (4 × 50 mL). The combined organic phases were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The oily residue was chromatographed to give a viscous oil that crystallized from isopropyl alcohol by cooling, giving white crystals of the title compound (3.55 g, 85% yield), mp 26–7 °C; ^1H NMR ($CDCl_3$) δ 1.23 (s, 4 H, $H_{cycloprop}$), 3.93 (s, 2 H, Ar–CH_2–Ar), 6.72–7.23 (m, 8 H, H_{arom}); mass spectrum, *m/e* (rel intens) 206 (M^+, 73), 205 (100), 204 (17), 203 (21), 202 (20), 191 (37), 189 (16), 178 (38), 176 (18). HRMS calcd for $C_{16}H_{14}$: 206.10955. Found: 206.10918.

9,10-Dihydro-9-phenyl-10-spiro[cyclopropaneanthracene]. Following the procedure of Nystrom[43] (method 2), to a stirred suspension of lithium aluminum hydride (0.38 g, 10 mmol) in dry diethyl ether (25 mL), a solution of granular aluminum chloride (1.33 g, 10 mmol) in dry diethyl ether (10 mL) was added dropwise. Five minutes later, 9,10-dihydro-9-phenyl-9-hydroxy-10-spiro[cyclopropaneanthracene][45] (2.98 g, 10 mmol), dissolved in dry diethyl ether (50 mL), was added dropwise at such a rate to produce gentle reflux. After 30 min, an addition of water (5 mL) and 6 N sulfuric acid (5 mL) was made and the reaction mixture was worked up as previously described for compound **18** to afford 9,10-dihydro-9-phenyl-10-spiro[cyclopropaneanthracene] (2.25 g, 80% yield), mp 121–3 °C (from light petroleum/benzene 4:1 v/v); ^1H NMR ($CDCl_3$) δ 0.92–1.80 (m, 4 H, $H_{cycloprop}$), 5.27 (s, 1 H, CH), 6.75–7.28 (m, 13 H, H_{arom}); mass spectrum, *m/e* (rel intens) 282 (M^+, 100), 281 (57), 267 (27), 265 (14), 252 (20), 205 (45), 204 (56), 203 (34), 202 (22), 191 (20). HRMS calcd for $C_{22}H_{18}$: 282.14085. Found: 282.14071.

Reaction of (1,1-$^2H_2$)-2-(9-Anthryl)ethyl Bromide (9b) with Tri-*n*-butyltin Hydride in the Presence of DPDC. A degassed solution of **9b** (0.6 g, 2.1 mmol), tri-*n*-butyltin hydride (9.0 g, 30.87 mmol), and DPDC (1.05 mL, 1.05 mmol) in benzene (30 mL) in a sealed vial was kept at 70 °C for 8 h. After cooling, the vial was opened and the solution was transferred into a round-bottomed flask; the solvent was removed under reduced pressure, and the residue chromatographed to give a mixture of *9-(1,1-$^2H_2$-ethyl)anthracene* and of *9-(2,2-$^2H_2$-ethyl)anthracene* (0.40 g, 92% yield), mp 58–9 °C (from light petroleum; lit.[46] mp 59 °C for the

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protic 9-ethylanthracene); the molar ratio of the two products was proved to be 1:1 by ^{1}H NMR spectroscopy; ^{1}H NMR (CDCl$_3$) δ 1.17–1.57 (m, 4 H, $\mathrm{CH_2{-}CD_2}H$ and $\mathrm{CD_2{-}C}H_3$), 3.52 (d, 2 H, $\mathrm{C}H_2\mathrm{{-}CD_2H}$), 7.13–8.37 (m, 18 H, H_{arom}); mass spectrum, *m/e* (rel intens) 208 (M$^+$, 100), 193 (76), 191 (87), 189 (19), 165 (9). HRMS calcd for $\mathrm{C_{16}H_{12}D_2}$: 208.12210. Found: 208.12188.

Reaction of 1,1-^{2}H$_2$-2-[9-(10-Phenylanthryl)]ethyl Bromide (10b) with Tri-*n*-butyltin Hydride in the Presence of DPDC. Following the procedure described for (1,1-^{2}H$_2$)-2-(9-anthryl)ethyl bromide, a degassed solution of **10b** (0.73 g, 2 mmol), tri-*n*-butyltin hydride (5.82 g, 20 mmol), and DPDC (1 mL, 1 mmol) afforded a mixture of *9-(1,1-^{2}H$_2$-ethyl)10-phenylanthracene* and of *9-(2,2-^{2}H$_2$-ethyl)10-phenylanthracene* (0.5 g, 88% yield), mp 108–10 °C (from light petroleum; lit.[47] mp 110 °C for the protic derivative); the molar ratio of the two products was proved to be 1:1 by ^{1}H NMR spectroscopy; ^{1}H NMR (CDCl$_3$) δ 1.18–1.58 (m, 4 H, $\mathrm{CH_2{-}CD_2}H$ and $\mathrm{CD_2{-}C}H_3$), 3.53 (d, 2 H, $\mathrm{C}H_2\mathrm{{-}CD_2H}$), 6.83–7.83 (m, 22 H, H_{arom}), 8.00–8.37 (m, 4 H, H_{arom}); mass spectrum, *m/e* (rel intens) 284 (M$^+$, 100), 269 (47), 267 (49), 265 (15), 252 (29). HRMS calcd for $\mathrm{C_{22}H_{16}D_2}$: 284.15340. Found: 284.15357.

Reaction of 2-(9-Anthryl)ethyl Bromide (9a) with Tri-*n*-butyltin Hydride in the Presence of AIBN. (i) A deoxygenated solution of **9a** (2.0 g, 7 mmol), tri-*n*-butyltin hydride (2.32 g, 8 mmol), and AIBN (1.31 g, 8 mmol) in benzene (200 mL) was refluxed under nitrogen atmosphere for 6 h until the bromo derivative disappeared. After cooling the solvent was removed under vacuum and the residue was chromatographed on a silica gel column to give *9-ethylanthracene* (1.01 g, 70% yield), mp 57–9 °C (lit.[46] mp 59 °C) and *9,9′-bis-(9,10-dihydro-10-spiro[cyclopropaneanthracene])* (**19**), 0.35 g, 25% yield), mp 250–1 °C (from benzene). ^{1}H NMR (CDCl$_3$) δ 0.87–2.07 (m, 8 H, $H_{\mathrm{cycloprop}}$), 4.37 (s, 2 H, $-\mathrm{C}H$), 6.17–7.33 (m, 16 H, H_{arom}); mass spectrum, *m/e* (rel intens) 410 (M$^+$, 3), 205 (100), 204 (18), 191 (4). Anal. Calcd for $\mathrm{C_{32}H_{26}}$: C, 93.62; H, 6.38. Found: C, 93.82; H, 6.40.

(ii) A deoxygenated solution of tri-*n*-butyltin hydride (2.45 g, 8.4 mmol) and AIBN (0.7 g, 4.2 mmol) in benzene (50 mL) was added dropwise during 75 min to a boiling and already deoxygenated solution of **9a** (2 g, 7 mmol) in benzene (150 mL). The reaction was refluxed until the starting material disappeared (ca. 3 h). The residue left after evaporation of the solvent under vacuum was chromatographed on a silica gel column to afford *9-ethylanthracene* (0.99 g, 68% yield), mp 58–9 °C (lit.[46] mp 59 °C) and *9,9′-bis-(9,10-dihydro-10-spiro[cyclopropaneanthracene])* (**19**, 0.33 g, 23% yield), mp 249–51 °C.

Decomposition of β-(9-Anthryl)propanoyl *m*-Chlorobenzoyl Peroxide (11). A solution of **11** (0.81 g, 2 mmol) in *o*-dichlorobenzene (50 mL) was refluxed for 4 days until the peroxide disappeared. The solvent was removed under reduced pressure, and the residue was chromatographed to furnish the following products: trace amounts of a mixture of isomeric *trichlorobiphenyls*; *aceanthracene* (**16**, 0.12 g, 30% yield), mp 116–7 °C (from light petroleum; lit.[48] mp 117 °C); *β-(9-anthryl)ethyl-m-chlorobenzoate* **15**, 0.29 g, 40% yield), mp 146–8 °C (from benzene); ^{1}H NMR (CDCl$_3$) δ 3.80–4.82 (m, 4 H, $\mathrm{C}H_2\mathrm{{-}C}H_2$), 7.00–8.48 (m, 13 H, H_{arom}); mass spectrum, *m/e* (rel intens) 362 (M$^+$ + 2, 9), 360 (M$^+$, 26), 204 (100), 191 (58), 189 (12), 165 (4), HRMS calcd for $\mathrm{C_{23}H_{17}ClO_2}$ 360.09171, found 360.09094; *m-chlorobenzoic acid* (0.04 g, 10% yield), mp 154–5 °C; *β-(9-anthryl)propanoic acid* (0.05 g, 5% yield), mp 194–6 °C (lit.[41] mp 194–5 °C).

Decomposition of β-[9-(10-Phenylanthryl)]propanoyl *m*-Chlorobenzoyl Peroxide (13). Following the same procedure described for the peroxide **11**, from **13** (0.65 g, 1.35 mmol) we obtained trace amounts of a mixture of *trichlorobiphenyl* isomers; *10-phenylaceanthracene* 0.1 g, 25% yield), mp 126–8 °C (from light petroleum); ^{1}H NMR (CDCl$_3$) δ 3.30–3.97 (m, 4 H, $\mathrm{C}H_2\mathrm{{-}C}H_2$), 6.97–8.15 (m, 12 H, H_{arom}); mass spectrum, *m/*e (rel intens) 280 (M$^+$, 100), 279 (25), 278 (15), 277 (15), 276 (15), 252 (11), 203 (12), 202 (12); HRMS calcd for $\mathrm{C_{22}H_{16}}$: 280.12520. Found: 280.12456; trace amounts of *m-chlorobenzoic acid* mp 154–5 °C, and of *β-[9-(10-phenylanthryl)]propanoic acid*, mp 218–20 °C.

Decomposition of *tert*-Butyl β-(9-Anthryl)perpropanoate (12). (i) In chlorobenzene. A degassed solution of **12**[34] (4.83 g, 15 mmol) in chlorobenzene (60 mL) in a sealed vial was maintained at 130 °C for 5 h. After cooling at −50 °C, the vial was opened and the content transferred into a round-bottomed flask; the solvent was removed under vacuum, and the residue chromatographed to afford the following compounds: *9-vinylanthracene* (0.31 g, 10% yield), mp 64–6 °C (lit.[49] mp 64.5–7 °C); *9-ethylanthracene* (0.12 g, 4% yield), mp 58–9 °C (lit.[46] mp 59 °C); *aceanthracene* (0.06 g, 2% yield), mp 116–7 °C (lit.[48] 117 °C); *β-(9-anthryl)ethyl-tert-butyl ether* (1.88 g, 45% yield), mp 77–9 °C (from light petroleum); ^{1}H NMR (CDCl$_3$) δ 1.15 (s, 9 H, $\mathrm{C(C}H_3)_3$), 3.43–4.03 (m, 4 H, $\mathrm{C}H_2\mathrm{{-}C}H_2$), 7.07–8.43 (m, 9 H, H_{arom}); mass spectrum, *m/e* (rel intens) 278 (M$^+$, 18), 205 (39), 204 (29), 203 (36), 202 (31), 191 (100), 189 (38), 165 (19); HRMS calcd for $\mathrm{C_{20}H_{22}O}$ 278.16706, found 278.16657; *9,9′-bis(9,10-dihydro-10-spiro[cyclopropaneanthracene])* (**19**, 0.062 g, 1%), mp 249–51 °C; *9,10-dihydro-9-tert-butoxy-10-[γ-(spirobutyro-γ-lactone)anthracene* (**17**, 0.48 g, 10% yield), mp 262–4 °C (from acetone); ^{1}H NMR (CDCl$_3$) δ 1.22 (s, 9 H, $\mathrm{C(C}H_3)_3$), 2.73 (s, 4 H, $\mathrm{C}H_2\mathrm{C}H_2$), 5.47 (s, 1 H, $\mathrm{C}H$), 7.00–7.62 (m, 8 H, H_{arom}); mass spectrum, *m/e* (rel intens) 322 (M$^+$, 1), 266 (10), 249 (100), 205 (34), 193 (54), 165 (83); HRMS calcd for $\mathrm{C_{21}H_{22}O_3}$: 322.15689. Found: 322.15723.

(ii) In benzene. A degassed solution of **12** (4.83 g, 15 mmol) in benzene (60 mL) in a sealed vial was maintained at 80 °C for 6 days. After the same work up described for the decomposition in chlorobenzene, the reaction gave the following compounds: *9-vinylanthracene* (0.19 g, 6% yield), mp 65–6 °C; *9-ethylanthracene* (0.06 g, 2% yield), mp 58–9 °C; *aceanthracene* (trace amounts), mp 115–7 °C; *β-(9-anthryl)ethyl-tert-butyl ether* (1.25 g, 30% yield), mp 78–9 °C; the *starting perester* (**12**, 0.35 g, 7%); *9,9′-bis(9,10-dihydro-10-spiro[cyclopropaneanthracene]* (**19**, trace amounts); *9,10-dihydro-9-tert-butoxy-10-[γ-(spirobutyro-γ-lactone)]anthracene* (**17**, 1.2 g, 25% yield), mp 262–4 °C.

Decomposition of *tert*-Butyl β-[9-(10-Phenylanthryl)]perpropanoate (14). Using the same procedure previously described for **12**, the decomposition of **14** (5.6 g, 14.1 mmol) in chlorobenzene (50 mL) afforded *9-vinyl-10-phenylanthracene* (0.32 g, 8% yield), mp 109–11 °C (from light petroleum); ^{1}H NMR (CDCl$_3$) δ 5.50–6.25 (m, 2 H, $\mathrm{CH{=}C}H_2$), 7.02–8.00 (m, 12 H, H_{arom} and $\mathrm{C}H\mathrm{{=}CH_2}$), 8.32–8.70 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 280 (M$^+$, 100), 279 (41), 203 (55), 202 (26); HRMS calcd for $\mathrm{C_{22}H_{16}}$ 280.12520, found 280.12471; *9-ethyl-10-phenylanthracene* (0.20 g, 5% yield), mp 107–9 °C (lit.[47] mp 110 °C); *10-phenylaceanthracene* (0.20 g, 5% yield), mp 126–8 °C; *β-[9-(10-phenylanthryl)]ethyl-tert-butyl ether* (2.0 g, 40% yield), mp 169–71 °C (from light petroleum/benzene 1:1 v/v); ^{1}H NMR (CDCl$_3$) δ 1.27 (s, 9 H, $\mathrm{C(C}H_3)_3$), 3.62–4.25 (m, 4 H, $\mathrm{C}H_2\mathrm{{-}C}H_2$), 7.13–7.93 (m, 11 H, H_{arom}), 8.33–8.68 (m, 2 H, H_{arom}); mass spectrum, *m/e* (rel intens) 354 (M$^+$, 50), 281 (19), 280 (19), 279 (14), 267 (100), 265 (27), 252 (31); HRMS calcd for $\mathrm{C_{26}H_{26}O}$ 354.19836, found 354.19756; an unidentified compound of general formula $C_{23}H_{18}O_2$ (0.69 g, 15% yield), mp 203–5 °C (from benzene); ^{1}H NMR (CDCl$_3$) δ 1.47–2.78 (m, 4 H), 5.33 (s, 1 H), 6.77–7.70 (m, 13 H, H_{arom}); mass spectrum, *m/e* (rel intens) 326 (M$^+$, 60), 271 (100), 267 (12), 193 (13), 165 (13); HRMS calcd for $\mathrm{C_{23}H_{18}O_2}$ 326.13068, found 326.13107.

Reaction of 9,10-Dihydro-9-spiro[cyclopropaneanthracene] with DPDC. A 1 M benzene solution of DPDC (5 mL, 5 mmol) containing 9,10-dihydro-9-spiro[cyclopropaneanthracene] (1.05 g, 5 mmol) was degassed and then kept at 70 °C under a nitrogen atmosphere until the peroxide disappeared (ca. 15 h). The solvent was removed under vacuum, and the residue chromatographed to afford the following compounds: *9-ethylanthracene* (0.10 g, 10% yield), mp 58–9 °C (lit.[46] mp 59 °C); *9,9′-bis-(9,10-dihydro-10-spiro[cyclopropaneanthracene])* (**19**, 0.82 g, 80% yield) mp 249–51 °C; *9,10-anthraquinone* (0.052 g, 5% yield), mp 284–6 °C.

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Supplementary Material Available: Tables of crystallographic data and bonding parameters for compound **19**, including fractional atomic coordinates, thermal parameters, bond angles, bond distances, and torsion angles (4 pages); structure factors for **19** (6 pages). Ordering information is given on any current masthead page.

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