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Stannous Chloride Mediated Formation of (9-Anthryl)methyl Dimers from (Halogenomethyl)anthracenes. Ground-State and Adiabatic Excited-State Reversibility of Intramolecular [4 + 2] Cycloadditions

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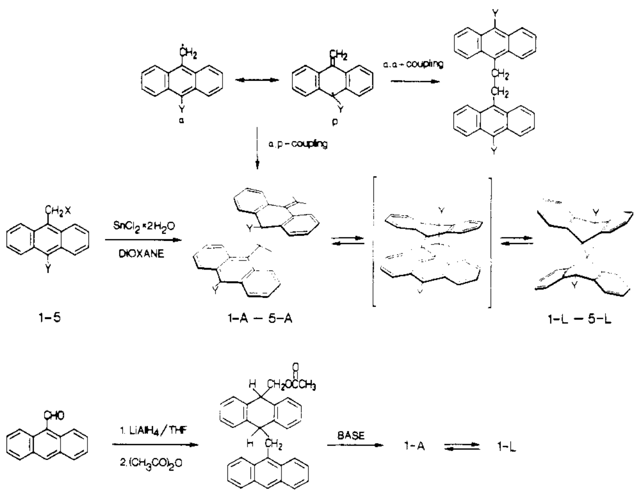
9-(Halogenomethyl)anthracenes react with stannous chloride dihydrate in dioxane solution to give tetrabenzotetracyclotetradecatetraenes ("lepidopterenes") in excellent yields. The involvement of [(9-anthryl)methyl]tin trihalides in the reaction is suggested, and the reversibility of intramolecular Diels–Alder additions of (9-anthryl)methyl *α,p* dimers is discussed. Novel (9-anthryl)methyl *p,p* dimers are found to rearrange into their *α,p* isomers and, consequently, into lepidopterenes. Upon photoexcitation, lepidopterenes undergo adiabatic cycloreversion as evidenced by exciplex emission near 600 nm.

The reductive dehalogenation of 9-(iodomethyl)anthracenes in dioxane in the presence of hydrochloric acid typically exemplifies the application of stannous chloride dihydrate as reducing agent in organic chemistry.[1] We have recently noted, however, that the reaction of stannous chloride with 9-methyl-10-(iodomethyl)anthracene (**2b**; X = I, Y = CH_3) in dioxane in the absence of hydrochloric acid does not give 9,10-dimethylanthracene but affords, by dehalogenative dimerization, the tetracyclic hydrocarbon dimethyllepidopterene (**2-L**, Y = CH_3).[2] Its formation was suggested to involve the 10-methyl-substituted (9-anthryl)methyl radical *α,p* dimer **2-A** (Y = CH_3) undergoing intramolecular Diels–Alder addition (see Scheme I). Conclusive evidence for the final step of the reaction sequence was obtained by the straightforward synthesis of the (9-anthryl)methyl *α,p* dimer **1-A** (Y = H) from 9-anthraldehyde. Indeed, **1-A** was found to be nonisolable at room temperature as the spontaneous intramolecular $[4_\pi + 2_\pi]$ cycloaddition gave the parent hydrocarbon lepidopterene (**1-L**, Y = H). Theretofore, **1-L** and **2-L** had been obtained inadvertently and sporadically as byproducts in the synthesis of the corresponding 1,2-bis(9-anthryl)ethanes, notably by reaction of the appropriate 9-(halogenomethyl)anthracenes with Grignard reagents.[3]

Scheme I



In the present paper, we report on the reaction of 9-(halogenomethyl)anthracenes with stannous chloride dihydrate and on the formation and cycloreversion of substituted lepidopterenes.

Results and Discussion

Addition of stannous chloride dihydrate (1 molar equiv) to a suspension of 9-(chloromethyl)anthracene (**1a**) or 9-(bromomethyl)anthracene (**1b**) in dioxane at 70 °C gives a yellow solution from which colorless crystals precipitate within minutes. Workup by addition of methanol, filtration, and recrystallization affords lepidopterene (**1-L**) in about 70% yield. A variety of 10-substituted 9-(halogenomethyl)anthracenes, **2**–**5** were found to react with

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(1) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1113.

(2) Becker, H.-D.; Sandros, K.; Arvidsson, A. *J. Org. Chem.* **1979**, *44*, 1336.

(3) Felix, G.; Lapouyade, R.; Castellan, A.; Bouas-Laurent, H.; Gaultier, J.; Hauw, C. *Tetrahedron Lett.* **1975**, 409. We have adopted the name "lepidopterene" which was proposed by these authors. The tetracyclic parent hydrocarbon lacking the benzo substituents of lepidopterene has been synthesized recently and was named $[2.2.2]^2$geminane: Park, H.; King, P. F.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 4773.

0022-3263/80/1945-4549$01.00/0

Table I. Dehalogenative Dimerization of 9-(Halogenomethyl)anthracenes 1–5 by $SnCl_2$

	X	Y	product	yield, %
1a	Cl	H	1-L	69
1b	Br	H	1-L	76
2a	Cl	CH_3	2-L	89
2b	I	CH_3	2-L	65
3	Cl	CH_2CH_3	3-L	81
4	Br	CH_2-C_6H_5	4-L	78
5	Br	C_6H_5	5-L	34

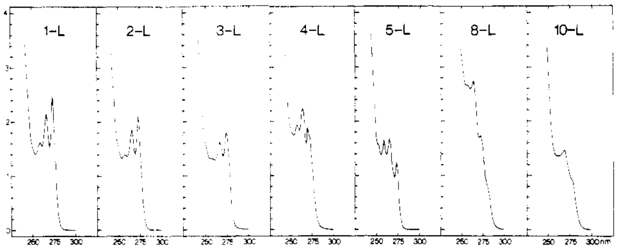


Figure 1. Electronic absorption spectra of lepidopterenes in cyclohexane solution.

stannous chloride in analogous manner to give substituted lepidopterenes **2-L**–**5-L** (cf. Table I).

The structures of **1-L**[4,5] and **2-L**[5] have been verified by X-ray methods, and the structures of **3-L**–**5-L** are supported by spectroscopic data. In the 270-MHz ^1H NMR spectra of **1-L**–**5-L**, the four different aromatic hydrogens of the lepidopterene skeleton are distinguishable by their different chemical shifts in conjunction with the typical splitting pattern (ortho coupling, 7 Hz; meta coupling about 1 Hz). Summarized in Table II are the ^1H NMR spectral data of **1-L**–**5-L**. In the ^1H NMR spectrum of diphenyllepidopterene (**5-L**), the ortho and meta protons of the phenyl substituent are pairwise equivalent, suggesting the rotation barrier to be lower than might be anticipated from molecular-model considerations.

The electronic absorption spectra of lepidopterenes are typical of the benzenoid chromophore and are characterized by vibrational fine structure (see Figure 1). Unsubstituted lepidopterene, we have pointed out previously,[2,6] is in temperature-dependent equilibrium with its Diels–Alder precursor **1-A**. At 25 °C in toluene solution, the equilibrium ratio of [**1-L**]:[**1-A**] is 630. Consequently, the electronic absorption of **1-A** due to its inherently strong $S_0 \rightarrow S_2$ transition around 250 nm contributes to the absorption spectrum of dissolved **1-L**. The presence of **1-A** in solutions of **1-L** is spectroscopically detectable by absorption around 350 nm, typical of the $S_0 \rightarrow S_1$ transition of anthracenes, and by the corresponding fluorescence spectrum (Figure 2). By contrast, the room-temperature equilibria of bridgehead-substituted lepidopterenes **2-L**–**5-L** are shifted far more to the side of the cycloaddition products. For example, the equilibrium ratio of [**2-L**]:[**2-A**] at 25 °C in toluene exceeds 10^7 (cf. Table III).

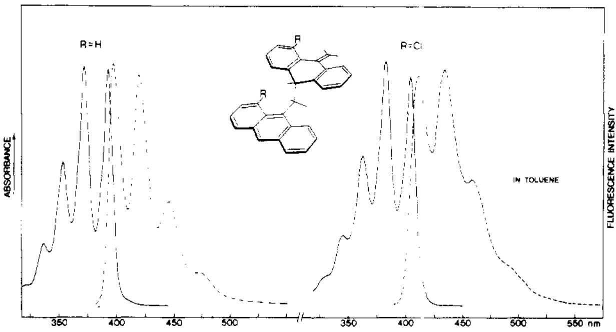


Figure 2. Electronic absorption (solid line) and emission spectra (dashed line) of **1-A** and **8-A** in toluene solution.

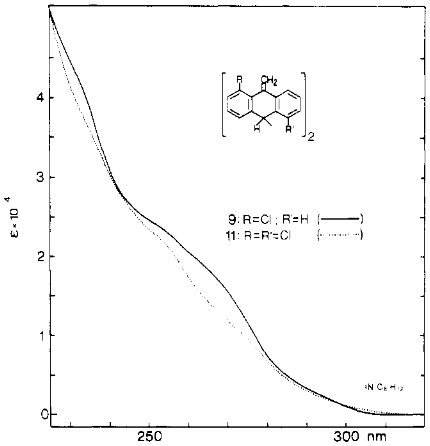
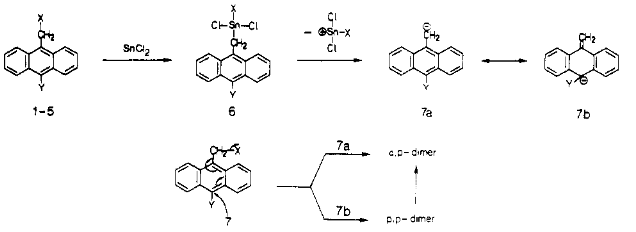


Figure 3. Electronic absorption spectra of *p,p* dimers **9a,b** (solid line) and **11a,b** (dotted line) in cyclohexane solution.

Scheme II



As for the mechanism of dehalogenative dimerization of 9-(halogenomethyl)anthracenes **1–5** by stannous chloride (Scheme II), a free-radical process appears unlikely in view of the negligible formation of 1,2-bis(9-anthryl)ethanes. Conceivably, 9-(halogenomethyl)anthracenes react with stannous chloride to give [(9-anthryl)methyl]tin trihalides **6** whose ionic dissociation may generate the (9-anthryl)methyl anions **7**.[7] Reaction of either **6** or **7** with 9-(halogenomethyl)anthracenes **1–5** to give the *α,p* dimers **1-A**–**5-A** by ionic substitution appears reasonable to us.[8]

There obviously exists, besides by way of *α,p* radical coupling or ionic substitution, a route to (9-anthryl)methyl *α,p* dimers which involves primary formation of thermodynamically less stable *p,p* dimers and their subsequent rearrangement.[9] Thus, 1-chloro-9-(bromomethyl)anthracene (**8**) was found to react with stannous chloride in dioxane to give as major product the *p,p* dimer **9** (56%

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(4) Gaultier, J.; Hauw, C.; Bouas-Laurent, H. *Acta Crystallogr., Sect. B*, **1976**, *B32*, 1220.

(5) In connection with a study on the relationship between fluorescence and molecular geometry, crystal structure analyses were carried out on a metastable modification of **1-L**, on **2-L**, and on two modifications of **10-L-1**: Becker, H.-D.; White, A. H.; et al., to be submitted for publication; cf. ref 6.

(6) Becker, H.-D.; Sandros, K. *Chem. Phys. Lett.* **1978**, *55*, 498.

(7) Stannous chloride is known to react with alkyl halides in the presence of trialkylantimony catalysts to give alkyltin trihalides: Bulten, E. J. *J. Organomet. Chem.* **1975**, *97*, 167. For a review, see: Bähr, G.; Pavlenko, S. In "Methoden der Organischen Chemie (Houben-Weyl)"; Kropf, H., Ed.; Georg Thieme Verlag: Stuttgart, 1978; Vol. 13, Part 6, p 181.

(8) The formation of **1-A** and, consequently, lepidopterene by an analogous reaction involving [(9-anthryl)methyl]magnesium halides had been proposed by: Henderson, W. W. Ph. D. Thesis, University of Minnesota, 1962.

(9) Concerning different modes of benzyl radical dimerization, see: Zahradnik, R.; Carsky, P. *Prog. Phys. Org. Chem.* **1973**, *10*, 327; Langhals, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543.

Scheme III

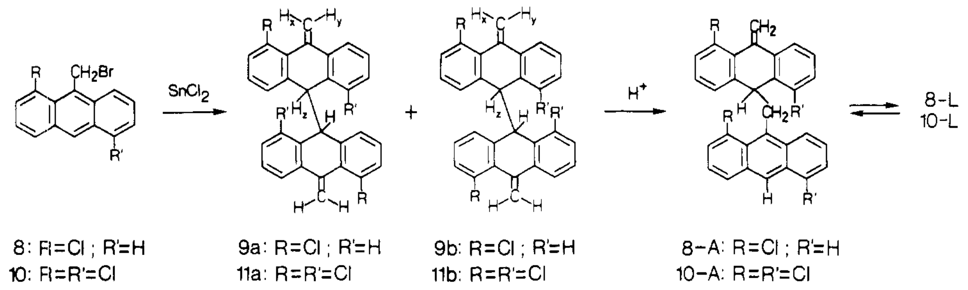


Table II. 270-MHz ^{1}H NMR Spectral Data (δ) of Lepidopterenes 1-L-5-L

	1-L	2-L	3-L	4-L[b]	5-L[b]
CH_2	2.90 (d, $J = 2.7$ Hz)	2.72 (s)	2.74 (s)	2.84 (s)	3.37 (s)
Y	4.63 (t, $J = 2.7$ Hz, H)	2.22 (s, CH_3)	2.78 (q, CH_2), 164 (t, $J = 7.5$ Hz, CH_3)	7.44 (d, H_a), 7.34-7.25 (m, $J = 6.9$ Hz, H_b, H_c), 4.24 (s, CH_2)	7.84 (d, H_a), 7.68 (t, H_b), 7.57 (t, H_c, $J = 7.4$ Hz)
aromatic H[a]	7.33 (dd), 6.99 (td), 6.80 (td), 6.72 (br d)	7.34 (dd), 7.02 (td), 6.80 (td), 6.73 (br d)	7.33 (d), 7.00 (t), 6.79 (t), 6.76 (d)	7.33 (d), 6.93 (t), 6.79 (t), 6.70 (d)	6.95-6.75

[a] $J_{o\text{-H}} = 7$ Hz; $J_{m\text{-H}} = 1$ Hz. [b] For Y the atom labeling is as follows:

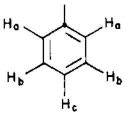
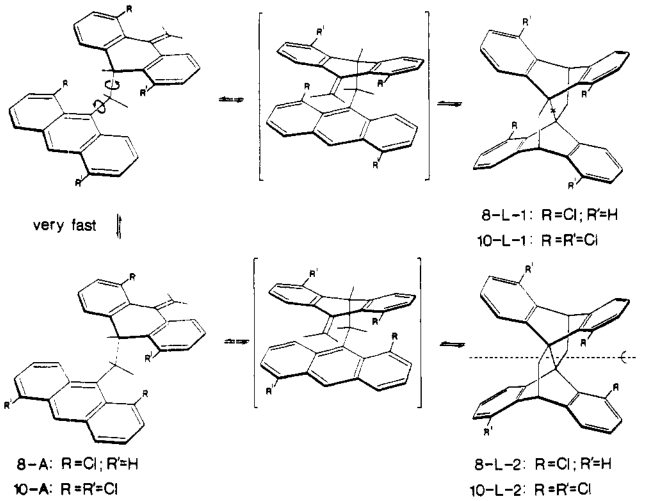


Table III. Equilibrium Constants for the Reaction A ⇄ L in Toluene at 25 °C

compd	[L]/[A]	compd	[L]/[A]
1-L	630	5-L	2×10^4
2-L	$>1 \times 10^7$	8-L	63
3-L	$>2 \times 10^6$	10-L	790
4-L	3×10^5	12-L	3×10^4

Scheme IV



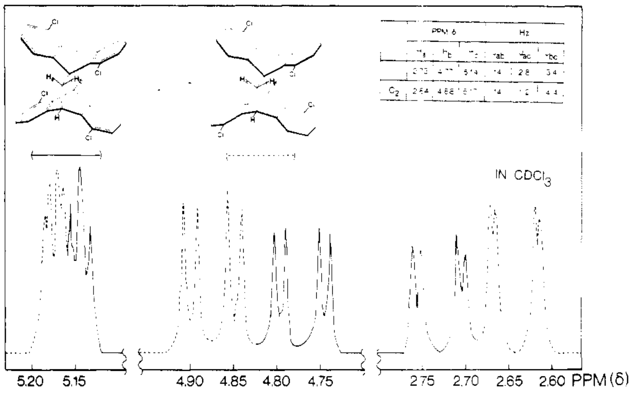


Figure 4. ABX portion of the 270-MHz ^{1}H NMR spectra of tetrachlorolepidopterenes 10-L-1 (solid line) and 10-L-2 (dashed line) in $CDCl_3$.

yield; see Scheme III). Dimer **9** was obtained as a mixture of isomers **9a** and **9b** (meso and racemic form, respectively) which we have not been able to separate. The structure of **9** is supported by the electronic absorption spectrum (Figure 3) and by the deceivingly "simple" ^{1}H NMR spectrum in which the chemical shifts of the methylidene protons (H_x/H_y) of the meso form differ from those of the racemic form, but the chemical shifts of all other protons appear to be the same in both isomers (cf. Table IV).

Treatment of *p,p* dimer **9** with hydrochloric acid in acetic acid solution smoothly afforded a mixture of the two possible dichlorolepidopterenes **8-L-1** and **8-L-2** of inversion and C_2 symmetry, respectively (cf. Scheme IV). Attempts to separate the two isomers have not been successful, but the ^{1}H NMR spectral data of the mixture (see Experimental Section) are in agreement with the assigned structures. We have found no evidence for homolytic dissociation of *p,p* dimer **9** at room temperature. Con-

Table IV. 270-MHz ^{1}H NMR Spectral Data of *p,p* Dimers 9a,b and 11a,b

	9a,b		11a,b	
	isomer 1	isomer 2	isomer 1	isomer 2
H_x	5.96 (d, $J_{xy} < 1$ Hz)	5.94 (d, $J_{xy} < 1$ Hz)	5.76 (s)	5.70 (s)
H_y	5.76 (d, $J_{xy} < 1$ Hz)	5.77 (d, $J_{xy} < 1$ Hz)	5.46 (s)	5.56 (s)
H_z	4.02 (s)	4.02 (s)	4.89 (s)	4.86 (s)
aromatic H	6.30-7.53		6.12-7.39	

Table V. Luminescence Properties of Lepidopterenes[a]

	1-L	2-L	3-L	4-L	5-L	8-L[b]	10-L[b]	12-L
quantum yield of emission from L^*	0.005	0.013	0.025	0.003	0.003	$<10^{-4}$	$<10^{-4}$	0.002
quantum yield of emission from E^*	0.58	0.54	0.28	0.34	0.52	0.15[c]	0.17[c]	0.39
λ_{max} of emission from E^*, nm	597	573	573	584	607	628	628	610

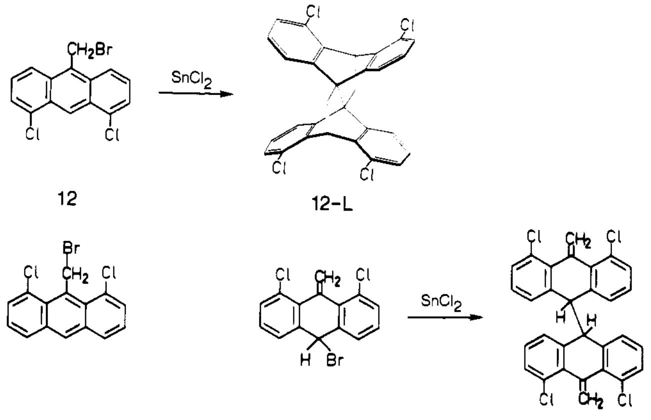
[a] In cyclohexane solution at room temperature. [b] Mixture of i and C_2 isomers. [c] Excitation wavelength 230 nm. In 8-L and 10-L the chloro substituents are situated so as to poke into the aromatic π system. In both these cases, E^* formation from higher vibronic levels of the excited singlet state competes more favorably and very fast radiationless deactivation processes. In all other lepidopterenes, the quantum yield of exciplex luminescence is independent of the wavelength of excitation.

ceivably, the acid-catalyzed rearrangement of **9** into the α,p dimer **8-A** (i.e., the Diels–Alder precursor of **8-L-1** and **8-L-2**) proceeds intramolecularly by a mechanism which is ionic in nature.[10]

From the reaction of 1,5-dichloro-9-(bromomethyl)anthracene (**10**) with stannous chloride, a mixture of isomeric (meso and racemic) *p,p* dimers **11** was isolable (see Experimental Section). The structural relationship between dimers **9** and **11** is apparent from a comparison of their electronic absorption spectra (Figure 3) and from ^{1}H NMR spectral data (see Table IV). Furthermore, analogous to the formation of dichlorolepidopterens **8-L-1**/**8-L-2** by acid-catalyzed rearrangement of **9**, treatment of *p,p* dimers **11** with mineral acid gave a mixture of isomeric tetrachlorolepidopterenes **10-L-1** and **10-L-2** of inversion and C_2 symmetry, respectively. Significantly, by slow crystallization from xylene solutions of the mixture of isomeric **10-L-1** and **10-L-2** only *one* isomer, namely, that of inversion symmetry[5] (**10-L-1**), was obtained, permitting unambiguous assignment of the ^{1}H NMR ABX spectra to the respective isomers. The ^{1}H NMR spectroscopic investigation of **10-L-1** furthermore revealed equilibration of the inversion (i) isomer with its C_2 isomer **10-L-2** (Figure 4). Lepidopterenes **10-L-1**/**10-L-2**, just like **8-L-1**/**8-L-2**, differ from lepidopterenes **1-L**–**5-L** by the absence of the mirror plane symmetry element, and the interconversion of the i and C_2 isomers is explicable by the reversibility of their formation by intramolecular Diels–Alder addition involving different rotamers of a common cycloreversion product (A; see Scheme IV). At 20 °C, the relaxation time for the equilibration is 170 min, and the equilibrium ratio of [**10-L-1**]:[**10-L-2**] is about 0.8. From the temperature dependence of the equilibration, the activation energy associated with the cycloreversion of **10-L-1** into **10-A** was calculated to be 11 kcal/mol, the enthalpy difference between the C_2 isomer **10-L-2** and the centrosymmetric isomer **10-L-1** being 1.9 kcal/mol.

Steric factors, most likely, are of importance in affecting the course of stannous chloride mediated (9-anthryl)methyl dimerization. Thus, bromination of 4,5-dichloro-9-methylanthracene smoothly affords 9-(bromomethyl)-4,5-dichloroanthracene (**12**) whose dehalogenative dimerization by stannous chloride gives peritetrachlorolepidopterene **12-L** (Scheme V). By contrast, bromination of 1,8-dichloro-9-methylanthracene does not give 9-(bromomethyl)-1,8-dichloroanthracene (**13**) but its isomer **14**. Upon treatment with stannous chloride, **14** undergoes dehalogenative *p,p* dimerization to give **15**.

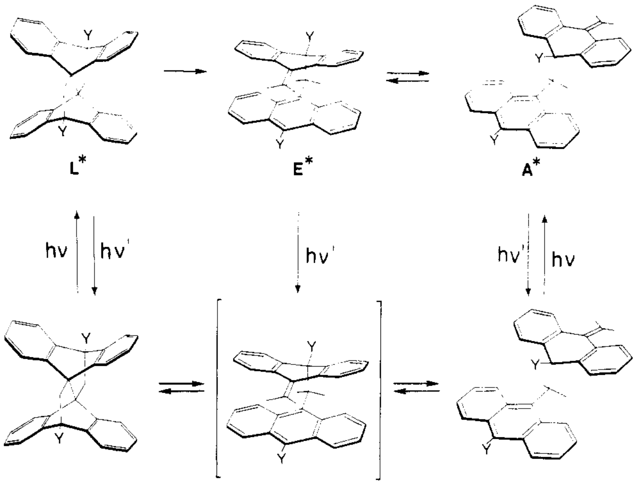
Scheme V



12 12-L

13 14 15

Scheme VI



Concerning the temperature-dependent equilibrium of chloro-substituted lepidopterenes with their retro Diels–Alder products A, the spectroscopically determined equilibrium ratios of [L]:[A] at 25 °C in toluene are 63, 790, and 3 × 10^4 for **8-L**, **10-L**, and **12-L**, respectively. Consequently, the presence of **8-A** and **10-A** in solutions of **8-L-1**/**8-L-2** and **10-L-1**/**10-L-2**, respectively, is easily detectable by the structured absorption around 370 nm and by the corresponding emission (see Figure 2 and Figure 6). As discussed for **1-L**, hidden under the absorption of **8-L** and **10-L** (Figure 1) is the absorption due to the $S_0 \rightarrow S_2$ transition of the respective cycloreversion product.

From a photochemical point of view, the lepidopterenes described in this paper are unique insofar as their excited-state cycloreversion occurs adiabatically (see Scheme VI), i.e., by a process which, in general, is rarely observed at room temperature.[6,11] Thus, all lepidopterenes were

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[10] Cf. the intramolecular rearrangement of *p*-quinamines: Miller, B. *J. Am. Chem. Soc.* **1964**, *86*, 1127.

[11] Turro, N. J.; Mcvey, J.; Ramamurthy, V.; Lechtken, P. *Angew. Chem.* **1979**, *91*, 597.

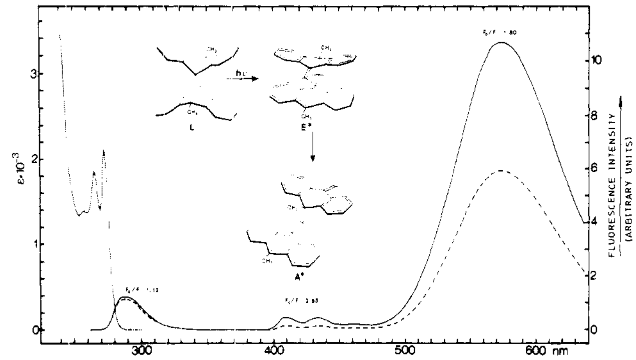

Figure 5. Absorption spectrum (dotted line) and triple emission spectrum of dimethyllepidopterene (2-L) in deaerated (solid line) and air-saturated (dashed line) cyclohexane solution at room temperature.

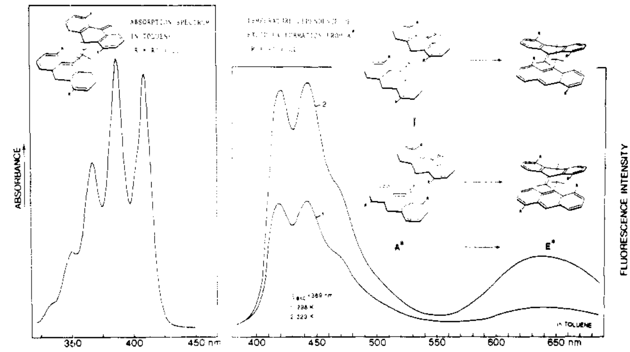

Figure 6. Absorption spectrum of **10-A** and its dual emission spectrum at 298 K (curve 1) and at 323 K (curve 2) in toluene solution. As a consequence of the substitution pattern of **10-A**, the formation of two different exciplexes E* is possible.

found to exhibit exciplex luminescence near 600 nm (see Table V). For example, photoexcitation of dimethyllepidopterene (**2-L**, λ_{exc} 276 nm) in cyclohexane at room temperature gives rise to prominent emission from its cycloreversion product **2-E*** of exciplex geometry ($\lambda_{em}{}^{max}$ 573 nm; luminescence quantum yield 0.54; see Figure 5). Radiative deactivation from the locally excited state **2-L*** ($\lambda_{em}{}^{max}$ 287 nm) and formation of the electronically excited retro-Diels–Alder product **2-A*** (structured emission around 425 nm) are of minor importance (cf. Table V). The adiabatic formation of **2-A*** in the reaction sequence L* → E* → A* is deducible from the observed ratios of the quantum yields in oxygen-free (F_0) and air-saturated (F) solution. The activation energy associated with the generation of **2-A*** from **2-E*** was found to be 9.3 kcal/mol.[12]

In the case of lepidopterenes **1-L**, **8-L**, and **10-L**, their ground-state equilibrium ratio [L]:[A] made it possible to generate the A* state by selective excitation around 375 nm of the corresponding retro-Diels–Alder products A. Radiative deactivation of A* to its Franck–Condon ground state was found to be highly efficient (84% in the case of **1-A***; cf. Figure 2); however, also detectable spectroscopically is the adiabatic process A* → E*. For example, selective photoexcitation of **10-A** (λ_{exc} 369 nm) clearly gives rise to emission from both the locally excited state **10-A*** and from the exciplex state **10-E*** (see Figure 6). The activation energy associated with the conversion of **10-A*** into **10-E*** was found to be 4 kcal/mol. In the case of **8-A***, its conversion into **8-E*** has an activation energy of 5.7 kcal/mol. The analogous process in the case of the parent compound **1-A** is associated with an activation energy of 10.3 kcal/mol and had previously[6] escaped detection.

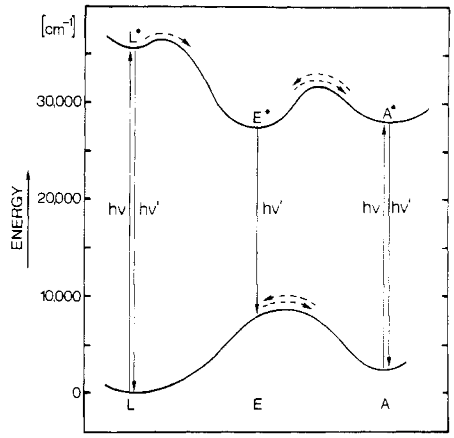

Figure 7. Ground-state and excited-state potential energy diagram relating to the formation and cycloreversion of lepidopterenes. The energy scale applies to the parent lepidopterene **1-L** and its cycloreversion product.

In summary, the photochemistry of lepidopterenes is characterized by efficient reversibility as schematically outlined in Figure 7 by the excited-state and ground-state potential energy curves. Clearly affected by the substituents of the lepidopterene skeleton are the activation barriers between the various states involved in the equilibria. Apparently, the geometrical prerequisites for the formation of luminescent exciplexes by photochemical cycloreversion of lepidopterenes are ideal, as are the geometrical conditions for the ground-state intramolecular [4 + 2] cycloaddition of (9-anthryl)methyl α,p dimers.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. Elemental analyses were performed by NOVO Microanalytical Laboratory. ^{1}H NMR spectra were recorded on a Bruker 270 instrument, and chemical shifts are given in parts per million downfield from Me_4Si. Absorption and emission spectra were obtained on a Beckman Acta III spectrophotometer and an Aminco SPF 500 (corrected spectra) spectrofluorometer, respectively.

Equilibrium Constants. In the case of **1-L**, **5-L**, **8-L**, and **10-L**, the equilibrium ratios of [L]:[A] were determined by absorption spectroscopy by assuming the molar extinction coefficient of the respective Diels–Alder precursor to be the same as that of the corresponding 10-Y-substituted 9-methylanthracene. The equilibrium constants of **2-L**, **3-L**, and **4-L** were determined emission spectroscopically by employing 10^{-2} M solutions (excitation wavelengths around 360 nm) and by assuming the fluorescence quantum yields of **2-A**, **3-A**, and **4-A** to be the same as that of **1-A** (0.84).[6]

9-(Halogenomethyl)anthracenes. **1a**,[13] **1b**,[14] **2a,b**,[15] **3**,[16] **4**,[17] **5**,[18] and **10**[19] were prepared according to the literature.

1-Chloro-9-(bromomethyl)anthracene (8). A solution of bromine (1.38 g, 8.6 mmol) in carbon disulfide (5 mL) was added to a stirred solution of 1-chloro-9-methylanthracene[20] (1.95 g, 8.6 mmol) in carbon disulfide (10 mL). A stream of nitrogen was

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[12] A detailed study of the photophysical properties of substituted lepidopterenes is in progress.

[13] Stewart, F. H. C. *Aust. J. Chem.* **1960**, *13*, 478.

[14] Akiyama, S.; Nakusuji, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2231.

[15] Badger, G. M.; Pearce, R. S. *J. Chem. Soc.* **1950**, 2314.

[16] By chloromethylation of 9-ethylanthracene; cf. ref 8, 17.

[17] Gibson, S.; Mosnaim, A. D.; Nonhebel, D. C.; Russell, J. A. *Tetrahedron* **1969**, *25*, 5047.

[18] Barnett, E. d. B.; Mathews, M. A. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1429.

[19] Barnett, E. d. B.; Cook, J. W.; Mathews, M. A. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2863.

[20] Bouas-Laurent, H.; Lapouyade, R. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 6922.

bubbled through the reaction mixture to remove part of the hydrogen bromide. After addition of petroleum ether (20 mL; bp 40–60 °C), the yellow crystalline precipitate was removed by filtration: yield 1.8 g (68%); mp 133–135 °C; ^{1}H NMR ($CDCl_3$, 0 °C) 5.45 (d, J = 11 Hz, 1 H), 6.64 (d, J = 11 Hz, 1 H), 7.29–8.58 (m, 8 arom H). By dynamic NMR, the barrier of rotation around the 9-anthryl–bromomethyl bond was calculated[21] to be 14.5 kcal/mol.[22] Anal. Calcd for $C_{15}H_{10}BrCl$ (mol wt 305.59): C, 58.96; H, 3.30. Found: C, 59.13; H, 3.85.

Lepidopterenes. The dehalogenative dimerization of 9-(halogenomethyl)anthracenes **1–5** with stannous chloride was carried out according to a standard experiment. Treatment of the crude reaction product with activated charcoal removed small amounts of fluorescent byproducts whose presence interfered with the emission spectroscopic investigation of the lepidopterenes.[12] In the case of diphenyllepidopterene (**5-L**), the elemental analysis gave a carbon value which was about 2% too low, as the compound retained solvent of recrystallization. Therefore, the molecular composition of **5-L** was ascertained by high-resolution mass spectrometry. The melting points of lepidopterenes were found to vary with the rate of heating, probably because of the thermal rearrangement of lepidopterenes into dianthrylethanes.

Lepidopterene (1-L). Standard Experiment. Powdered stannous chloride dihydrate (1.13 g, 5 mmol) was added to a stirred solution of 9-(bromomethyl)anthracene (1.36 g, 5 mmol) in dioxane (15 mL) at 70 °C under nitrogen. An orange-brown solution formed immediately, and after 2 min, a colorless crystalline product precipitated. The reaction mixture was kept at 70 °C for 30 min and then diluted with methanol (15 mL). Filtration gave a pale yellow product (820 mg) which was dissolved in methylene chloride and filtered to remove traces of insoluble material. The filtrate was treated twice with activated charcoal to give a colorless filtrate from which lepidopterene was precipitated by addition of methanol: yield 730 mg (76%); mp 317–323 °C (lit.[3] mp 298 °C; Henderson[8] reported 320–321 °C).

Dimethyllepidopterene (2-L). Colorless crystals were obtained from methylene chloride solution by addition of methanol; mp 308–312 °C (lit.[3] mp 345 °C). For details of the preparation of **2-L** from **2b**, see ref 2.

Diethyllepidopterene (3-L). Recrystallization from methylene chloride solution by addition of methanol gave colorless crystals, mp 292–295 °C (lit.[8] mp 308–310 °C). Anal. Calcd for $C_{34}H_{30}$ (mol wt 438.61): C, 93.11; H, 6.89. Found: C, 92.76; H, 6.76.

Dibenzyllepidopterene (4-L). Recrystallization from methylene chloride solution by addition of methanol gave colorless crystals, mp 256–260 °C. Anal. Calcd for $C_{44}H_{34}$ (mol wt 562.75): C, 93.91; H, 6.09. Found: C, 93.58; H, 5.96.

Diphenyllepidopterene (5-L). For removal of a fluorescent byproduct [according to NMR analysis, 1,2-bis(10-phenyl-9-anthryl)ethane], repeated treatment of **5-L** with activated charcoal was necessary. Recrystallization from methylene chloride solution by addition of methanol gave colorless crystals: mp 273–277 °C; high-resolution mass spectrum, m/e 534.2309, $C_{42}H_{30}$ requires m/e 534.2347.

Reaction of 1-Chloro-9-(bromomethyl)anthracene with Stannous Chloride. Powdered stannous chloride dihydrate (1 g) was added to a solution of **8** (1 g) in dioxane (10 mL) at 45 °C. Filtration after 2 h at 45 °C gave 20 mg of insoluble dichlorolepidopterene **8-L-1**/**8-L-2** (vide infra). Addition of methanol (25 mL) to the yellow-orange filtrate gave a colorless crystalline precipitate which was recrystallized by being dissolved in ether and precipitated with methanol: yield 417 mg (56%) of isomeric **9a,b**; mp 170–180 °C dec. Anal. Calcd for $C_{30}H_{20}Cl_2$ (mol wt 451.40): C, 79.83; H, 4.47. Found: C, 79.27; H, 4.49.

Acid-Catalyzed Rearrangement of 9a,b. Dichlorolepidopterenes 8-L-1/8-L-2. Concentrated hydrochloric acid (1 mL) was added to a boiling solution of **9a,b** (50 mg) in acetic acid (10 mL). After 5 min, a colorless crystalline precipitate formed. Filtration after 2 h gave dichlorolepidopterenes **8-L-1**/**8-L-2**: 40 mg (80% yield); mp ~265 °C dec. Recrystallization from toluene or xylene always gave the mixture of isomers. In $CDCl_3$ at 25 °C, the ^{1}H NMR spectroscopically determined ratio of [**8-L-1**]:[**8-L-2**] was about 0.6. Listed in Table VI are relevant ^{1}H NMR spectral data. As for the assignment of the spectra to the respective isomers, we have assumed the chemical shift differences in the ABX spectrum of the centrosymmetric **8-L-1** to be analogous to those of **10-L-1**, which was analyzed by X-ray crystallography.

Table VI. ^{1}H NMR Spectral Data of **8-L-1**, **8-L-2**, **10-L-1**, and **10-L-2** (Cf. Figure 4)

	chemical shift, δ				coupling const, Hz		
	H_a	H_b	H_c	aromatic H	J_{ab}	J_{ac}	J_{bc}
8-L-1	2.78	4.79	4.59	7.45–6.74	14	2.1	3.4
8-L-2	2.71	4.87	4.59		14	1.0	4.3
10-L-1	2.73	4.77	5.14	7.39–6.74	14	2.8	3.4
10-L-2	2.64	4.88	5.17		14	1.2	4.4

Reaction of 1,5-Dichloro-9-(bromomethyl)anthracene with Stannous Chloride. Powdered stannous chloride dihydrate (1.53 g) was added to a suspension of **10** (2.3 g) in dioxane (23 mL) at 70 °C under nitrogen to give a clear orange solution. Filtration after 2 h gave 10 mg of insoluble material which was not further investigated. Addition of methanol (15 mL) to the filtrate gave 740 mg of colorless crystalline precipitate which, according to ^{1}H NMR analysis, consisted of a mixture of *p,p* dimer **11a,b** (26%, based on **10**) and tetrachlorolepidopterenes **10-L-1**/**10-L-2** (16%, based on **10**). Separation of tetrachlorolepidopterene **10-L** from *p,p* dimer **11** was accomplished by fractional crystallization from methylene chloride in which **11a,b** is more easily soluble. The *p,p* dimer can be precipitated with methanol, and the ratio of meso and racemic forms can vary from fraction to fraction. The melting point of the *p,p* dimer, consequently, may vary as well (205–220 °C dec). Anal. Calcd for $C_{30}H_{18}Cl_4$ (mol wt 520.28): C, 69.26; H, 3.49. Found: C, 69.51; H, 3.61.

Acid-Catalyzed Rearrangement of 11a,b. Tetrachlorolepidopterenes 10-L-1/10-L-2. A stirred suspension of **11a,b** (80 mg) in acetic acid (7 mL) and concentrated hydrochloric acid (1 mL) was placed in a screw-cap vial and kept at 80 °C for 45 min. Filtration gave a colorless crystalline residue which was washed with methylene chloride to give 40 mg of insoluble product: yield 50%; mp 282–286 °C dec.[23] Anal. Calcd for $C_{30}H_{18}Cl_4$ (mol wt 520.28): C, 69.26; H, 3.49. Found: C, 68.81; H, 3.53. ^{1}H NMR spectral data of **10-L-1**/**10-L-2** are listed in Table VI. The partial ^{1}H NMR spectrum shown in Figure 4 is that of an equilibrium mixture at 25 °C. Isomer **10-L-1** was obtained from a solution of the isomer mixture by slow crystallization from xylene solution.

Reaction of 4,5-Dichloro-9-(bromomethyl)anthracene with Stannous Chloride. Peritetrachlorolepidopterene 12-L. Powdered stannous chloride dihydrate (1.13 g) was added to a stirred solution of **12**[24] (1.70 g) in dioxane (40 mL) at 90 °C under nitrogen to give an orange solution. After 15 min, a colorless precipitate formed. After 2 h, the reaction mixture was diluted with methanol (5 mL), and the pale yellow crystalline precipitate (944 mg) was removed by filtration. Recrystallization from 2.5 L of methylene chloride in the presence of charcoal gave 744 mg (57%) of colorless crystals: mp 300–310 °C dec; 270-MHz ^{1}H NMR ($CDCl_3$) 7.10 (d, 4 H, J = 8 Hz), 6.96 (t, 4 H, J = 8 Hz), 6.68 (d, 4 H, J = 8 Hz), 5.30 (t, 2 H, J = 3 Hz), 2.86 (d, 4 H, J = 3 Hz). Anal. Calcd for $C_{30}H_{18}Cl_4$ (mol wt 520.28): C, 69.26; H, 3.49. Found: C, 69.16; H, 3.37.

Reaction of 10-Bromo-1,8-dichloro-9-methylene-9,10-dihydroanthracene with Stannous Chloride. Powdered stannous chloride dihydrate (0.68 g) was added to a stirred suspension of **14**[24] (1.02 g) in dioxane (10 mL) at 70 °C under nitrogen. An orange solution formed immediately, and a colorless precipitate formed within 1 min. After 20 min, the reaction mixture was

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[21] Kost, D.; Carlson, E. H.; Raban, M. *Chem. Commun. 1971*, 656.

[22] The free energy of activation associated with the rotation around the aryl 9-bromomethyl bond in **10** also was found to be 14.5 kcal/mol.

[23] The reaction of **10** with methylmagnesium iodide has been reported (see ref 19) to give a colorless product melting at 287 °C. We have repeated the reaction and found the colorless reaction products to be identical with those we obtain from **10** by treatment with stannous chloride. As to whether the reaction of **10** with Grignard reagents leads to predominantly *p,p* dimers **11** or to tetrachlorolepidopterenes **10-L** appears to depend on the mode of workup which involves acidification.

[24] Barnett, E. d. B.; Goodway, N. F.; Wiltshire, J. L. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 472.

diluted with methanol (10 mL), and the colorless precipitate (637 mg) was removed by filtration. Recrystallization by dissolving the precipitate in methylene chloride followed by addition of methanol gave 561 mg (72%) of *p,p* dimer **15**, mp 307–311 °C. Its UV absorption spectrum in cyclohexane is virtually identical with that of *p,p* dimer **11**: 270-MHz ^{1}H NMR (CDCl$_3$) 7.28 (d, 4 H, J = 8 Hz), 6.85 (t, 4 H, J = 8 Hz), 6.40 (s, 4 H, methylene H), 6.27 (d, 4 H, J = 8 Hz), 4.01 (s, 2 H). Anal. Calcd for $C_{30}H_{18}Cl_4$ (mol wt 520.28): C, 69.26; H, 3.49. Found: C, 69.10; H, 3.56.

Thermodynamic and Kinetic Measurements. Thermodynamic and kinetic data for the equilibration of tetrachlorolepidopterenes **10-L-1** ⇄ **10-L-2** were obtained in CDCl$_3$ solution at 10, 25, and 35 °C by integration over the ABX spectra shown in Figure 4. The solubility of **10-L-1** in CDCl$_3$ is about 1 mg/mL.

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Registry No. 1a (X = Cl; Y = H), 24463-19-2; **1b** (X = Br; Y = H), 2417-77-8; **1L**, 55614-27-2; **2a** (X = Cl; Y = CH$_3$), 25148-26-9; **2b** (X = I; Y = CH$_3$), 27998-91-0; **2L**, 55657-77-7; **3**, 24451-22-7; **3L**, 74998-96-2; **4**, 24451-67-0; **4L**, 74998-97-3; **5**, 24451-66-9; **5L**, 74998-98-4; **8**, 74998-99-5; **8-L-1**, 75010-79-6; **8-L-2**, 75045-10-2; **9a**, 74999-00-1; **9b**, 75010-80-9; **10**, 74999-01-2; **10-L-1**, 74999-02-3; **10-L-2**, 75044-20-1; **11a**, 74999-03-4; **11b**, 74999-04-5; **12**, 74999-05-6; **12L**, 74999-06-7; **14**, 74999-07-8; **15**, 74999-08-9; stannous chloride, 7772-99-8; 1-chloro-9-methylanthracene, 4535-08-4.

Photosensitized Electron-Transfer-Induced Reactions of Some Cyclopropene Derivatives

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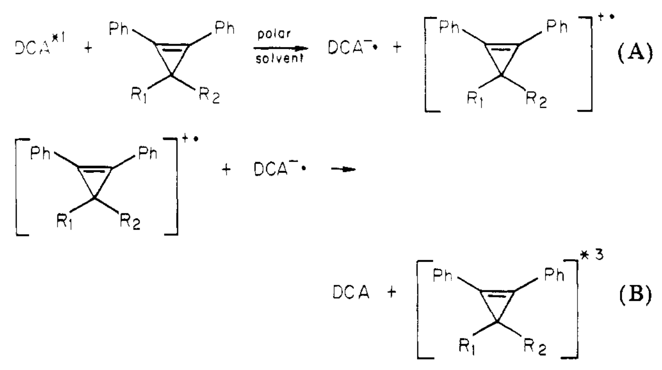
The 9,10-dicyanoanthracene-sensitized rearrangement of several 3-phenyl-substituted cyclopropenes to indenes in acetonitrile has been studied. When an unsymmetrically 1-phenyl-2-methyl-substituted cyclopropene was used, the major indene obtained corresponds to cleavage of the cyclopropene bond attached to the phenyl group. This stands in marked contrast to the results obtained on direct irradiation. The mechanism proposed to rationalize the results involves a number of steps. The first step consists of selective excitation of dicyanoanthracene. Step 2 involves an electron transfer which ultimately leads to a solvent-separated radical ion pair. The calculated ΔG value for this process indicates that the electron-transfer reaction should be spontaneous. The initially produced radical cation undergoes cleavage of the ring followed by a subsequent cyclization onto the ortho position of the neighboring aromatic ring. Reaction of the resulting radical cation with dicyanoanthracene radical anion leads to an isoindene which undergoes rearomatization. The radical cation path nicely accommodates the regioselectivity observed. Thus, ring opening occurs in the direction leading to the most stable radical cation.

Scheme I



The reactions of exciplexes and electron-transfer processes have attracted considerable attention in recent years.[1-5] It is clear that, in many cases where electronic energy transfer is endothermic, the primary process leading to quenching is formation of an exciplex, the stability of which should depend on the electron-donating and -accepting properties of the quencher and excited state, respectively. Whereas exciplexes are usually formed in nonpolar solvents, the formation of solvated radical ions occurs on irradiation in polar solvents. The electron-transfer reactions of cyclopropenes are particularly interesting because of the unusual intermediates that are involved. Independent work by Arnold[7] and Farid[8] has shown that the [2 + 2] photocycloaddition of cyclopropenes with electron-deficient olefins proceeds via an electron-transfer reaction. Diphenyl-substituted cyclopropenes have also been found to react with the singlet-state of 9,10-dicyanoanthracene (DCA*^{1}) at a diffusion-controlled rate to produce the radical ions of the cyclopropene and anthracene (see Scheme I).[7,8] The free-energy (ΔG) change for such a process, leading to the formation of a radical-ion pair, can be calculated from the Weller equation (eq 1).[3]

$$\Delta G_1 = (E_D^{Ox} - E_A^{Red}) - \Delta E(A^{*1}) \qquad (1)$$

In this expression E_D^{Ox} and E_A^{Red} are the electrochemically determined potentials for the one-electron oxidation of the donor and reduction of the acceptor, respectively. $\Delta E(A^{*1})$ is the zero–zero transition energy of the lowest excited singlet state of the acceptor. Substitution of the appropriate values into the Weller equation results in the conclusion that electron transfer from a diphenyl-substituted

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