Structural Effects Controlling the Rate of the Retro-Diels–Alder Reaction in Anthracene Cycloadducts

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We have undertaken a fairly broad study of how the structure of an anthracene cycloadduct affects the rate of its cycloreversion reaction. Based on the rate constants for retro-Diels–Alder (rDA) reactions of a variety of anthracene-type adducts conducted in diphenyl ether, we draw the following conclusions. The rDA reaction of anthracene cycloadducts is influenced by *diene* substituents in the following ways: (1) electron-donating groups increase the reaction rate, and the accelerating effect is subject to geometric modulation for a conjugating substituent like dimethylamino; (2) electron-withdrawing groups may decrease or increase the reaction rate, although the effect is rarely large; and (3) steric acceleration is relatively small and demonstrates an unprecedented bell-shaped structure–reactivity profile. Peripheral substitution of the adduct with siloxy groups results in a significant acceleration, even though the groups are three bonds removed from the reaction site. The same reaction is influenced by *dienophile* substituents in the following ways: (1) electron-withdrawing groups increase the rate of the reaction; (2) strongly conjugating substituents make the reaction much faster than predicted by classical electron-withdrawing or -donating ability due to a change to polar mechanism; and (3) there is no observable steric effect.

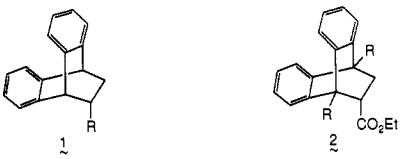
While the factors that influence the rate of the Diels–Alder (DA) reaction are rather well established, there remains little predictive ability in knowing at what temperature a retro-Diels–Alder (rDA)[1,2] reaction will occur. A survey of the substituent effect on the rDA reaction has not been reported; such information is essential to our group's work on the design of cycloaddition/cycloreversion-based catalysts.[3] In addition, recent syntheses in which rDA reactions played a key role[4] point to the need to understand how these reactions can be done at less than pyrolytic temperatures. Consequently, we have examined how the substitution of an anthracene cycloadduct affects the rate of its cycloreversion reaction; some of these results have been published previously in abbreviated form.[5]

Synthetic Methods

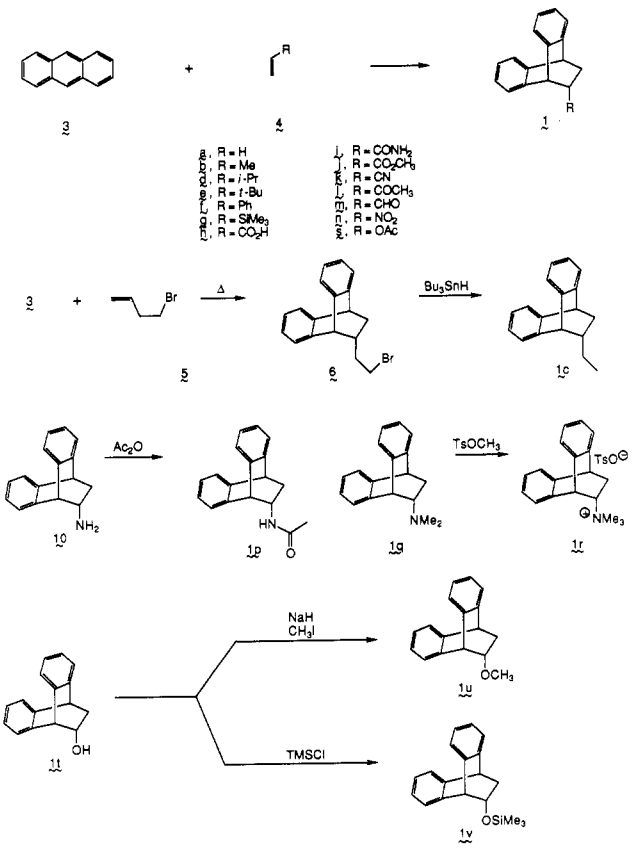
For this work, we required samples of cycloadducts variously substituted on the dienophile (**1**) and diene (**2**) portions of the adduct framework (Chart I). The compounds (43) used for kinetic studies are shown in Table I, together with a summary of the synthetic methods used for their preparation. As shown in Scheme I, many of the "dienophile-substituted" adducts could be prepared by direct cycloaddition of anthracene with the appropriate dienophile (**4a,b,d–n,s**). We prepared the ethyl adduct (**1c**) by reaction of 1-bromo-3-butene (**5**) with anthracene to afford the bromoethyl adduct (**6**), which was subsequently reduced with tri-*n*-butyltin hydride. Acylation of the amino adduct (**1o**) readily afforded acetamido adduct **1p**. Methylation of dimethylamino adduct **1q** gave the trimethylammonium tosylate **1r**; methylation of hydroxy adduct **1t** gave methoxy adduct **1u**. Reaction of hydroxy adduct **1t** with trimethylsilyl chloride provided siloxy adduct **1v**.

Most of the "diene-substituted" adducts were made by direct cycloaddition of a 9,10-disubstituted anthracene

Chart I



Scheme I



(1) For synthetic reviews of the retro-Diels–Alder reaction, see: (a) Ripoll, J.-L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. (b) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 229. (c) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415. (d) Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121. (e) Ichihara, A. *Synthesis* **1987**, 207.

(2) For mechanistic reviews of the retro-Diels–Alder reaction, see: (a) Reference 1c. (b) Smith, G. G.; Kelly, F. W. *Prog. Phys. Org. Chem.* **1971**, *8*, 201. (c) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(3) (a) Czarnik, A. W. *Tetrahedron Lett.* **1984**, *25*, 4875. (b) Nanjappan, P.; Czarnik, A. W. *J. Am. Chem. Soc.* **1987**, *109*, 1826.

(4) For example, see: (a) Knapp, S.; Ornaf, R. M.; Rodriques, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 5494. (b) Kodpinid, M.; Siwapinyoyos, T.; Thebtaranonth, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4862. (c) Anderson, W. K.; Milowsky, A. S. *J. Org. Chem.* **1985**, *50*, 5423. (d) Magnus, P.; Cairns, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 217.

(5) (a) Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1986**, *51*, 2851. (b) Chung, Y.-S.; Duerr, B.; Nanjappan, P.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 1334.

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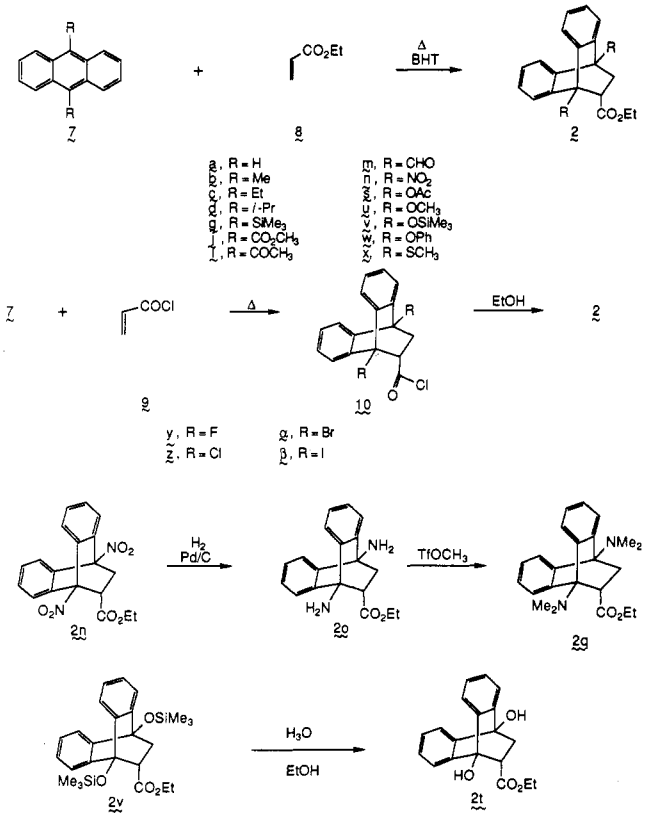
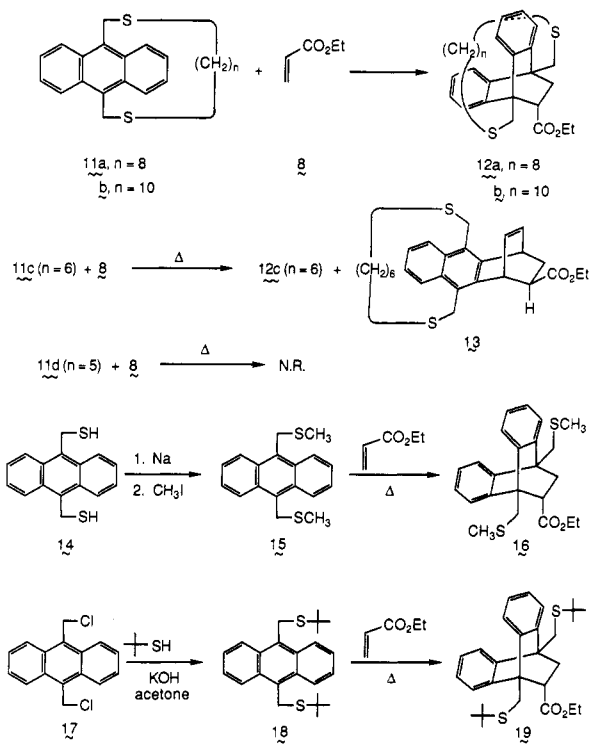
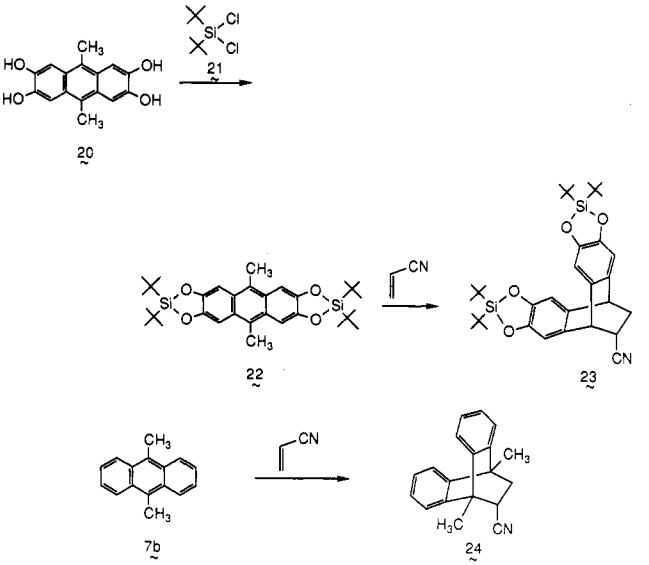
Scheme II



Scheme III



Scheme IV



(**7a–d,g,j,l,n,s,u–x**) with ethyl acrylate (Scheme II). While many of the anthracenes required were either commercially available or were obtained by using the literature procedures indicated in Table I, we were able to make anthracenes **7b,c,g,j,l,y,β** conveniently by the reaction of 9,10-dilithioanthracene with an appropriate electrophile.[6] Halogens **7y,z,α,β** were too unreactive for the direct reaction with ethyl acrylate; however, cycloaddition with acryloyl chloride **9** followed by ethanolysis readily afforded the requisite compounds. Interestingly, 9,10-dicyanoanthracene (**7k**) and 9,10-bis(dimethylamino)anthracene (**7q**; prepared by tetramethylation of 9,10-diaminoanthracene[7]) were unreactive toward ethyl acrylate; **7k** was also unreactive toward acryloyl chloride. Several adducts of the general structure **2** were prepared by functional group manipulation of other adducts. Catalytic hydrogenation of dinitro adduct **2n** gave diamino adduct **2o**, which in turn served as starting material for bis(dimethylamino) adduct **2q** via methyl triflate methylation. Acid-catalyzed hydrolysis of bis(trimethylsiloxy) adduct **2v** readily provided dihydroxy adduct **2t** with no observable retro-aldol products.

The ethyl acrylate adducts of anthracenophanes **11a**[8a] and **11b** could also be made by the direct route (Scheme III). Reaction of ethyl acrylate with anthracenophane **11c**[8b] afforded a mixture of adducts from cycloaddition at the central ring (**12c**) and at the terminal ring (**13**), based on the ^{1}H NMR spectrum of the crude reaction product. Attempted reaction of ethyl acrylate with anthracenophane **11d**[8b] yielded only starting material, again based on the ^{1}H NMR spectrum of the crude reaction product. Anthracenes **15** and **18** were prepared from the dithiol (**14**) and dichloride (**17**), respectively; conversions to the reference cycloadducts **16** and **19** were accomplished in neat ethyl acrylate.

(Silylenedioxy)anthracene adduct **23** was prepared by using the route shown in Scheme IV. 2,3,6,7-Tetrahydroxy-9,10-dimethylanthracene (**20**), prepared by modifications of the literature procedure,[9] and triethylamine were allowed to react with di-*tert*-butyldichlorosilane (**21**)[10] in acetonitrile to afford anthracene **22** in >90% yield after aqueous workup and crystallization from chloroform. The corresponding silyl ditriflate related to **21** was not useful for the preparation of **22**. Condensation of **22** in neat acrylonitrile at 85 °C provided cycloadduct **23**. For com-

(6) Duerr, B. F.; Chung, Y.-S.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 2120.
(7) Schiedt, V. B. *J. Prakt. Chem.* **1941**, *157*, 203.
(8) (a) Vogtle, F.; Koo Tze Mew, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 60. (b) Chung, J.; Rosenfeld, S. M. *J. Org. Chem.* **1983**, *48*, 387.
(9) (a) Boldt, P. *Chem. Ber.* **1967**, *100*, 1275. (b) Lindsey, A. S. *Chem. Ind.* **1965**, 1685.
(10) Obtained from the Aldrich Chemical Company, Milwalkee, WI.

Table I. Methods of Preparation and Physical Data for Some Cycloadducts Used in This Study[a]

compd	R	method of synthesis (conditions: °C, h)	yield, %	mp, °C	chromatography and/or crystallization systems	anal.[58]
1a	H	B[10] (170/R1/48)	17	143–144	S7, C8	C, H
2a	H	C[10] (165/R1/24)	88	98–99	C4	C, H
1b	Me	A[41]	68	89–91	S7, C7	C, H
2b	Me	C[6] (110/R2/16)	71	101–103	S3, C4	C*, H
1c	Et	D		76–77	S7, C8	C, H
2c	Et	C[6] (100/R2/45)	50	102–103	S3, C4	C, H
1d	*i*-Pr	B[10] (200/R1/72)	43	89–91	C1	C, H
2d	*i*-Pr	C[42] (80/R2/72)	80	83.4–84.5	S3, C7	C*, H
1e	*t*-Bu	B[10] (225/R1/96)	3	75–76	S7, C1	C, H
1f	Ph	A[43]		99–100	S7, C7	C, H
1g	$SiMe_3$	B[10] (220/R1/68)	78	75–76	C1	C, H
2g	$SiMe_3$	C[6] (90/R2/72)	20	132–135	S1, C1	C, H
1h	COOH	A[44] (160/R1/24)	93	189–192	C6	C, H
1i	$CONH_2$	A[45]		243–245	S5, C3	C, H, N
1j	$COOCH_3$	A[44]		117–118	S5, C4	C, H
2j	$COOCH_3$	C[6] (180/R2/48)	49	144–145	S1, C1	C, H
1k	CN	A[46]		118–120	S5, C5	C, H
1l	$COCH_3$	A[47]		149–151	C6	C, H
2l	$COCH_3$	C[6] (130/R2/48)	65	126–128	S1	C, H
1m	CHO	A[48]		103–105	C4	C, H
2m	CHO	C[49] (150/R2/24)	63	143–145	S1, C1	C*, H
1n	NO_2	A[50]		107–108	S5, C7	C, H, N
2n	NO_2	C[51] (170/R2/24)	61	119–120	S1, C1	C, H
1o	NH_2	A[44]		104–105	C11	C, H, N
2o	NH_2	D		83–84	S2	C*, H, N
1p	NHAc	D		198–200	C9	C*, H, N
1q	NMe_2	A[44]		122–125	C8	C, H
2q	NMe_2	D		74–76	S1 & S2	C, H, N
1r	NMe_3TsO	D		226–228	C10	C*, H
1s	OAc	A[52]		100–101	C1	C, H
2s	OAc	C[53] (150/R1/24)	92	176–177	S1, C1	C, H
1t	OH	A[44]		140–141	C1	C, H
2t	OH	D		148–150	S2, C2	C*, H
1u	OCH_3	D		116–117	S4, C7	C, H
2u	OCH_3	C[54] (120/R2/48)	85	110–112	S1, C1	C, H
1v	$OSiMe_3$	D		83–85	S6, C4	C, H, Si
2v	$OSiMe_3$	C[55] (120/R2/72)	25	79–80	S1, C1	C, H
2w	OPh	C[56] (160/R2/48)	10	132–134	S1, C1	C, H
2x	SCH_3	C[56] (160/R2/20)	47	134–137	S4, C7	C, H, S
2y	F	D	61	oil	S3	no anal.
2z	Cl	D	47	102–105	S4, C7	C, H, Cl
2α	Br	D	67	105–108	S4, C7	C, H, Br
2β	I	D	49	106–107	S5, C4	C, H, I

[a] method of synthesis: (A) compound prepared by literature procedure, the reference is for the synthetic procedure used; (B) D-A of known dienophile with anthracene (temp, time), the reference is for the preparation of the dienophile; (C) D-A of ethyl acrylate with known anthracene (temp, time), the reference is for the preparation of the anthracene; (D) multistep procedure described in the Experimental Section. Reaction solvent (with small amount of hydroquinone or BHT): R1, xylene; R2, neat ethyl acrylate. Chromatography solvent systems (all on silica gel): S1, $CHCl_3$/hexane (2:1); S2, ethyl acetate; S3, CH_2Cl_2/hexane (1:1); S4, $CHCl_3$; S5, $CHCl_3$/hexane (1:1); S6, hexane/$CHCl_3$ (5:1); S7, petroleum ether (30–60 °C). Crystallization of solvent systems: C1, methanol; C2, $CHCl_3$; C3, $CHCl_3$/hexane (3:1); C4, hexane; C5, ether; C6, benzene; C7, ethanol; C8, petroleum ether (30–60 °C); C9, ethanol/water; C10, methanol/ether; C11, pure compound crystallized on standing.

parison, the acrylonitrile adduct of 9,10-dimethylanthracene (**7b**) was also prepared.

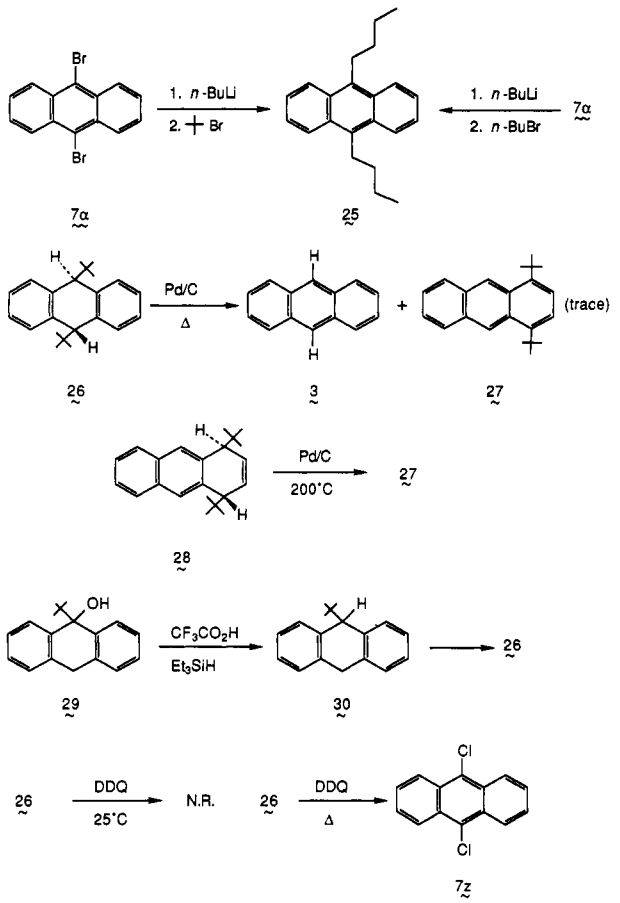
We have been unable to prepare the highly strained 9,10-di-*tert*-butylanthracene (**7**, R = *t*-Bu) to date, even though its use would have been quite important to this study and consequently commensurate effort was directed toward its synthesis. Some of our attempts as summarized in Scheme V warrant discussion. The synthesis of 9,10-di-*tert*-butylanthracene has been reported by the reaction of 9,10-dilithioanthracene with *tert*-butyl bromide[11] and its use in various physical studies described.[12] Unfortunately, we have been unable to prepare 9,10-di-*tert*-butylanthracene using this method; while we obtain a product in low yield with the same melting point reported,[11] that product analyzes as 9,10-di-*n*-butylanthracene (**25**). It seems likely that the 9,10-dilithioanthracene formed in the reaction of **7α** with *n*-butyllithium reacts instead with some of the *n*-butyl bromide formed as a byproduct of the halogen–metal exchange. To verify this possibility, we converted **7α** to **25** using excess added *n*-butyl bromide; the product (**25**) proved identical with that obtained in the reaction using *tert*-butyl bromide. Attempted dehydrogenation of the known *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracene (**26**)[13] with palladium on carbon afforded mainly anthracene as product, but a low yield of a *tert*-butylanthracene could be isolated. The product analyzed not as the desired 9,10-isomer but instead as the 1,4-isomer

(11) Karger-Kocsis, J. Ph.D. Thesis, Budapesti Muszaki Egyetem, 1976. We thank Dr. Jozsef Reffy, Department of Chemistry, Budapesti Muszaki Egyetem, Budapest, Hungary, for sending us a copy of the pertinent pages of this thesis and for his advice concerning 9,10-di-*tert*-butylanthracene.

(12) (a) Reffy, J.; Karger-Kocsis, J. *Magy. Kem. Koly.* **1977**, *83*, 410. (b) Tamas, V.; Reffy, J.; Karger-Kocsis, J. *Magy. Fem. Foly.* **1978**, *84*, 101. (c) Karger-Kocsis, J.; Reffy, J. *Magy. Kem. Foly.* **1978**, *84*, 413.

(13) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1145.

Scheme V



27. For verification of our structure assignment, the heretofore unknown 1,4-di-*tert*-butylanthracene (**27**) was prepared by the dehydrogenation of the known dihydro derivative (**28**);[13] this product proved indistinguishable from the minor product obtained by dehydrogenation of **26**. We suspect that the sample of **26**, prepared by addition of *tert*-butyllithium to anthracene followed by alkylation with *tert*-butyl bromide,[13] contains an impurity of **28** even after extensive chromatographic and crystallative purification; indeed, the difficulty in separating isomers of **26** by column chromatography has been described previously.[13] We prepared a "pure" sample of **26** by initial reduction of alcohol **29**[14] with triethylsilane in TFA to provide **30**[15] apparently uncontaminated by other isomers. Conversion of **30** to **26** by the literature procedure[13] gave a homogeneous sample of *trans*-9,10-di-*tert*-butyl-9,10-dihydroanthracene (**26**). Attempted dehydrogenation of this sample with Pd/C affords only anthracene as product. Attempted oxidation with DDQ at room temperature gave only starting materials back, but at higher temperature we unexpectedly obtained 9,10-dichloroanthracene (**7z**) as a product. The ability of DDQ to act as a source of electrophilic chlorine at elevated temperature has been observed previously.[16]

Difficulties in the literature syntheses of 9,10-difluoroanthracene (**7y**) lead us[6] to develop a new synthesis, based on the reaction of 9,10-dilithioanthracene with a source of electrophilic fluorine, *N*-tert-butyl-*N*-fluorobenzenesulfonamide;[17,18] the direct fluorination affords **7y** in 60% yield in one step. However, obtaining a sample of *N*-tert-butyl-*N*-fluorobenzenesulfonamide (an oil) still requires its synthesis by fluorination with elemental fluorine. Recent reports[19] of fluorinations using *N*-fluoropyridinium salts **32**–**34** interested us for two reasons: first, the fluorinating agents are relatively stable, free-flowing, colorless solids and, second, they are presently available commercially in Japan in multigram quantities. As we have reported previously,[6] attempted reaction of 9,10-dilithioanthracene with **32** led only to proton abstraction and anthracene formation; in fact, the literature suggests that lithium salts are not good starting materials for fluorinations with the *N*-fluoropyridinium triflates.[19] However, direct fluorinations using anthracene (**3**) itself as the starting material are successful (Scheme VI). As shown in Table II, reaction of anthracene with the least activated fluorinating agent, **32**, provides a 25% yield of **7y**. While the yield is low, the method is probably preferable to all previously published inasmuch as the fluorinating agent does not need to be prepared. Other products in the reaction include 9-fluoroanthracene (**31**) in 30% and unreacted anthracene in 45%. Fluorination with reagent **33** provides the fluorinated anthracene products in comparable yields. However, reaction with the most activated reagent, **34**, affords mainly polyfluorinated anthracene products as indicated by TLC and mass spectral data.

Scheme VI

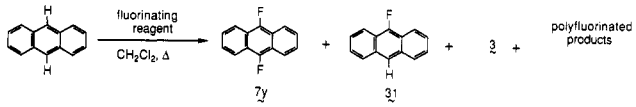
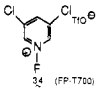


Table II

Reagent	Product Distribution			
 (FP-T300)	25%	30%	45%	trace
 (FP-T500)	24%	25%	not isolated	not isolated
 (FP-T700)	≤10%	≤10%	≤10%	major products

Kinetic Methods

For each of the cycloreversion reactions we ran, a 1.1–1.2 × 10^{-4} M solution of the adduct in dry diphenyl ether was prepared; in cases where the effect of solvent polarity was examined, the solution was prepared in dry pentadecane. The formation of anthracene product was assayed by monitoring the absorbance at that anthracene's long wavelength λ_{max}.[20] At the start of the run, the absorbance at the monitored wavelength was always ≤0.05 inasmuch as neither the adduct nor diphenyl ether absorb in this region. Adducts **1a**–**v** (at 250 °C), **12a**, **12b**, **16**, and **17** (at 200 °C) were heated in sealed ampules, ca. 80% submerged

(14) Parish, R. C.; Stock, L. M. *J. Org. Chem.* **1966**, *31*, 4265.
(15) Compound **30** has been reported previously: Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Strothers, J. B.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5912.
(16) Roberts, R. M. G. *J. Organomet. Chem.* **1976**, *110*, 281 (see p 287).
(17) Barnette, W. E. *J. Am. Chem. Soc.* **1984**, *106*, 452.
(18) Lee, S. H.; Schwartz, J. *J. Am. Chem. Soc.* **1986**, *108*, 2445.
(19) (a) Umemoto, T.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 3271. (b) Umemoto, T.; Kawada, K.; Tomita, K. *Tetrahedron Lett.* **1986**, *27*, 4465. We thank the Onoda Cement Company of Tokyo, Japan, for generously providing us with samples of compounds **32**–**34**.
(20) The formation of anthracene was followed at 362 nm as originally reported in ref 5a. The λ_{max} of many substituted anthracenes is reported in ref 5b. The γ_{max} of **7y** is 376 nm; that of **22** is 378 nm. Because our UV slit width is 2 nm, all λ_{max}'s reported are ±1 nm.

Table III. First-Order Rate Constants of Retro-Diels–Alder Reactions at 250 °C in Diphenyl Ether

R	compd	10^5k_1, s^{-1}
H	**1a**	1.21
Me	**1b**	1.14
Et	**1c**	1.09
i-Pr	**1d**	0.97
t-Bu	**1e**	0.88
Ph	**1f**	146
$SiMe_3$	**1g**	19.6
CO_2H	**1h**	168
$CONH_2$	**1i**	39.8
CO_2CH_3	**1j**	69.0
CN	**1k**	81.9
$COCH_3$	**1l**	217
CHO	**1m**	304
NO_2	**1n**	20.1
NH_2	**1o**	100
NHAc	**1p**	16.7
NMe_2	**1q**	3006[a]
$NMe_3^+TsO^-$	**1r**	2030
OAc	**1s**	0.40
OH	**1t**	1.62
OCH_3	**1u**	2.70
$OSiMe_3$	**1v**	2.73

[a] Due to the fast reaction rate at 250 °C, k_1 was extrapolated from the temperature dependence.

in an oil bath heated to the appropriate temperature; adducts **2a**–*β*, **23**, and **24** (all at 200 °C) were added to preheated diphenyl ether in a three-neck flask and the temperature of the solution was monitored by an internal thermometer. While it was not possible to monitor the internal temperature of the sealed ampule reactions, subsequent kinetic experiments using several adducts of type **1** in the three-neck system suggest the temperature of the ampule solutions to have been about 2–3 degrees less than that of the surrounding oil bath. Therefore, while the relative rates of cycloreversion in series **1** are internally comparable, the absolute rate constants are likely those at 247 °C instead of 250 °C. The determination of first-order rate constants and of kinetic activation parameters (reported as ± one standard deviation) was accomplished by using the computer program LSTSQ, available from Serena Software, 489 Serena Lane, Bloomington, IN 47401, and run on an IBM-AT microcomputer.

Most of the adducts we examind revealed clean first-order behavior for the formation of the anthracene product; no attempt was made to isolate or quantify the dienophile component of the rDA reaction. In two cases (**2o** and **2t**), oxidation of the anthracene under the conditions of the cycloreversion was extremely fast; the formation of oxidized products at 304 and 326 nm, respectively, was monitored instead. Rapid oxidation of anthracenes **7o**[7] (R = NH_2) and **7t**[21] (R = OH) was confirmed by adding a sample of each anthracene to deoxygenated diphenyl ether at 200 °C; the UV spectrum, taken within 15 s, in each case showed no anthracene absorptions, only peaks at 304 and 326 nm, respectively. The reaction of **23** demonstrated first-order kinetic behavior for only 1 half-life, owing to a concurrent decomposition of product **22** (likely oxidative and confirmed by using **22** itself under identical conditions). A rate constant for **23** was determined by using the A_∞ calculated from the adduct concentration and the data for the first 50% of the reaction.

Results

First-order rate constants for the rDA reactions of adducts substituted on the dienophile portion of the structure

(21) Landucci, L. L.; Ralph, J. *J. Org. Chem.* **1982**, *47*, 3486.

Table IV. First-Order Rate Constants of Retro-Diels–Alder Reactions at 200 °C in Diphenyl Ether

R	compd	10^5k_1, s^{-1}
H	**2a**	1.72
Me	**2b**	3.87
Et	**2c**	34.7
i-Pr	**2d**	13.6
$SiMe_3$	**2g**	4.63
CO_2CH_3	**2j**	0.415
$COCH_3$	**2l**	3.10
CHO	**2m**	8.32
NO_2	**2n**	0.031
NH_2	**2o**	4000
NMe_2	**2q**	239
OAc	**2s**	3.40
OH	**2t**	628
OCH_3	**2u**	69.0
$OSiMe_3$	**2v**	453
OPh	**2w**	198
SCH_3	**2x**	34.0
F	**2y**	0.317
Cl	**2z**	1.39
Br	**2α**	0.808
I	**2β**	1.40
$-CH_2S(CH_2)_8SCH_2-$	**12a**	40.3
$-CH_2S(CH_2)_{10}SCH_2-$	**12b**	26.1
CH_2SCH_3	**16**	26.4
$CH_2SC(CH_3)_3$	**19**	48.4

Table V. Kinetic Activation Parameters for Some Representative Substituents in the Retro-Diels–Alder Reactions of Anthracene Adducts in Diphenyl Ether

compd	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)	T(avg), °C
1b	44 ± 1.7	2.9 ± 3.2	245
1e	50 ± 2.0	14 ± 4.0	245
1j	38 ± 0.38	−1.8 ± 0.74	245
1q	29 ± 0.11	−11 ± 0.22	220
1u	43 ± 3.4	2.0 ± 6.5	245
2a	34.8 ± 1.4	−7.9 ± 2.7	230
2b	37.8 ± 1.9	0.4 ± 3.9	223
2c	36.1 ± 3.5	−0.1 ± 7.2	210
2d	35.7 ± 0.9	−3.7 ± 1.9	220
2m	40.0 ± 1.1	6.5 ± 2.3	215
2u	32.3 ± 1.0	−5.5 ± 2.0	215
2w	36.2 ± 1.2	4.6 ± 2.6	195
2t	31.2 ± 1.9	−3.7 ± 4.0	165
12a	32.6 ± 0.4	−6.0 ± 0.9	210
12b	37.2 ± 4.2	3.1 ± 8.5	215

Table VI. Polar Solvent Effects for Some Representative Substituents in the Retro-Diels–Alder Reactions of Anthracene Adducts

compd	rate in diphenyl ether (10^5k_1, s^{-1})	rate in pentadecane (10^5k_1, s^{-1})	reactn temp (°C)
1b	1.14	1.15	250
1q	3006	519	250
2c	34.7	25.1	200
2q	239	219	200
2t	628	212	200
2v	453	381	200

are compiled in Table III; those for adducts substituted on the diene portion are compiled in Table IV. Siladioxy adduct **23** cycloreverted with a rate constant of 4.5×10^{-4} s^{-1} in diphenyl ether at 200 °C; reference adduct **24** cycloreverted with a rate constant of 2.4×10^{-5} s^{-1} under the same conditions. The dideuteroxy adduct (**2γ**, R = OD), prepared by dissolution of dihydroxy adduct **2t** in CD_3OD followed by evaporation to dryness, cycloreverted with a rate constant of 1.62×10^{-3} s^{-1} (average of three runs) in pentadecane at 200 °C.

Kinetic activation parameters for some representative substituents are shown in Table V. The effect of solvent polarity was determined by comparing the rate of rDA

reaction in diphenyl ether with that in the less polar pentadecane at the same temperature (Table VI).

Cyclic voltammetry of several compounds was used to measure the electron-donating ability of amine substituents as a function of their potential for p–π overlap with the aromatic ring. An acetonitrile solution with tetrabutylammonium hexafluorophosphate as the supporting electrolyte was used to establish chemically irreversible oxidations at peak potentials of 1.20 V (aniline, **35**), 0.95 V (*N*,*N*-dimethylaniline, **36**), 0.18 V (9,10-diaminoanthracene, **7o**), and 0.55 V (9,10-bis(dimethylamino)-anthracene, **7q**) vs an Ag/AgCl reference. A platinum electrode was used at a scan rate of 100 mV/s.

Discussion

Objectives of This Study and Some Limitations in Interpreting the Results. Our impetus for determining structural effects on the rDA reaction is this group's interest in developing a one-pot cycloaddition/cycloreversion sequence as part of a catalytic cycle.[3] We intended (and still intend) to examine the development of synthetic catalysts based on reversible covalent bond formation as opposed to the reversible non-covalent binding most enzymes use. Reversible intermolecular cycloaddition reactions have been observed at room temperature with highly activated dienophiles[22] or at higher temperatures with less activated ones.[23] We were interested in finding whether or not such reversible cycloadditions with a moderately activated dienophile like ethyl acrylate could be accomplished at a reasonable temperature. Because the DA reaction is generally exothermic and the rDA reaction is endothermic, the cycloreversion step would be the slow half of the equilibrium at all but very low dienophile concentrations. In addition, the structure/reactivity profile for the DA reaction is quite well studied (although additional systematic work would certainly be appropriate given the DA reaction's importance in synthesis).

However, it quickly became clear that the structure/reactivity profile of the rDA reaction had not been examined previously in an extensive and systematic way.[24] To us, this appeared to be a rather large gap in what is a very fundamental reaction in organic chemistry. The rDA reaction was first used as a synthetic tool by Diels in 1938,[25] but it had not been used in a planned sense very extensively before about 15 years ago. Of course, the rDA reaction enjoys extensive useage as a "deprotection" step and in the generation of high energy species.[1] Therefore, the current study seemed to us an excellent opportunity to both pursue our own research goals as well as to contribute to the understanding of a very fundamental and understudied reaction.

Because of a seemingly limitless synthetic and mechanistic interest in the DA reaction, a study of its microscopic reverse, the rDA reaction, would be expected to lend mechanistic insight to this reaction pathway. Indeed, an advantage of using the rDA reaction to study the DA mechanism is that one can carry out rDA reactions that must fail in the opposite direction; for example, attempted cycloaddition of anthracene with ethylenamine would lead simply to polymerization of the dienophile. However, some perils exist. For one, there is no guarantee that the rDA reaction run by necessity at a high (e.g., 200 °C) temperature will transverse the same mechanistic pathway followed in a lower temperature DA reaction. For another, the choice of a general structure for the adduct must bias any general conclusions. We have chosen to work initially with anthracene as the diene because cycloaddition at the terminal ring can only yield a single product and because cycloreversion yields a highly stable chromophoric product that lends itself nicely to UV quantitation. *However, as compared to adducts of the prototypic diene, butadiene, anthracene adducts may be unusually prone to stepwise rDA mechanisms*; anionic, radical, and cationic intermediates will form more readily by using anthracene adducts because of the doubly benzylic stabilization available. For both these reasons, conclusions based on this work regarding "the" DA reaction will be made only when the temptation is overwhelming.

Also of importance is our arbitrary choice of ethyl acrylate as the dienophile with which adducts of 9,10-disubstituted anthracenes were fashioned. While the ethylene-bridged adducts might have offered a less ambiguous choice for studying the *stricto sensu* rDA reaction, there were two major advantages to the ethyl acrylate tack: (1) operationally, it is much easier to use neat ethyl acrylate as reactant and solvent than to carry out ethylene reactions at higher temperature and in a pressure apparatus and (2) rDA reactions of the slowest members of adduct type **2** but with an ethylene bridge would likely be excruciatingly slow even at 200–250 °C. Perhaps most importantly, our intention of designing synthetic catalysts has as its goal reactions on acrylate-type "substrates" (methyl acrylate, acrylonitrile, acrylamide, acrolein, etc.); therefore, a detailed knowledge of their rDA kinetics was most useful to us.

Finally, there is the issue of whether to use 9-monosubstituted or 9,10-disubstituted dienes for this work. Obviously, making adducts with 9-monosubstituted anthracenes removes any possible interplay of two substituents at different positions on the adduct. Of particular importance would be the lessening of anchimeric assistance in a system such as amino adduct **2o**. Using the "m-isomer" (ester and amino groups at opposite ends of the bridge) of a monoaminosubstituted adduct would provide a measure of the amino group's purely inductive effect; using the "o-isomer" (ester and amino groups on the same end of the bridge) would give a measure of the combined inductive effect and of the enhanced tendency toward a dipolar retro-Mannich type intermediate. However, this entails what is likely to be the difficult separation of the o- and m-isomers of some 21 type-**2** adducts, in addition to doubling the number of kinetic runs necessary. We early chose not to go this route for purely practical reasons. In retrospect, the potential of electron-donating groups to favor polar transition structures appears less than originally considered; polar solvent effects shown in Table VI indicate that even the presence of such electron-rich sub-

(22) (a) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 150. (b) Sauer, J.; Schroder, B.; Wiemer, R. *Chem. Ber.* **1967**, *100*, 306.

(23) (a) Wassermann, A. *Trans. Faraday Soc.* **1938**, *34*, 128. (b) Bachman, W. E.; Kloetzel, M. C. *J. Am. Chem. Soc.* **1938**, *60*, 481. (c) Khambata, B. S.; Wassermann, A. *J. Chem. Soc.* **1939**, 375. (d) Cope, A. C.; Haven, A. C.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867. (e) Kresze, G.; Rau, S.; Sabelus, G.; Goetz, H. *Ann.* **1961**, *648*, 57. (f) Kiselev, V. D.; Konovalov, A. I.; Veisman, E. A.; Ustyugov, A. N. *Zh. Org. Khim. (Engl. Transl.)* **1978**, *14*, 128. (g) Lee, M. W.; Herndon, W. C. *J. Org. Chem.* **1978**, *43*, 518. (h) Jenner, G.; Papadopoulos, M.; Rimmelin, J. *J. Org. Chem.* **1983**, *48*, 748. (i) Sellers, S. F.; Dolbier, W. R., Jr.; Koroniak, H.; Al-Fekri, D. M. *J. Org. Chem.* **1984**, *49*, 1033.

(24) Some work on structure–reactivity relationships in the rDA reaction has been reported previously: (a) Herndon, W. C.; Manion, J. M. *J. Org. Chem.* **1968**, *33*, 4504 (and previous papers in this series). (b) Kabakoff, D. S. *Diss. Abstr. Int. B* **1974**, *35*, 2099. (c) Brown, A. C. *Diss. Abstr. Int.* **1984**, *45*, 1468. (d) George, A. V.; Isaacs, N. S. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1845. (e) Van Mele, B.; Boon, G.; Huybrechts, G. *Int. J. Chem. Kinet.* **1986**, *18*, 537. In addition, substituent effects in the bicyclooctadiene series are being concurrently investigated by Professor D. Hasselman, Ruhr-Universitat Bochum, Lehrstuhl fur Organische Chemie II, to whom we are grateful for sharing his results with us.

(25) Diels, O.; Thiele, W. E. *Ber.* **1938**, *71*, 1173.

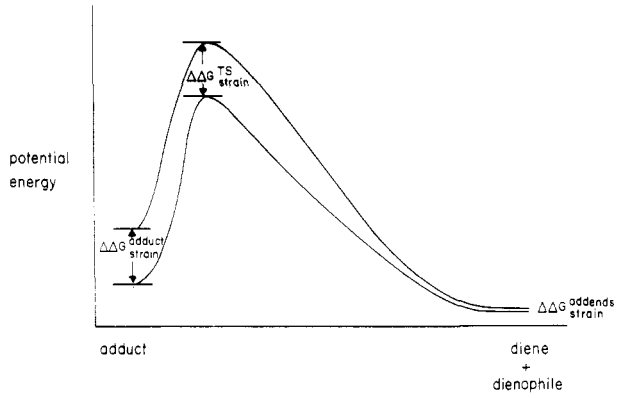


Figure 1. Reaction coordinate for cycloreversion indicating relative strain energies in sterically conjested vs unconjested adducts and in their corresponding transition structures and addends.

stituents as dimethylamino (**2q**) and trimethylsiloxy (**2v**) do not result in a dipolar mechanism. While the hydroxy substituent *does* result in a change in mechanism (**2t**), this ultimately proves to be due to deprotonation of the hydroxyl group and not to the effect of the neutral substituent (see later discussion, this section).

Steric Effects. An Unprecedented Bell-Shaped Structure–Reactivity Curve. The suggestion that strain in adducts results in accelerated rDA reactions has been made previously, and experimental evidence providing credence to it has been reported.[26] In the forward direction, increasing the steric bulk of a diene or dienophile is well known to decelerate DA reactions, and so acceleration in the rDA direction is a perfectly reasonable concept. Therefore, it was with some surprise that we have found very limited acceleration attributable to the relief of strain in the rDA transition structure. For adducts of type **1**, increasing the size of the R group progressively from H to *tert*-butyl (**1a,b,c,d,e**) induces a negligible (1.4-fold) change in the rate constant, and the effect of increasing size is to *decrease* the rate contrary to prediction. Molecular mechanics calculations[27] predict that the most stable conformations of these compounds will be relieved of 0.37 (Me), 0.36 (Et), 1.1 (*i*-Pr), and 2.3 (*t*-Bu) kcal/mol more strain energy than will the H-substituted adduct (**1a**) on cycloreversion; this ordering, as well as being computationally rigorous, is consistent with intuition. We have rationalized this apparent contradiction by recalling that the DA reaction has a transition structure whose geometry closely resembles that of the adduct;[28] le Noble has reported the same conclusion based on the observed $\Delta V^{\ddagger}$ for the DA reaction.[29] In the rDA direction, this means that strain energy stored in the adduct is felt equally by the transition structure, and so its eventual release comes too late to provide a rate acceleration. This notion is depicted in Figure 1, which, in summary, indicates that the difference in strain energies for two adducts and for their respective rDA transition structures is about the same. It should be noted that the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ terms of adducts **1b** and **1e** affect $\Delta G^{\ddagger}$ in opposite ways; because we cannot speculate on the origins of these trends with any confidence, only the rate constants at 250 °C have been compared.

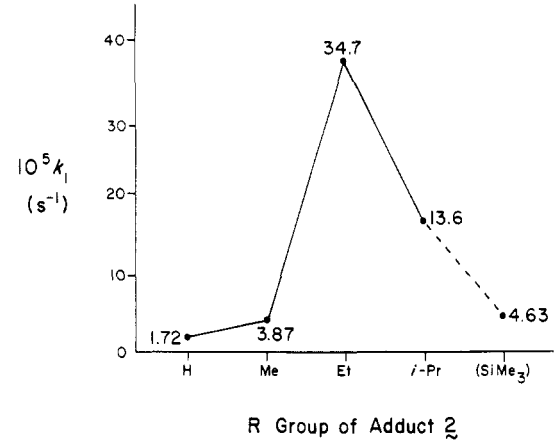


Figure 2. Bell-shaped structure–reactivity profile for the rDA rate constant as a function of substituent in the 9,10-dialkylanthracene series.

Steric acceleration in the adduct type-**2** series was also interesting and unexpected. On progressing from adduct **2a** (R = H) to adduct **2c** (R = Et), we find a 20-fold increase in rate; while this is not an enormous increase, it is much larger than anything seen in the type-**1** series and forces a reexamination of our idea put forth in Figure 1. Evidently, moving the locus of congestion into direct confluence with the already congested bridgehead position results in a qualitatively different result. However, progression to the next member of this homologous series, adduct **2d** (R = *i*-Pr), yields a rate *decrease*. While it would have been optimal to compare these data with those of the di-*tert*-butyl adduct, we have to date been unable to prepare the highly strained 9,10-di-*tert*-butylanthracene. Instead, one may consider (with appropriate reservation)[30] the reactivity of disilyl adduct **2g**, which is again slower than diisopropyl adduct **2d**. A plot of rate vs (crudely) steric bulk is shown in Figure 2, which reveals a bell-shaped structure–reactivity relationship unprecedented for a size-based structure parameter. Our analysis of this bell-shaped reactivity relationship centers on the question how much does the transition structure "know" about steric problems in the anthracene it is going to? It is reasonable to conclude, based on molecular mechanics calculations and examinations of space-filling models, that increasing steric bulk of the substituents results in greater strain energies of *both* adducts and anthracenes. However, steric strain in the adducts, in which a "gear-like" orientation between substituent and adduct framework can exist, is less than strain in the anthracenes, in which bad contacts with the peri hydrogens cannot be avoided *beginning with the isopropyl group*. In other words, at some hypothetical point between ethyl and isopropyl groups the generation of strain in the transition structure wins out over the release of strain in the starting material and the reaction slows.

The results here are relevant to an issue relating to the DA reaction. 9,10-Dimethylanthracene proves to be about 10^3-fold more reactive in the DA reaction than is anthracene; this acceleration is substantially greater than that obtained by using 9,10-dimethoxyanthracene. This rate data by Sauer[2c] remains something of an enigma, because

(26) For example, see ref 4d.
(27) Molecular mechanics programs adapted from Allinger's "MMP1" were obtained from Serena Software, 489 Serena Lane, Bloomington, IN 47401; this version (name: "MMPM") with the accompanying graphics routine was run on an IBM-AT microcomputer.
(28) Wiberg, K. B. In *Physical Organic Chemistry*; John Wiley and Sons, 1966; p 376.
(29) le Noble, W. J. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 207.
(30) Because the Si–C bond is longer than the C–C bond, the purely steric effect of a $Si(CH_3)_3$ group is expected to be smaller than that of a $C(CH_3)_3$ group; the inductive electronic effects are predicted to be similar, based on σ_p values. It is difficult to predict what the resonance effect of the vacant silicon d orbital would be, although as a rDA dienophile substituent, $Si(CH_3)_3$ is faster than $C(CH_3)_3$ by about 22-fold at 250 °C (cf. ref 5a).

it is surprising that the conjugated diene methoxy groups prove less activating than methyl groups. Obviously, this cannot be due strictly to a polar substituent effect. The ethyl acrylate adduct of 9,10-dimethoxyanthracene (**2u**) cycloreverts 40 times faster than does that of anthracene at 200 °C; the adduct of 9,10-dimethylanthracene (**2b**) cycloreverts only 2.25 times faster, strongly suggesting that there is no "special" electronic effect of the methyl group here. Our view is that 9,10-dimethylanthracene experiences a "stress" (strain without distortion) due to repulsion of the methyls with the peri hydrogens; this stress is relieved on attaining the TS geometry (which resembles that of the adduct), in which a gear-like staggering is possible.

Finally, based on entries **12a**, **12b**, **16**, and **19**, our notion that strain induced by bridging substituents would accelerate cycloreversions significantly appears unfounded, perhaps for the same reasons described above. Each of these adducts cycloreverts at about the same rate as does adduct **2c** (R = Et), indicating no special effect of the anthracenophane bridge at least for these chain lengths. It should be noted, however, that shorter chain lengths than used in this study have been found to affect both the DA rates and the positions of ensuing cycloaddition equilibria in reactions with tetracyanoethylene.[31]

Polar Inductive Effects. It is well-documented that DA reactions of "normal" electron demand are accelerated when an electron-rich diene and/or an electron-deficient dienophile is used. While this trend need not have held for the rDA reaction,[32] we find experimentally that it does. In the type-1 adducts, electron-withdrawing substituents on the dienophile fragment of the adduct accelerate the rDA reaction as compared to H (**1a**) by factors of 139 (CO_2H; **1h**), 33 ($CONH_2$; **1i**), 251 (NO_2; **1n**), and so forth. For type-2 adducts, electron-donating substituents on the diene fragment of the adduct accelerate the reaction as compared to H (**2a**) by factors of 20 (SPh; **2x**), 40 (OMe; **2u**), 2330 (NH_2; **2o**), etc.

We find that rDA rates are often not slowed by the *opposite* electronic trends. For example, methoxy adduct **1u** in which an electron-donating substituent is on the dienophile fragment of the adduct actually cycloreverts 2.2 times faster than does reference adduct **1a**. Similarly, CO_2CH_3, $COCH_3$, and CHO substituents on the diene (adducts **2j,l,m**) all react within 5 times the rate of reference adduct **2a**. This may be an indication of movement toward a biradical mechanism. In this entire series of compounds, the only adduct that reacted significantly more slowly than did its reference was dinitro adduct **2n**, which cycloreverted 55 times more slowly than did **2a**. While nitro was the most electron-withdrawing substituent (based on σ_p values) used in the type-2 series, it is not clear why there is a qualitative difference between the nitro group (**2n**; $\sigma_p = 0.78$) and the acetyl group (**21**; $\sigma_p = 0.50$).

Bridgehead siloxy acceleration of the rDA reaction has been reported previously by Grimme,[33] and we find the same effect. Adduct **2v** (R = $OSiMe_3$) cycloreverts 263 times more quickly than does the reference compound (**2a**); furthermore, the small solvent effect observed (Table VI) indicates that the mechanism has not changed to dipolar. While such an anthracene might be considered an excellent candidate for our synthetic catalyst work, this substitution pattern is not ideal for our purposes because (1) steric hindrance is expected to slow the cycloaddition leading to the adduct's synthesis and (2) for our catalysis work, it would be optimal to place a catalytic group near the site of reaction instead. Consequently, we have examined the potential of siloxy groups distal to the reaction center as accelerating substituents and find that a substantial rate acceleration is obtained even when the substituent is three bonds removed from the reaction site. The rate constants obtained at 200 °C in diphenyl ether are 4.5×10^{-4} s^{-1} for siladioxy adduct **23** and 2.4×10^{-5} s^{-1} for reference adduct **24** and reveal a 19-fold rate increase for the siloxy-substituted compound as compared to the reference. While this acceleration is quite significant for a remote substituent, anthracene **22** did not prove useful for setting up reversible low temperature cycloaddition equilibria because of the ease with which **22** oxidizes (competitive with the rDA rate even in deoxygenated solvent).

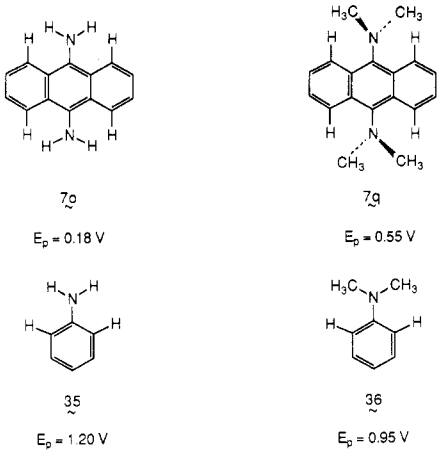
As a side note, we were interested in the idea that the *tert*-butyl groups of anthracene **22** might provide some selectivity for dienophiles, and a size discrimination was observed. Details concerning the cycloaddition steric requirements of anthracene **22** were obtained by measuring the rates of reaction of **22** and **7b** with substituted maleimides. In chloroform at 25 °C, the ratio (k^{Me}/k^{H}) of second-order rate constants using maleimide (H) and *N*-methylmaleimide (Me) is 3.01 for **22** and 3.43 for **7b**; this indicates that, in the absence of a major steric perturbation, electronic changes of the dienophile affect the reactions of both anthracenes about equally. However, k^{Ph}/k^{H} is 0.84 for **22** and 2.51 for **7b**; presumably, the perpendicular phenyl group of *N*-phenylmaleimide is finally large enough to interact with one of the siladioxy *tert*-butyl groups in **22**. An examination of CPK molecular models corroborates this conclusion.

Nonpolar Conjugative Effects. Two substituents examined in this study, phenyl and silyl, do not exert a large polar inductive effect on reactions, at least as measured by their small σ_p values (0.01 and –0.07, respectively). However, each group is capable of interacting with an adjacent p orbital by conjugation and might therefore indicate to what extent transition structure conjugation is important. Once again, a mechanistic ambiguity arises because conjugative interactions would stabilize adjacent radicals (in a stepwise mechanism) just as they would an adjacent double bond (in a concerted reaction). It seems that a conjugative effect should be most pronounced in the type-1 adducts because something like a phenyl group must end up perpendicular to the anthracene product in the type-2 adduct; in addition, because we observe essentially no steric effect in this adduct type, an acceleration in a type-1 adduct cannot be attributed to strain relief. As shown in Table II, adduct **1f** (R = Ph) cycloreverts 146 times faster than does reference adduct **1a**. This is a very large rate enhancement, comparable to that afforded by a strongly electron-withdrawing substituent. Either the partial double bond character of the transition structure dienophile benefits from conjugation with the phenyl group or the biradical mechanism is enhanced by this doubly benzylic system.

In addition, we note that adduct **1g** (R = $SiMe_3$) cycloreverts about 20 times faster than does the reference adduct. It is a fair guess that this is not due to steric acceleration of the reaction inasmuch as adducts in this series reveal no such effect in the alkyl series. Because of current interest in silicon's ability to stabilize an adjacent carbon radical,[34] our rDA result takes on a special significance. What that significance is, we are not quite sure

(31) S. Rosenfeld, Smith College, unpublished results.
(32) The heats of formation of adducts with polar substituents cannot be estimated with accuracy, making it impossible to calculate a structure–reactivity profile for the rDA reaction.
(33) Papies, O.; Grimme, W. *Tetrahedron Lett.* **1980**, 2799.
(34) Swenton, J. S.; Platz, M.; Venham, L. D. *J. Org. Chem.* **1988**, *53*, 2764.

Chart II

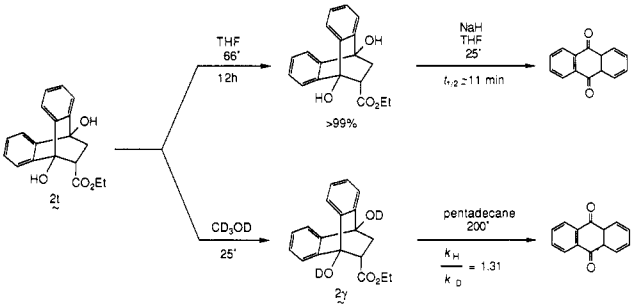


because silicon may be accelerating the reaction in any one of several ways. For stepwise mechanisms, these include (1) stabilization of an α radical (although recent work suggest that this effect is small);[34] (2) stabilization of a β radical; (3) stabilization of an α carbanion; and (4) stabilization of a β carbocation. The trimethylsilyl group could also be stabilizing the forming double bond in a concerted process; this would also be a significant conclusion, because Hine's extensive survey of double-bond stabilizing substituents[35] did not include any trialkylsilyl substituents. Magnus has previously reported an rDA acceleration resulting from β-trimethylsilyl substitution of an adduct.[36]

Geometric Attenuation of Polar Conjugative Effects. Electron-donating groups on a diene accelerate the rDA reaction, but substituents that are both electron donating and conjugating afford the greatest rate increases. In the series-**2** adducts, relative rates for R = H (1), Me (2), OMe (40), and NH_2 (2330) illustrate this point well. Of course, diene substitution by an alkoxide substituent that conjugates to the forming double bonds as the reaction proceeds has been shown to accelerate dramatically the rDA reaction of anthracene adducts, to the point that they may be carried out at room temperature.[33,37]

There is, however, an intriguing discrepancy in our rDA data for this class of substituent. On the basis of σ_p values, the dimethylamino group (−0.83) is a stronger electron-donating group than is the amino group (−0.66); this conclusion is also consistent with intuition, given that methyl is more electron donating than hydrogen. It was quite unexpected, then, to find that adduct **2q** (R = NMe_2) cycloreverts almost 17 times slower than does adduct **2o** (R = NH_2). The resolution to this conundrum is found in a consideration of the conjugating ability of each substituent in the transition structure. It seems likely, based on an examination of space-filling models, that **2o** can populate a conformation in which the amino group is in a position to conjugate with the forming C=C bond of the anthracene. Conversely, steric repulsion by the methyl groups of **2q** ensure that this conformation is not accessible and therefore that the amine lone pair cannot readily overlap with the forming anthracene π bonds in the transition structure. While we cannot model this steric inhibition to resonance for the transition structure, we can model it by using the anthracene products. To test the

Scheme VII



idea that the NMe_2 group in anthracene **7q** is not coplanar with the anthracene ring, we determined the oxidation peak potentials of anthracenes **7o** and **7q** by cyclic voltammetry (Chart II). As anticipated, while the planar *N,N*-dimethylaniline (**36**) is easier to oxidize by 250 mV than is aniline (**35**) itself, 9,10-bis(*N,N*-dimethylamino)-anthracene (**7q**) is *harder* to oxidize than is 9,10-diaminoanthracene (**7o**) by 370 mV. We suggest that the larger size of the more electron-donating dimethylamino group forces it out of planarity with the anthracene ring due to repulsion with the peri hydrogens; our molecular mechanics calculations predict that (i) both dimethylamino groups in **7q** are roughly perpendicular to the anthracene in the ground state and (ii) a 180° rotation of one perpendicular dimethylamino group passes over a 23 kcal/mol energy barrier. In addition, X-ray structures of 9-mono and 9,10-disubstituted anthracenes reveal such a nonplanarity in the case of two-dimensional substituents such as the nitro group.[38] Such a deconjugation in the dimethylamino adduct would lessen any p−π overlap and thereby lessen resonance interactions. It therefore seems clear that the transition structure for cycloreversion reflects the aromatic character of the anthracene product to a significant extent even if its geometry closely resembles that of the adduct; this finding is consistent with the idea that, *energetically* (as opposed to geometrically),[29] the DA reaction has an early (i.e., addends-like) transition structure. It is not likely that even adduct **2q** cycloreverts by an ionic mechanism based on the relative insensitivity of this cycloreversion to solvent polarity effects (Table VI).

Amino substituents on the dienophile portion of an adduct also accelerate the cycloreversion, but at least in the case of anthracene adducts this seems to involve a change to a polar mechanism. This time, because no steric constraints to conjugation exist, the NMe_2 compound **1q** demonstrates the greatest acceleration, with relative rates of R = H (1), NH_2 (83), and NMe_2 (2480). In fact, for this adduct type the "strongest" electron-donating group, dimethylamino, makes the reaction even faster than does the "strongest" electron-withdrawing group, trimethylammonium. However, cycloreversion of adduct **1q** slows by a factor of about 6 when transferred from diphenyl ether to pentadecane, indicating a polar mechanism; by comparison, the rate of adduct **1b** (R = Me) cycloreversion varies by less than 1% in the two solvent systems.

Rate-Limiting Deprotonation: A Special Case. The rapid cycloreversion rate of **2t** (R = OH)[59] as compared to **2u** (R = OMe) suggested that different mechanisms might be involved in these two reactions. The solvent polarity effect on reaction rate confirmed that the mechanism by which **2t** cycloreverts involves a charged transition structure. Less biased rDA reactions are known to

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be highly insensitive to solvent effects, occurring at nearly the same rate in solution and gas phases.[39] However, as shown in Table VI, dihydroxy adduct **2t** exhibits a large deceleration on changing from diphenyl ether to pentadecane solvent; that 3-fold deceleration represents an unusually large solvent effect and suggests that deprotonation (either full or partial) of a tertiary alcohol in **2t** is the rate-limiting step. Dramatic acceleration of the rDA reaction by alkoxide substituents has been reported previously by Grimme,[33] and we observe the same effect. As shown in Scheme VII, a THF solution of adduct **2t** at reflux (66 °C) shows no (less than 1%) cycloreversion after 120 h. After cooling to room temperature, addition of excess NaH results in rapid cycloreversion ($t_{1/2}$ about 11 min).

As support for our contention of O–H bond cleavage in the transition structure of **2t**, we measured the remote deuterium isotope effect on this cycloreversion. As shown in Scheme VII, deuterium exchange of dihydroxy adduct **2t** to dideuteroxy adduct **2γ** was accomplished by dissolving in CD_3OD solution and evaporating to dryness; the exchange was confirmed by using ^1H NMR. In pentadecane solution and 200 °C, triplicate runs of each cycloreversion reaction gave the following rate constants: **2t**, 0.137, 0.124, 0.121 min^{-1}, avg = 0.127 min^{-1}; **2γ**, 0.095, 0.105, 0.091 min^{-1}, avg = 0.097 min^{-1}. Because anthrahydroquinone (**7t**) oxidizes to anthraquinone within seconds of addition to pentadecane at 200 °C, we see only absorptions due to anthraquinone in this reaction; additionally, this means that the isotope effect cannot be due to the oxidation step of this two-step process. Using the averages from above, we calculated a k_H/k_D of 1.31 for this cycloreversion. Because neither the D–O nor the O–C bond requires breaking for a concerted rDA reaction of **2γ**, one would not expect a significant isotope effect unless a change in mechanism occurred that did involve one of these in a rate-determining step. The only reasonable choice here is that the H(D)–O bond is broken, and we conclude that this results from deprotonation of **2t** in the transition structure. That deprotonation need not be complete; for example, a half-broken H–O bond would still place significantly more electron density on the oxygen, which would still be expected to accelerate the reaction, albeit to a proportionately smaller extent than a full alkoxide would. Still, because the acceleration afforded by a fully formed alkoxide group is enormous (est. 10^6-fold),[33] even partial H–O bond cleavage would be expected to result in a large acceleration.

Recent results from Rickborn's group[60] on the novel oxyanion-accelerated forward DA reaction of anthrone indicate that the reaction product varies with the base used, triethylamine providing cycloadduct products and alkoxide yielding Michael type products. We have observed that the cycloreversion rates of dihydroxy adduct **2t** at 180 °C are not increased by addition of 1 equiv (i.e., 10^{-4} M) of benzyldimethylamine (bp 184 °C), pyridine, or *p*-toluenesulfonic acid. However, 1 equiv of added sodium ethoxide results in enormous acceleration, with complete reaction at 180 °C within 1 min. This finding suggests a special role for triethylamine, which is apparently basic enough to deprotonate anthrone but is insufficiently basic to deprotonate the resulting adduct bridgehead alcohol and therefore unable to catalyze its rDA reaction.

Summary

The retro-Diels–Alder reaction of anthracene cycloadducts is influenced by *diene* substituents in the following ways: (1) electron-donating groups increase the reaction rate, and the accelerating effect is subject to geometric modulation for a conjugating substituent like dimethylamino; (2) electron-withdrawing groups may decrease or increase the reaction rate, although the effect is rarely large; and (3) steric acceleration is relatively small and demonstrates an unprecedented bell-shaped structure–reactivity profile. Peripheral substitution of the adduct with siloxy groups results in a significant acceleration, even though the groups are three bonds removed from the reaction site.

The same reaction is influenced by *dienophile* substituents in the following ways: (1) electron-withdrawing groups increase the rate of the reaction; (2) strongly conjugating substituents make the reaction much faster than predicted by classical electron-withdrawing or -donating ability due to a change to polar mechanism; and (3) there is no observable steric effect.

Experimental Section

General. Melting points were taken on an Electrothermal melting point apparatus and are uncorrected. Microanalyses were carried out at Canadian Microanalytical Service, New Westminster, B.C. Mass spectra were obtained by use of a Kratos-30 mass spectrometer. FT-NMR spectra were obtained at 11.75 T (500 MHz) or 7.0 T (300 MHz). All starting materials were purchased from the Aldrich Chemical Company, Milwaukee, WI. The synthetic methods used for the preparation of many adducts, together with their melting points and microanalytical data, are compiled in Table I.

Adduct 1a: ^1H NMR ($CDCl_3$) δ 1.53–1.72 (m, 4, CH_2CH_2), 4.33 (br s, 2, H-9 and H-10), 7.10–7.12 (m, 4, Ar H), 7.23–7.28 (m, 4, Ar H); EI mass spectrum, *m/e* 206 (M^+, 10), 178 (M^+ – 28, 100);

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(58) While the carbon analyses for the adducts marked by an asterisk were not within the 0.4% limit expected for structure verification, all spectroscopic data were consistent with our assignment. All these "off" microanalyses fall within the 0.4% limit upon addition of 0.1–0.5 equiv of water to the molecular formula.
(59) Our previously[6] reported activation parameters for adduct **2t** have been revised based on a more extensive temperature–rate study for the cycloreversion of this adduct. Accordingly, the rate constant at 200 °C has been likewise revised.
(60) Rickborn, B., University of California-Santa Barbara, private communication.

see Table I for mp and microanalysis data.

Adduct 1b: ^{1}H NMR ($CDCl_3$) δ 0.63 (d, 3, C*H*$_3$), 0.75–1.00 (m, 1, C*H*HCHCH$_3$ cis to CH$_3$), 1.72–2.00 (m, 2, C*H*CH$_3$ and CH*H*-CHCH$_3$ trans to CH$_3$), 3.85 (d, H-9), 4.08 (t, 1, H-10), 6.89–7.25 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1d: ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 3, C*H*$_3$), 0.85 (m, 1, C*H*HCHC$_3$H$_7$ cis to *i*-C$_3$H$_7$), 1.05 (s, 3, C*H*$_3$), 1.20 (m, 1, CH*H*C-HC$_3$H$_7$ trans to *i*-C$_3$H$_7$), 1.44 (m, 1, C*H*(CH$_3$)$_2$), 1.94 (m, 1, C*H*CH(CH$_3$)$_2$), 4.18 (t, 1, H-10), 4.30 (d, 1, H-9), 7.15 (m, 8, Ar H); FAB mass spectrum, *m/e* 249 (M + 1, 14), 178 (100); see Table I for mp and microanalysis data.

Adduct 1e: ^{1}H NMR ($CDCl_3$) δ 0.72 (s, 9, *t*-Bu), 1.64 (m, 3, C*H*$_2$C*H*-C(CH$_3$)$_3$), 4.25 (t, 1, H-10), 4.38 (d, 1, H-9), 7.19 (m, 8, Ar H); FAB mass spectrum, *m/e* 263 (M + 1, 24), 178 (100); see Table I for mp and microanalysis data.

Adduct 1f: ^{1}H NMR ($CDCl_3$) δ 1.68–1.98 (m, 1, C*H*HCHC$_6$H$_5$ cis to C$_6$H$_5$), 2.15–2.50 (m, 1, CH*H*CHC$_6$H$_5$ trans to C$_6$H$_5$), 3.10–3.33 (m, 1, C*H*C$_6$H$_5$), 4.18 (d, 1, H-9), 4.40 (t, 1, H-10), 6.50–6.68 (m, 2, Ar H), 6.95–7.45 (m, 11, Ar H); see Table I for mp and microanalysis data.

Adduct 1g: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9, Si(C*H*$_3$)$_3$), 1.03 (m, 1, C*H*HCHSi(CH$_3$)$_3$ cis to Si(CH$_3$)$_3$), 1.64 (m, 1, C*H*Si(CH$_3$)$_3$), 1.89 (m, 1, CH*H*CHSi(CH$_3$)$_3$ trans to Si(CH$_3$)$_3$), 4.30 (t, 1, H-10), 4.37 (d, 1, H-9), 7.10 (m, 4, Ar H), 7.25 (m, 4, Ar H); EI mass spectrum, *m/e* 278 (M$^+$, 18), 240 (3), 178 (100); see Table I for mp and microanalysis data.

Adduct 1h: ^{1}H NMR ($CDCl_3$) δ 2.21 (m, 2, C*H*$_2$), 2.88 (m, 1, C*H*COOH), 4.32 (t, 1, H-10), 4.65 (d, 1, H-9), 7.15 (m, 8, Ar H), 9.50 (br s, 1, COO*H*); see Table I for mp and microanalysis data.

Adduct 1i: ^{1}H NMR ($CDCl_3$) δ 1.80–2.25 (m, 2, C*H*$_2$), 2.60–2.92 (m, 1, C*H*CONH$_2$), 4.40 (t, 1, H-10), 4.52 (d, 1, H-9), 5.12 (br s, 2, N*H*$_2$), 7.05–7.54 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1j: ^{1}H NMR ($CDCl_3$) δ 1.81–2.34 (m, 2, C*H*$_2$), 2.75–3.02 (m, 1, C*H*CO$_2$CH$_3$), 3.6 (s, 3, C*H*$_3$), 4.35 (t, 1, H-10), 4.68 (d, 1, H-9), 7.00–7.48 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1k: ^{1}H NMR ($CDCl_3$) δ 2.15 (m, 2, C*H*$_2$), 2.88 (m, 1, C*H*CN), 4.40 (t, 1, H-10), 4.57 (d, 1, H-9), 7.32 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1l: ^{1}H NMR ($CDCl_3$) δ 1.75–2.15 (m, 2, C*H*$_2$), 2.10 (s, 3, C*H*$_3$), 2.75–2.98 (m, 1, C*H*COCH$_3$), 4.32 (t, 1, H-10), 4.58 (d, 1, H-9), 7.00–7.48 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1m: ^{1}H NMR ($CDCl_3$) δ 1.82–2.25 (m, 2, C*H*$_2$), 2.62–2.90 (m, 1, C*H*CHO), 4.40 (t, 1, H-10), 4.68 (d, 1, H-9), 7.05–7.50 (m, 8, Ar H), 9.48 (d, 1, C*H*O); see Table I for mp and microanalysis data.

Adduct 1n: ^{1}H NMR ($CDCl_3$) δ 2.14–2.68 (m, 2, C*H*$_2$), 4.39 (t, 1, H-10), 4.70–4.90 (m, 1, C*H*NO$_2$), 5.00 (d, 1, H-9), 7.01–7.50 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 1s: ^{1}H NMR ($CDCl_3$) δ 1.40–1.61 (m, 1, C*H*HCHO-COCH$_3$ cis to OCOCH$_3$), 1.89 (s, 3, C*H*$_3$), 2.18–2.42 (m, 1, CH*H*-CHOCOCH$_3$ trans to OCOCH$_3$), 4.25 (t, 1, H-10), 4.52 (d, 1, H-9), 5.00–5.21 (m, 1, C*H*OCOCH$_3$), 7.02–7.45 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 6. A mixture of anthracene (1.0 g, 5.6 mmol), 4-bromo-1-butene (5.0 g, 37.0 mmol), and hydroquinone (10 mg) in xylene (5 mL) was heated in a sealed tube at 240–250 °C for 20 h. The reaction was cooled and evaporated in vacuo; the resulting black residue was treated with hexane and a black flocculent solid formed. The solid was collected by filtration and the hexane was removed by evaporation. The compound was further purified by flash chromatography using petroleum ether (30–60 °C) as solvent. Appropriate fractions were pooled and evaporated in vacuo and finally recrystallized from petroleum ether (30–60 °C) to yield the desired compound (1.0 g, 46%): mp 101–103 °C; ^{1}H NMR ($CDCl_3$) δ 1.03–1.22 (m, 1, C*H*HCHCH$_2$C-H$_2$Br cis to CH$_2$CH$_2$Br), 1.40–1.70 (m, 2, C*H*CH$_2$CH$_2$Br and CH*H*CHCH$_2$CH$_2$Br trans to CH$_2$CH$_2$Br), 1.92–2.22 (m, 2, C*H*$_2$CH$_2$Br), 3.28–3.50 (m, 2, C*H*$_2$Br), 4.08 (d, 1, H-9), 4.22 (t, 1, H-10), 6.95–7.34 (m, 8, Ar H); FAB mass spectrum, *m/e* 314 (M + 1, 3), 313 (9), 178 (100).

Adduct 1c. To a solution of adduct **6** (1.0 g, 3.2 mmol) in dry benzene (50 mL) was added tributyltin hydride (0.93 g, 3.2 mmol) and azobis(isobutyronitrile) (AIBN) (0.011 g, 2 mol %), and the solution was heated under nitrogen at 80 °C for 4 h. The contents of the flask were evaporated in vacuo to give a yellow oil that was subjected to silica gel flash chromatography with petroleum ether (30–60 °C) as solvent. The appropriate fractions were pooled and evaporated in vacuo to give a colorless solid containing the desired compound along with a small amount of anthracene. During recrystallization from petroleum ether (30–60 °C), a small amount of anthracene was obtained on cooling (ice), which was removed by filtration. The desired product was obtained on recrystallization of the sample twice more (0.30 g, 40%): ^{1}H NMR ($CDCl_3$) δ 1.05 (m, 6, C*H*$_2$C*H*$_3$ and C*H*HCHCH$_2$CH$_3$ cis to CH$_2$CH$_3$), 1.98 (m, 2, C*H*CH$_2$CH$_3$ and CH*H*CHCH$_2$CH$_3$ trans to CH$_2$CH$_3$), 4.10 (d, 1, H-10), 4.25 (t, 1, H-9), 7.19 (m, 8, Ar-H); FAB mass spectrum, *m/e* 234 (M + 1, 1), 178 (100); see Table I for mp and microanalysis data.

Adduct 1p. To a solution of adduct **1o** (500 mg, 1.9 mmol) in pyridine (5 mL) was added acetic anhydride (2.0 g, 20 mmol), and the reaction was heated at 100 °C for 10 h and then allowed to cool to room temperature. The reaction mixture was poured onto crushed ice (200 g) with stirring. The colorless crystalline precipitate was filtered and dried. Recrystallization from ethanol/water yielded **1p** (0.450 g, 76%): ^{1}H NMR ($CDCl_3$) δ 1.10–1.40 (m, 1, C*H*HCHNHCOCH$_3$ cis to NHCOCH$_3$), 1.82 (s, 3, C*H*$_3$), 2.20–2.55 (m, 1, CH*H*CHNHCOCH$_3$ trans to NHCOCH$_3$), 4.28 (t, 1, H-10), 4.30–4.55 (2 overlapping sets of peaks, m, 1, C*H*N-HCOCH$_3$ and d, 1, H-9), 4.82–5.18 (br s, 1, N*H*), 7.05–7.48 (m, 8, Ar H); FAB mass spectrum, *m/e* 264 (M + 1, 100), 205 (M–NHAc, 75), 178 (M – H$_2$C=CHNHAc); high resolution FAB mass spectrum, calcd for C$_{18}$H$_{18}$NO [(M + H)$^+$] 264.138, measured 264.136; see Table I for mp and microanalysis data.

Adduct 1r. Methyl *p*-toluenesulfonate (0.5 g, 2.7 mmol) was added dropwise to a solution of **1q** (0.2 g, 0.8 mmol) in ether (10 mL) and kept at room temperature for 10 h. After adding ether (50 mL) to the reaction mixture, a solid formed that was collected and washed with ether. Recrystallization from methanol/ether yielded **1r** (0.34 g, 99%): ^{1}H NMR (DMSO-d_6) δ 2.30 (s, 3, C$_6$H$_4$C*H*$_3$), 2.52 (m, 1, C*H*HCHN$^+$(CH$_3$)$_3$Ar cis to N$^+$(CH$_3$)$_3$Ar), 2.90 (s, 9, N$^+$(C*H*$_3$)$_3$Ar), 3.85 (m, 2, CH*H*C*H*N$^+$(CH$_3$)$_3$ trans to N$^+$(CH$_3$)$_3$Ar), 4.48 (t, 1, H-10), 5.12 (d, 1, H-9), 7.17 (m, 7, Ar H), 7.41 (m, 4, Ar H), 7.58 (m, 1, Ar H); FAB mass spectrum, *m/e* 265 (M + 1, 23), 264 (100), 205 (88); see Table I for mp and microanalysis data.

Adduct 1u. Under nitrogen atmosphere a solution of **1t** (500 mg, 2.3 mmol) and sodium hydride (0.2 g, 4.2 mmol) (washed with petroleum ether, 60–90 °C, 2 × 20 mL) in benzene (30 mL) was refluxed for 2 h. The solution was then cooled to room temperature and methyl iodide (5.0 g, 35.2 mmol) was added and the resulting solution was stirred at room temperature for 15 h. Methanol (20 mL) was added to the reaction mixture and the resulting solution was poured into water (100 mL). Extraction with ether (2 × 100 mL), washing with water, and evaporation in vacuo yielded a light yellow solid that was further purified by silica gel flash chromatography. Elution with $CHCl_3$, pooling, and evaporation of the appropriate fractions and recrystallization from ethanol yielded **1u** (0.13 g, 25%): ^{1}H NMR ($CDCl_3$) δ 1.50 (m, 1, C*H*HCHOCH$_3$ cis to OCH$_3$), 2.13 (m, 1, CH*H*CHOCH$_3$ trans to OCH$_3$), 3.34 (s, 3, OC*H*$_3$), 3.79 (m, 1, C*H*OCH$_3$), 4.25 (t, 1, H-10), 4.58 (d, 1, H-9), 7.20 (m, 8, Ar H); FAB mass spectrum, *m/e* 237 (M + 1, 2), 236 (2), 205 (100), 178 (81); see Table I for mp and microanalysis data.

Adduct 1v. Into a flask was placed **1t** (1.5 g, 6.75 mmol), triethylamine (10 mL), *p*-(dimethylamino)pyridine (0.15 g), and dichloroethane (40 mL). Trimethylsilyl chloride (10 g, 92 mmol) was added slowly while stirring and a dense white precipitate formed. When the addition was complete the reaction mixture was allowed to stir for 6 h. The solution was then cooled in an ice/salt bath for 2 h. To this mixture were added hexane (150 mL) and saturated sodium bicarbonate (50 mL). The hexane solution was washed with water and the organic phase was dried over $MgSO_4$. Removal of hexane yielded a light yellow oil that crystallized upon standing. The product was further purified by silica gel flash chromatography ($CHCl_3$/hexane, 1:5 solvent). Pooling of the appropriate fractions and evaporation in vacuo yielded a colorless oil that solidified upon standing. The resulting solid was recrystallized from hexane to yield **1v** (1.4 g, 71%): ^{1}H NMR ($CDCl_3$) δ 0.5 (s, 9, Si(C*H*$_3$)$_3$), 1.35–1.45 (m, 1, C*H*HCHO-

$Si(CH_3)_3$ cis to $OSi(CH_3)_3$), 2.10–2.40 (m, 1, $CHHCHOSi(CH_3)_3$ trans to $OSi(CH_3)_3$), 4.16–4.43 (m, 3, H-9, H-10, and $CHOSi(CH_3)_3$), 7.05–7.41 (m, 8, Ar H); see Table I for mp and microanalysis data.

Adduct 2a: ^1H NMR ($CDCl_3$) δ 1.15 (t, 3, OCH_2CH_3), 1.92–2.23 (m, 2, CH_2), 2.83–2.92 (m, 1, H-11), 4.04 (q, 2, OCH_2CH_3), 4.30 (t, 1, H-10), 4.56 (d, 1, H-9), 7.05–7.35 (m, 8, Ar H); high resolution mass spectrum, calcd for $C_{19}H_{18}O_2$ 278.131, measured, 278.132; see Table I for mp and microanalysis data.

Adduct 2b: ^1H NMR ($CDCl_3$) δ 1.09 (t, 6, OCH_2CH_3), 1.81–2.15 (m, 2, CH_2), 2.00 (d, 6, CH_3), 2.55–2.81 (dd, 1, H-11), 3.84–4.15 (q, 2, OCH_2CH_3), 7.05–7.50 (m, 8, Ar H); EI mass spectrum, m/e 306 (M^+, 2), 206 (100); see Table I for mp and microanalysis data.

Adduct 2c: ^1H NMR ($CDCl_3$) δ 1.12 (t, 3, OCH_2CH_3), 1.32–1.42 (dt, 3, CH_2CH_3), 1.73–1.81 (m, 1, $CHHCHCO_2C_2H_5$ cis to $CO_2C_2H_5$), 2.19 (t, 1, H-11), 2.50–2.62 (m, 4, CH_2CH_3), 2.93–3.00 (m, 1, $CHHCHCO_2C_2H_5$ trans to $CO_2CH_2CH_3$), 3.90–4.08 (m, 2, OCH_2CH_3), 7.04–7.38 (m, 8, Ar H); EI mass spectrum, m/e 334 (M^+, 1), 234 (100), 219 (40); see Table I for mp and microanalysis data.

Adduct 2d: ^1H NMR ($CDCl_3$) δ 1.09 (t, 3, OCH_2CH_3), 1.50–1.67 (m, 14, $CH(CH_3)_2$ and $CH(CH_3)_2$), 2.88–3.01 (m, 2, H-12), 3.02–3.16 (m, 1, H-11), 3.85–4.04 (m, 2, OCH_2CH_3), 7.05–7.67 (3 multiplets, 8, Ar H); high resolution mass spectrum, calcd for $C_{25}H_{30}O_2$ 362.225, measured 362.224; see Table I for mp and microanalysis data.

Adduct 2g: ^1H NMR ($CDCl_3$) δ 0.70 (d, 18, $SiMe_3$), 1.04 (t, 3, CH_3), 1.69–2.26 (m, 2, CH_2), 2.89 (dd, 1, CH), 3.90 (q, 2, OCH_2), 7.02–7.43 (m, 8, Ar H); mass spectrum, m/e 422 (M^+), 322 (M^+ – 100, 28), 250 (100); see Table I for mp and microanalysis data.

Adduct 2j: ^1H NMR ($CDCl_3$) δ 1.10 (t, 3, CH_3), 2.03–2.66 (m, 2, CH_2), 3.30 (dd, 1, CH), 3.82–4.06 (m, 2, OCH_2), 4.03 (d, 6, OCH_3), 7.10–8.12 (m, 8, Ar H); mass spectrum, m/e 394 (M^+), 294 (M^+ – 100, 100); see Table I for mp and microanalysis data.

Adduct 2l: ^1H NMR ($CDCl_3$) δ 1.14 (t, 3, CH_3), 1.92–2.60 (m, 2, CH_2), 2.70 (d, 6, OCH_3), 3.19 (dd, 1, CH), 3.97 (q, 2, OCH_2), 7.14–7.80 (m, 8, Ar H); mass spectrum, m/e 362 (M^+), 262 (M^+ – 100, 100), 247 (50); see Table I for mp and microanalysis data.

Adduct 2m: ^1H NMR ($CDCl_3$) δ 1.14 (t, 3, CH_3), 2.10–2.59 (m, 2, CH_2), 3.38 (dd, 1, CH), 4.05 (q, 2, OCH_2), 7.24–8.0 (m, 8, Ar H), 10.91 (d, 2, CHO); mass spectrum, m/e 334 (M^+), 234 (M^+ – 100, 100), 206 (71); high resolution mass spectrum, calcd for $C_{21}H_{18}O_4$ 334.120, measured 334.119; see Table I for mp and microanalysis data.

Adduct 2n: ^1H NMR ($CDCl_3$) δ 1.12 (t, 3, CH_3), 2.44–3.13 (m, 2, CH_2), 3.74 (dd, 1, CH), 4.03 (q, 2, OCH_2), 7.1–7.95 (m, 8, Ar H); mass spectrum, m/e 368 (M^+), 322 (70), 268 (M^+ – 100, 100); see Table I for mp and microanalysis data.

Adduct 2s: ^1H NMR ($CDCl_3$) δ 1.07 (t, 3, CH_3), 2.54 (s, 6, $COCH_3$), 2.52–3.02 (m, 2, CH_2), 3.95 (q, 2, OCH_2), 4.27 (dd, 1, CH), 7.10–7.55 (m, 8, Ar H); mass spectrum, m/e 294 (M^+ – 100), 210 (100); see Table I for mp and microanalysis data.

Adduct 2u: ^1H NMR ($CDCl_3$) δ 1.10 (t, 3, CH_3), 2.30 (d, 2, CH_2), 3.57 (dd, 1, CH), 3.93 (d, 6, OCH_3), 3.88–4.0 (m, 2, OCH_2), 7.10–7.52 (m, 8, Ar H); mass spectrum, m/e 238 (M^+ – 100), 223 (100); Table I for mp and microanalysis data.

Adduct 2v: ^1H NMR ($CDCl_3$) δ 0.48 (d, 18, $SiMe_3$), 1.11 (t, 3, CH_3), 2.09–2.51 (m, 2, CH_2), 3.19 (dd, 1, CH), 4.05 (q, 2, OCH_2), 7.24–7.64 (m, 8, Ar H); mass spectrum, m/e 354 (M^+ – 100); see Table I for mp and microanalysis data.

Adduct 2w: ^1H NMR ($CDCl_3$) δ 1.12 (t, 3, CH_3), 2.18 (d, 2, CH_2), 3.17 (t, 1, CH), 3.98 (q, 2, OCH_2), 6.86–7.53 (m, 18, Ar H); mass spectrum, m/e 362 (M^+ – 100); see Table I for mp and microanalysis data.

Adduct 2x: ^1H NMR ($CDCl_3$) δ 1.20 (t, 3, OCH_2CH_3), 2.15–2.50 (m, 2, CH_2), 2.40 (d, 6, SCH_3), 3.11–3.30 (m, 1, H-11), 3.90–4.21 (q, 2, OCH_2CH_3), 7.25–7.35 (m, 4, Ar H), 7.68–7.90 (m, 4, Ar H); EI mass spectrum, m/e 325 ($M^+ - OC_2H_5$, 2), 270 (100), 255 (45); see Table I for mp and microanalysis data.

Adduct 2y. Anthracene **7y** (80 mg, 0.37 mmol) was placed in a pressure tube along with freshly distilled **9** (4 mL) and dry xylene (16 mL). Hydroquinone (50 mg) was added and the tube was sealed and heated at 80–90 °C overnight. Absolute ethanol (5 mL) was added to the tube and it was heated at 80 °C for 1 h. The resulting solution was then evaporated in vacuo to a thick oil that was subjected to silica gel flash chromatography (hexane/CH_2Cl_2, 1:1). The appropriate fractions were pooled (R_f 0.25, silica gel) and evaporated in vacuo to give an oil that resisted all attempts at crystallization (47 mg, 40%): ^1H NMR ($CDCl_3$) δ 1.17 (t, 3, OCH_2CH_3), 2.33–2.41 (m, 2, CH_2), 3.16–3.24 (m, 1, H-11), 4.02–4.13 (m, 2, OCH_2CH_3), 7.24–7.33 (m, 4, Ar H), 7.44–7.56 (m, 4, Ar H); high resolution mass spectrum, calcd for $C_{19}H_{16}F_2O_2$ 314.1118, measured 314.1116; see Table I for mp and microanalysis data.

Adduct 2z: ^1H NMR ($CDCl_3$) δ 1.20 (t, 3, OCH_2CH_3), 2.30–2.75 (m, 2, H-12), 3.14–3.33 (m, 1, H-11), 3.97–4.20 (q, 2, OCH_2CH_3), 7.31–7.42 (m, 4, Ar H), 7.70–7.85 (m, 4, Ar H); EI mass spectrum, m/e 346 (M^+, 3), 248 (65), 246 (100); see Table I for mp and microanalysis data.

Adduct 2α: ^1H NMR ($CDCl_3$) δ 1.14 (t, 3, OCH_2CH_3), 2.40–2.92 (m, 2, H-12), 3.20–3.45 (m, 1, H-11), 4.05 (q, 2, OCH_2CH), 7.20–7.45 (m, 4, Ar H), 7.72–7.93 (m, 4, Ar H); EI mass spectrum, m/e 436 (M^+, 3), 336 (100); see Table I for mp and microanalysis data.

Adduct 2β: ^1H NMR ($CDCl_3$) δ 1.12 (t, 3, OCH_2CH_3), 2.70–3.18 (m, 2, H-12), 3.38–3.67 (m, 1, H-11), 4.00–4.28 (q, 2, OCH_2CH_3), 7.25–7.35 (m, 4, Ar H), 7.61–7.80 (m, 4, Ar H); EI mass spectrum, m/e 431 (M^+, 24), 430 (100), 403 (42); see Table I for mp and microanalysis data.

Adduct 2o. To a sample of 10% Pd/C (50 mg) in a 20-mL test tube was added a solution of 9,10-dinitro-11-carbethoxy-9,10-ethanoanthracene (**2n**; 500 mg, 1.37 mmol) dissolved in ethanol (10 mL). The tube was placed in a bottle and the mixture was shaken under hydrogen gas (60 psi) at room temperature for 30 h. The Pd/C was filtered by using Celite and the filtrate was concentrated on a rotary evaporator. Purification by silica gel column chromatography using ethyl acetate as eluent afforded **2o** (285 mg, 68%): ^1H NMR ($CDCl_3$) δ 1.07 (t, 3, CH_3), 2.05 (d, 2, CH_2), 2.36 (br s, 4, NH_2), 2.79 (dd, 1, CH), 3.94 (q, 2, OCH_2), 7.12–7.66 (m, 8, Ar H); mass spectrum, m/e 208 (M^+ – 100); high resolution FAB mass spectrum, calcd for $C_{19}H_{21}N_2O_2$ [$(M + H)^+$] 309.160, measured 309.159; see Table I for mp and microanalysis data.

Adduct 2q. To a stirred solution of 9,10-diamino-11-carbethoxy-9,10-ethanoanthracene (**2o**; 150 mg, 0.49 mmol), benzene (10 mL), and methyl trifluoromethanesulfonate (0.6 g, 3.5 mmol) was added a small amount of 2,6-di-*tert*-butylpyridine (0.5 mL). The mixture was stirred at room temperature for 3 days under a nitrogen atmosphere and then was diluted with chloroform, and poured into a 5% sodium carbonate solution (60 mL). The organic layer was separated, dried over magnesium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (chloroform/hexane 2:1, then ethyl acetate) to afford **2q** (180 mg, 90%): ^1H NMR ($CDCl_3$) δ 1.04 (t, 3, CH_3), 1.76–2.12 (m, 2, CH_2), 3.01–3.07 (m, 1, CH), 3.06 (d, 6, NMe_2), 3.91 (m, 2, OCH_2), 7.11–7.64 (m, 8, Ar H); mass spectrum, m/e 264 (M^+ – 100), 249 (100); see Table I for mp and microanalysis data.

Adduct 2t. To a solution of 9,10-bis(trimethylsiloxy)-11-carbethoxy-9,10-ethanoanthracene (**2v**; 300 mg, 0.66 mmol) in ethanol (5 mL) was added several drops each of water and 3 N HCl. The mixture was stirred at room temperature for 2 h, neutralized with sodium bicarbonate solution, and concentrated on a rotatory evaporator. The resulting residue was extracted with chloroform, which was dried over magnesium sulfate. Evaporation of chloroform in vacuo afforded **2t** as a colorless solid (195 mg, 95%): ^1H NMR ($CDCl_3$) δ 1.09 (t, 3, CH_3), 2.17–2.38 (m, 2, CH_2), 2.68 (s, 1, OH), 2.93 (dd, 1, CH), 4.04 (q, 2, OCH_2), 5.24 (s, 1, OH), 7.2–7.67 (m, 8, Ar H); mass spectrum, m/e 210 (M^+ – 100); see Table I for mp and microanalysis data.

9,10-Bis(dimethylamino)anthracene (7q). To a solution of 9,10-diaminoanthracene[7] (1 g, 4.8 mmol) in methanol (5 mL) were added iodomethane (11.4 g, 0.08 mol) and a solution of sodium carbonate (2.2 g, 0.022 mol) in water (5 mL). The mixture was stirred at room temperature for 16 h and then was refluxed for 1 day. The mixture was concentrated, dissolved in chloroform, and washed with aqueous sodium carbonate solution. The organic layer was separated, dried over magnesium sulfate, and concentrated in vacuo. Purification by silica gel column chromatography (chloroform/hexane, 2:1) gave **7q** as a bright yellow solid (1.1 g, 87%): ^1H NMR ($CDCl_3$) δ 3.24 (s, 12, NMe_2), 7.47 (q, 4, Ar H), 8.34 (q, 4, Ar H); mass spectrum, m/e 264 (M^+), 249 (100).

Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.82; H, 7.58; N, 10.61. Found: C, 81.56; H, 7.59; N, 10.57.

Anthracenophane 11b. With use of the general procedure reported by Rosenfeld,[8b] solutions of 9,10-bis(chloromethyl)anthracene (1.7 g, 6.25 mmol) in toluene (900 mL) and 1,10-decanedithiol (1.29 g, 6.25 mmol) and KOH (0.7 g, 12.5 mmol) in a mixture of ethanol (200 mL, 95%) and toluene (700 mL) were added simultaneously and at equal rates under a nitrogen atmosphere to refluxing toluene (100 mL) with stirring over 2.5 h. After completion of the addition, the reaction mixture was refluxed for an additional 15 h. The yellow oil obtained after removal of the solvent under reduced pressure was purified by flash chromatography on silica gel with $CHCl_3$ as eluant to afford a yellow crystalline solid (1.0 g, 40%): mp 153–155 °C; ^{1}H NMR ($CDCl_3$) δ 1.28 (m, 12, -$SCH_2CH_2(CH_2)_6CH_2CH_2S$-), 1.68 (m, 4, -$SCH_2CH_2(CH_2)_6CH_2CH_2S$-), 2.65 (t, 4, -$SCH_2(CH_2)_8CH_2S$-), 4.62 (br s, 4, benzylic CH_2), 7.54 (m, 4, Ar H), 8.38 (m, 4, Ar H); EI mass spectrum, m/e 408 (M^+, 4).

Anal. Calcd for $C_{26}H_{32}S_2$: C, 76.42; H, 7.89; S, 15.69. Found: C, 76.32; H, 7.83; S, 15.65.

Adduct 12a. A solution of 2,11-dithia[12](9,10)-anthracenophane[8a] (**11a**; 0.20 g, 0.53 mmol), ethyl acrylate (5.0 g, 50.0 mmol), and BHT (0.02 g) was heated at 140 °C for 2 days in a sealed glass tube. The yellow syrup obtained after removal of the excess ethyl acrylate under reduced pressure was chromatographed on silica gel (50 g). Elution with chloroform afforded a paste that, after crystallization from ethanol, gave a cream colored crystalline solid (0.080 g, 34%): mp 90–91 °C; ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3, $C(O)OCH_2CH_3$), 1.42 (m, 8, -SCH_2CH_2-$(CH_2)_4CH_2CH_2S$-), 1.63 (m, 4, -$SCH_2CH_2(CH_2)_4CH_2CH_2S$-), 1.08 (m, 1, C*H*-CHC(O)OC_2H_5, cis to ester), 1.36 (m, 1, C*H*-CHC(O-)OC_2H_5, trans to ester), 2.75 (t, 4, $SCH_2(CH_2)_6CH_2S$), 3.24 (m, 1, $CHC(O)OC_2H_5$), 3.58 (m, 2, benzylic CH_2S), 3.89 (m, 4, C(O)O-CH_2CH_3 and other benzylic CH_2S), 7.11 (m, 4, Ar H), 7.32 (m, 3, Ar H), 7.52 (m, 1, Ar H).

Anal. Calcd for $C_{29}H_{36}S_2O_2$: C, 72.46; H, 7.55; S, 13.34. Found: C, 72.36; H, 7.51; S, 13.40.

Adduct 12b. A mixture of 2,13-dithia[14](9,10)-anthracenophane (**11b**; 0.20 g, 0.49 mmol), BHT (10 mg), and ethyl acrylate (5.0 g, 50 mmol) was heated at 180 °C for 40 h in a sealed tube. After removal of excess ethyl acrylate by co-evaporation with $CHCl_3$ under reduced pressure, the viscous yellow liquid was chromatographed on silica gel (35 g). Elution with $CHCl_3$ gave a light yellow pasty material that, after further purification by preparative TLC (elution with $CHCl_3$), afforded a very light yellow gum (0.11 g, 44%): ^{1}H NMR ($CDCl_3$) δ 1.10 (t, 3, $C(O)OCH_2CH_3$), 1.38 (m, 12, -$SCH_2CH_2(CH_2)_6CH_2CH_2S$-), 1.82 (m, 5, -$SCH_2CH_2(CH_2)_6CH_2CH_2S$- and C*H*-CH-C(O)$OC_2H_5$, cis to ester), 2.38 (m, 1, C*H*-CH-C(O)C_2H_5, trans to ester), 2.75 (t, 4, -SCH_2-$(CH_2)_8CH_2S$-), 3.28 (m, 1, $CHC(O)OC_2H_5$), 3.74 (br s, 2, benzylic CH_2), 3.86 (br s, 2, benzylic CH_2), 4.15 (m, 2, $C(O)OCH_2CH_3$), 7.15 (m, 4, Ar H), 7.40 (m, 3, Ar H), 7.60 (m, 1, Ar H); FAB mass spectrum, m/e 409 ($[M + 1]^+$, 7).

Anal. Calcd for $C_{31}H_{40}S_2O_2$: C, 73.18; H, 7.92; S, 12.60. Found: C, 73.10; H, 7.95; S, 12.55.

9,10-Bis[(methylthio)methyl]anthracene (15). Sodium metal (0.81 g, 35.0 mmol) in small bits was added to cold methanol (150 mL) with stirring. When all the sodium had reacted, 9,10-anthracenedimethanedithiol[57] (**14**; 4.0 g, 14.8 mmol) was added and the solution was refluxed for 30 min. Methyl iodide (10 g, 70.4 mmol) in methanol (10 mL) was then added to the reaction mixture over 10 min at 40 °C and stirred at that temperature for 4 h. The reaction mixture was then poured into water (200 mL). The bright yellow solid was collected by filtration and purified by flash chromatography on silica gel (50 g) using $CHCl_3$/hexane (1:1) as eluant. Crystallization from CH_2Cl/hexane (3:1) gave a yellow solid (2.5 g, 55%): mp 191–193 °C; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 6, SCH_3), 4.72 (s, 4, CH_2S), 7.55 (m, 4, Ar H), 8.44 (m, 4, Ar H); EI mass spectrum, m/e 298 (M^+, 5), 204 (100).

Anal. Calcd for $C_{18}H_{18}S_2$: C, 72.44; H, 6.08; S, 21.48. Found: C, 72.40; H, 6.04; S, 21.52.

Adduct 16. A solution of 9,10-bis[(methylthio)methyl]-anthracene (**15**; 0.20 g, 0.67 mmol), ethyl acrylate (5.0 g, 50.0 mmol), and BHT (10 mg) was heated in a sealed tube at 160 °C for 24 h. After evaporation of the excess of ethyl acrylate under diminished pressure, the yellow syrup was chromatographed on silica gel (35 g). Elution with $CHCl_3$/hexane (1:1) afforded a colorless waxy solid that, after crystallization from ethanol, yielded a colorless solid (0.20 g, 75%): mp 90–91 °C; ^{1}H NMR ($CDCl_3$) δ 1.13 (t, 3, $C(O)OCH_2CH_3$), 1.54 (m, 1, C*H*-CHC(O)OC_2H_5, cis to ester), 1.91 (m, 1, C*H*-CHC(O)OC_2H_5, trans to ester), 2.34 (s, 3, SCH_3), 2.37 (s, 3, SCH_3), 3.23 (m, 1, $CHC(O)OC_2H_5$), 3.65 (m, 2, CH_2S), 3.83 (m, 2, CH_2S), 4.03 (m, 2, $C(O)OCH_2CH_3$), 7.17 (m, 4, Ar H), 7.39 (m, 3, Ar H), 7.58 (m, 1, Ar H).

Anal. Calcd for $C_{23}H_{26}S_2O_2$: C, 69.31; H, 6.57; S, 16.09. Found: C, 69.36; H, 6.55; S, 16.02.

9,10-Bis[(*tert*-butylthio)methyl]anthracene (18). To a refluxing solution of 9,10-bis(chloromethyl)anthracene[57] (**17**; 2.0 g, 7.3 mmol) in acetone (50 mL) was added a solution of *tert*-butylmercaptan (2.0 g, 22.2 mmol) and KOH (1.5 g, 26.5 mmol) in 95% ethanol (50 mL) over 10 min. The reaction mixture was then refluxed with stirring for 5 h. The yellow solid that formed after reducing the volume to 30 mL under reduced pressure was filtered and crystallized from a CH_2Cl_2/hexane (3:1) mixture to afford yellow needles (2.56 g, 92%): mp 259–260 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.62 (s, 18, $SC(CH_3)_3$), 4.71 (s, 4, CH_2S)e, 7.58 (m, 4, Ar H), 8.42 (m, 4, Ar H); EI mass spectrum, m/e 382 (M^+, 6), 204 (100).

Anal. Calcd for $C_{24}H_{30}S_2$: C, 75.34; H, 7.90; S, 16.76. Found: C, 75.25; H, 7.97; S, 16.55.

Adduct 19. A mixture of 9,10-bis[(*tert*-butylthio)methyl]-anthracene (**18**; 0.50 g, 1.3 mmol), ethyl acrylate (5.0 g, 50.0 mmol), and BHT (0.02 g) was heated in a sealed glass tube at 140 °C for 20 h. The light yellow syrup obtained after removal of excess ethyl acrylate under reduced pressure was chromatographed on silica gel (50 g). On elution with chloroform a colorless gum was obtained that, on crystallization from ethanol, afforded a colorless crystalline solid (0.45 g, 71%): mp 136–137 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14 (t, 3, $C(O)OCH_2CH_3$), 1.48 (s, 9, $SC(CH_3)_3$), 1.55 (s, 9, $SC(CH_3)_3$), 1.82 (m, 1, C*H*-CHC(O)OC_2H_5, cis to ester), 2.44 (m, 1, C*H*-CHC(O)OC_2H_5, trans to ester), 3.18 (m, 1, $CHC(O)$-OC_2H_5), 3.64 (m, 3, CH_2S and one diastereotopic proton of another CH_2S), 3.98 (m, 3, $C(O)OCH_2CH_3$ and one diastereotopic proton of CH_2S), 7.16 (m, 4, Ar H), 7.46 (m, 1, Ar H), 7.75 (m, 1, Ar H).

Anal. Calcd for $C_{29}H_{38}S_2O_2$: C, 72.15; H, 7.93; S, 13.28. Found: C, 72.07; H, 7.88; S, 13.04.

9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene (20). Reagents and reaction conditions are a combination of those cited by Boldt[9a] and Lindsey.[9b] To an ice-cold solution of veratrole (32 mL, 250 mmol) in acetic acid (125 mL) was slowly added an ice-cooled solution of acetaldehyde (21 mL, 375 mmol) in methanol (20 mL). The resulting solution was stirred for 1 h. Concentrated H_2SO_4 (95%, 125 mL) was added dropwise over 90 min. The reaction was stirred at 0 °C for 20 h and then poured over ice water (1400 mL) to give a yellow/pink mixture. The beige solid was collected, crystallized from chloroform, and dried to provide 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene (9.13 g, 22.4%) as pale yellow flakes: mp> 340 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 4, Ar H), 4.10 (s, 12, OCH_3), 2.95 (s, 6, Ar CH_3); mass spectrum, m/e 326 (M^+, base peak), 327 ($M^+ + 1$), 311 ($M^+ - CH_3$), 283 ($M^+ - C_3H_7$), 268 ($M^+ - C_3H_7CH_3$); high-resolution mass spectrum, m/e 326.1523 ($C_{20}H_{22}O_4$ requires 326.1518).

9,10-Dimethyl-2,3,6,7-tetramethoxyanthracene (8.0 g, 24.5 mmol) was suspended in freshly dried and distilled dichloromethane (350 mL). Boron tribromide (6.5 mL, 69 mmol) was injected quickly. After 90 min the reaction mixture reached a greenish yellow color. The crude product, a bright yellow solid, was collected, washed with water (2 × 100 mL), crystallized from acetic acid (crystallization from ethanol also provides some purification), and dried for 24 h at 80 °C to yield **20** (5.56 g, 84%) as greenish brown needles: decomposes without melting at 235–250 °C; ^{1}H NMR (DMSO-d_6) δ 9.45 (br s, 1, Ar O*H*), 7.40 (s, 4, Ar H), 2.71 (s, 6, Ar CH_3); mass spectrum, m/e 270 (M^+, base peak), 271 ($M^+ + 1$), 255 ($M^+ - CH_3$), 253 ($M^+ - OH$), 242 ($M^+ - C_2H_4$), 241 ($M^+ - C_2H_5$), 227 ($M^+ - C_3H_7$); high-resolution mass spectrum, m/e 270.0886 ($C_{16}H_{14}O_4$ requires 270.0892).

Bis(silylenedioxy)anthracene 22. 9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene (**20**; 400 mg, 1.48 mmol) was dissolved in dry acetonitrile (50 mL). Freshly distilled triethylamine (0.8 mL, 5.74 mmol) was injected and a yellow precipitate formed immediately. Di-*tert*-butyldichlorosilane (0.7 mL, 3.3 mmol) was added dropwise over 5 min and the temperature was increased

to gentle reflux for 16 h. The reaction mixture was concentrated under reduced pressure to a dark solid, taken up in chloroform (300 mL), and partitioned between chloroform and aqueous sodium bicarbonate solution. The chloroform layer was then washed with a saturated salt solution, dried over potassium carbonate, and evaporated under reduced pressure to give a pale yellow-green solid, which was recrystallized from chloroform to afford **22** (810 mg, 99%): ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 36, *t*-Bu), 2.90 (s, 6, CH_3), 7.61 (s, 4, Ar H); ^{13}C NMR ($CDCl_3$) δ 14.90 (Ar CH_3), 21.56 (CCH_3), 26.17 ($C(CH_3)_3$), 104.55 (Ar *C*H), 124.75 (C-*C*-CH_3), 126.64 (unassigned quaternary C), 148.79 (C-OR); mass spectrum, *m/e* 550 (M^+); high resolution mass spectrum, calcd for $C_{32}H_{46}O_4Si_2$ 550.2935, measured 550.2942.

Adduct 23. Bis[(di-*tert*-butylsilylene)dioxy][*b,i*]-9,10-dimethylanthracene (**22**; 231 mg, 0.42 mmol) was added to a pressure tube with acrylonitrile (10 mL) and BHT (2 crystals). The pressure tube was sealed, wrapped in aluminum foil, and placed in an oil bath at 85 °C for 44 h. The resulting orange solution was evaporated under reduced pressure to an orange oil that was taken up in a minimal amount of hot CCl_4. Upon cooling, impurities precipitated. The orange mixture was eluted through a Celite plug with carbon tetrachloride and the filtrate was evaporated to yield **23** (213 mg, 84%): ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 36, *t*-Bu), 1.80 (s, 3, CH_3), 1.81 (dd, 1, CH trans to CN), 2.05 (s, 3, CH_3), 2.06 (dd, 1, CH cis to CN), 2.65 (dd, 1, CH), 6.90 (s, 4, Ar H) mass spectrum, *m/e* 603 (M^+), 550 (M^+ – acrylonitrile, 100).

Adduct 24. 9,10-Dimethylanthracene (182 mg, 88 mmol) was placed in a pressure tube with acrylonitrile (10 mL) and 2,6-di-*tert*-butyl-4-methylphenol (2 crystals). The pressure tube was sealed, wrapped in aluminum foil, and warmed in an oil bath at 50 °C for 21 h. The resulting solution was evaporated to dryness and recrystallized from ethanol to afford **24** (206 mg, 98%): ^{1}H NMR ($CDCl_3$) δ 1.46 (dd, 1, CH trans to CN), 1.98 (s, 3, $NCCCCCH_3$), 2.11 (dd, 1, CH cis to CN), 2.17 (s, 3, $NCCCCH_3$), 2.75 (dd, 1, CH), 7.30 (m, 8, Ar H).

9,10-Di-*n*-butylanthracene (25). 9,10-Dibromoanthracene (2.0 g, 5.95 mmol) was placed in a dry 50-mL three-neck flask that was sealed with septa. Anhydrous diethyl ether (30 mL) was added and the solution was stirred under argon while *n*-butyllithium (4.76 mL of a 2.5 M solution, 11.9 mmol) was added slowly over 5 min. The solution was stirred for 30 min, then *n*-butyl bromide (1.3 mL, 12 mmol) was added, and the solution was heated to reflux for 15 h. Extraction of the ether layer with H_2O, drying over $MgSO_4$, and evaporation to dryness resulted in a yellow oil. The oil was subjected to silica gel chromatography (hexane solvent) and the appropriate fractions were pooled and evaporated to give a fluorescent oil that crystallized upon standing. The solid was recrystallized from methanol to give **25** as light green fluorescent needles (648 mg, 38% yield): mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.04–1.52 (t, 6, CH_3), 1.57–1.79 (m, 4, CH_2), 1.80–1.85 (m, 4, CH_2), 3.57–3.63 (m, 4, Ar-CH_2), 7.47–7.51 (m, 4, Ar H), 8.28–8.33 (m, 4, Ar H); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 23.4 ($CH_2CH_2CH_3$), 27.9 ($CH_2CH_2CH_2CH_3$), 35.6 ($CH_2CH_2CH_2CH_3$), 124.7 and 125.2 (Ar *C*-H), 129.4 and 133.8 (quaternary Ar *C*); high resolution mass spectrum, calcd for $C_{22}H_{26}$ 290.203, measured 290.204.

Attempted Dehydrogenation of 9,10-Di-*tert*-butyl-9,10-dihydroanthracene (26). Into a pressure tube were placed **26** (536 mg, 1.82 mmol), 10% palladium on carbon (500 mg), and hexane (8 mL). The tube was sealed and heated in a salt bath at 250 °C for 6 h, then removed from the salt bath, and allowed to cool. The contents of the tube were passed through a short silica gel plug, eluting with hexane to remove the palladium on carbon. The resulting solution was evaporated in vacuo to give a solid that was subjected to silica gel chromatography (hexane eluant). Fractions were analyzed by TLC and UV. Pooling and evaporation of the appropriate fractions showed that the product composition consisted of **3** and a trace amount of **27**. The products were further characterized by using EI mass spectroscopy and ^{1}H and ^{13}C NMR by comparison to authentic samples.

1,4-Di-*tert*-butylanthracene (27). A 10-in. pressure tube was filled with 1,4-di-*tert*-butyl-1,4-dihydroanthracene (195 mg, 0.67 mmol), 10% palladium on carbon (256 mg), and hexane (8 mL) as solvent. The tube was heated for 5 h at 200 °C, cooled, and filtered through a silica gel plug to remove the palladium on carbon. The hexane solution was evaporated to dryness and the solid was subjected to silica gel flash chromatography (hexane solvent). The appropriate fractions were pooled and evaporated to give a white solid (164 mg, 86%): mp 123–125 °C; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 18, *t*-Bu), 7.47 (s, 2, Ar H), 7.49–7.56 (m, 2, Ar H), 8.05–8.10 (m, 2, Ar H), 9.15 (s, 2, Ar H); ^{13}C NMR δ 32.11 ($C(CH_3)_3$), 35.94 ($C(CH_3)_3$), 122.3, 125.3, 126.7, 128.2 (Ar *C*-H), 129.3, 131.5, 144.3 (quaternary Ar *C*); high resolution mass spectrum, calcd for $C_{22}H_{26}$ 290.203, measured 290.204.

9-*tert*-Butyl-9,10-dihydroanthracene (30). Into a 100-mL flask were placed **29** (2.0 g, 7.9 mmol) and CH_2Cl_2 (25 mL). The flask was flushed with argon and trifluoroacetic acid (1.3 mL, 17 mmol) was added. The solution turned black as it was allowed to stir for 6 min, and then triethylsilane (2.7 mL, 17 mmol) was added. After 5 min the solution was evaporated in vacuo to a dark oil that was extracted into ether (100 mL) and washed with 20% sodium bicarbonate (2 × 20 mL) and water (2 × 20 mL). The ether layer was dried over $MgSO_4$ and evaporated in vacuo to give a light oil that was chromatographed on silica gel (hexane solvent). Pooling and evaporation of the appropriate fractions gave a colorless solid that was used without further purification (620 mg, 33%): mp 124–125 °C (lit.[15] mp 122.5 °C); ^{1}H NMR (CCl_4) δ 0.86 (s, 9, *t*-Bu), 3.5 (s, 1, benzylic) 3.9 (q, 2, benzylic), 7.0-7.5 (m, 8, Ar H).

Reaction of 26 with DDQ at High Temperature. Into a pressure tube were placed **26** (200 mg, 0.68 mmol) and DDQ (300 mg, 1.32 mmol). Benzene (8 mL) was added as solvent and the tube was sealed and heated at 140 °C for 14 h. The contents of the tube were cooled and passed through a short silica gel plug (elution with hexane) to remove the DDQ. TLC of the resulting solution (hexane on silica gel) showed two spots. The solution was evaporated in vacuo to give a light green solid that was dissolved in hexane and subjected to silica gel flash chromatography (hexane elutent). The two bands that eluted from the column were evaporated to remove the hexane; analysis by ^{1}H NMR, UV, and mass spectrometry showed the compounds to be 9,10-dichloroanthracene (59 mg, 35%) and anthracene (79 mg, 65%) by comparison to authentic samples.

Direct Fluorination of Anthracene. A 50-mL flask was flame-dried, fitted with a condenser, and flushed with argon. Into the flask were placed **3** (104 mg, 0.58 mmol) and **33** (300 mg, 1.21 mmol). Dry, degassed 1,2-dichloroethane (35 mL) was added as solvent and the solution was heated at reflux for 5 h. The solution was cooled and quenched with water, then was extracted into ether, washed with water (2 × 15 mL), dried over $MgSO_4$, and evaporated to provide a light yellow solid. The crude product was subjected to silica gel flash chromatography (hexane eluant); the first two fluorescent bands that eluted from the column were collected and pooled to give **7y** (30 mg, 24%) and **31** (28 mg, 25%), respectively. The products obtained gave mp, mass spectrometry, and ^{1}H NMR data identical with those previously reported.[40]

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Micellar-Induced Selectivity and Rate Enhancement in the Acid-Catalyzed Cyclization and Rearrangement of Monoterpenes. The Solvolysis of Linalyl and Geranyl Acetates

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The monoterpene linalyl acetate (**1**) undergoes acid-catalyzed solvolysis/cyclization at pH 3 in HCl/citrate buffer to yield three major acyclic alcohols, geraniol (**2**), linalool (**3**), and nerol (**4**), and one cyclic alcohol, α-terpineol (**5**). The acyclic/cyclic alcohol ratio is 2.7 in no sodium dodecyl sulfate (SDS) controls after ca. 3 half-lives, compared to 8.5 when the reaction is carried out in a SDS micelle. No micellar rate effect was observed. The SDS-induced selectivity is explained in terms of the micelle-favoring acyclic conformers of linalyl acetate. In contrast to linalyl acetate, solvolysis of geranyl acetate (**6**) in the SDS micelle at pH 2 gives little product selectivity but yields a 7-fold rate effect relative to no SDS controls. This rate effect results in very different product distributions after 90% completion of the reaction. The observed SDS rate effect for geranyl acetate is compatible with a difference in solvolysis mechanism for linalyl and geranyl acetate.

Introduction

Despite the importance of functionalized mono- and polyene acid-catalyzed cyclizations,[1] rearrangements,[2] and ester solvolyses,[3] both to the synthesis and biogenesis of terpenes, reports of the effects of micelles on these reactions have been sparse. In fact, only a few reports of micellar effects on nonphotochemical cyclization reactions have appeared.[4-6]

We recently reported[4] a relatively large micellar-induced stereoselectivity and a modest rate enhancement in an acid-catalyzed "ene" cyclization of the monoterpene citronellal. Bunton and Cori[6] have also observed some micellar-induced selectivity in the cyclization/rearrangement of geranyl and neryl phosphates and pyrophosphates. In addition, sodium dodecyl sulfate (SDS) rate inhibition has been noted for some unusual neryl esters,[7] and the effect of compressed vs expanded films on nerol and geraniol solvolyses has been reported.[8]

We now report our observations showing that SDS micelles exert considerable product selectivity in the solvolysis of linalyl acetate with no rate acceleration, while a modest rate acceleration with very little selectivity was observed in the solvolysis of geranyl acetate. Even though hundreds of kinetic studies of organic substrates in micelles have been reported, very few involve complete quantitative product analysis over the course of the reaction as reported here. This type of detailed analysis is necessary to observe selectivity in complex reactions, and thus relatively few reports exist describing micellar selectivity. Studies limited to analysis of starting materials would have yielded very little information for the systems discussed here.

Due to their implication in terpene biogenesis, the acid-catalyzed solvolyses of geranyl, linalyl, and neryl systems employing many different esters and other substituents have been widely reported.[3] Specifically, the acetates have been investigated[9] in aqueous acid under conditions similar to those reported here. As noted by Juršič et al.,[7] water is the solvent of choice for studying

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