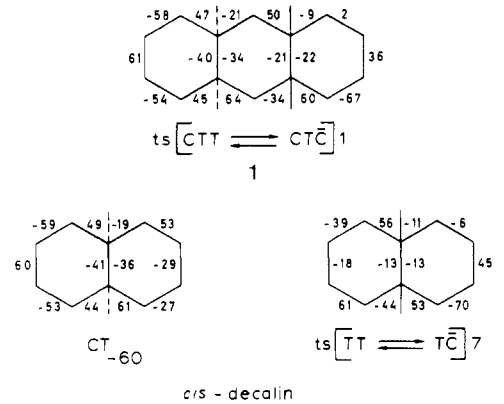

Figure 8. Endocyclic torsion angles of a higher lying transition state of 1; comparison with *cis*-decalin conformations.

groups forming ring C and the rings B and A are absent so that one may expect that this transition state of 1 has the same strain as its component *cis*-decalin transition state: 13.5 kcal mol^{-1}, a value satisfactorily close to the 13.8 kcal mol^{-1} obtained in the full computation. We actually also found a transition state of 1 that combines the lowest *cis*-decalin transition state with a relatively unstable chair–twist form (Figure 8), but its energy lies 0.9 kcal mol^{-1} higher.

In summary one can say that the rate-determining transition states of 1 and 2 are composed of the same most stable chair–twist moiety of *cis*-decalin for rings C and B combined with different chair–twist to twist–twist transition-state geometries for rings B and A; the BA moiety of the transoid isomer assumes a conformation of higher energy.

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Registry No. 1, 29863-91-0; 2, 19128-78-0.

Supplementary Material Available: Tables I and II contain the conformational energy, the endocyclic torsion angles of the three six-membered rings, and one exocyclic torsion angle at both ring-fusion sites for each stationary state of 1 and 2. A great number of non-rate-determining chair to twist transition states on the various reaction paths between the different forms depicted in Scheme I are analyzed in Tables III–VIII and are discussed in terms of *cis*-decalin forms. The pseudorotation within the various manifolds of 1 and 2 is elucidated in Figures 9–13 and in Table IX and is discussed in the same manner (25 pages). Ordering information is given on any current masthead page.

Chemistry of Bridged Aromatics. A Study of the Substituent Effect on the Course of Bond Cleavage of 9,10-Dihydro-9,10-ethanoanthracenes and an Oxyanion-Assisted Retro-Diels–Alder Reaction†

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The retro-Diels–Alder reactions of 9,10-dihydro- and 1,4,9,10-tetrahydro-9,10-ethanoanthracenes are dramatically accelerated by an oxyanion substitution on the 2π component, i.e., the ethano bridge. Studies of related systems bearing anionic, cationic, and radical substituents indicate that the cycloreversion is concerted and occurs only if both 4π and 2π fragments are highly resonance stabilized.

The retro-Diels–Alder reaction continues to receive much synthetic[1] as well as mechanistic[2] attention. However, high temperatures, frequently above 250 °C, required to effect the reaction compromise synthetic utility. Recently Grimme et al.[3] have reported that cycloreversion of some Diels-Alder adducts is dramatically accelerated by anionic substituents. For example, cycloreversion of some Diels–Alder adducts of 5-cyanocyclopentadiene is strongly accelerated by deprotonation,[3a] and an alkoxide substituent on the 4π component (at C_1) of the bicyclo[2.2.2]octadiene system accelerates the rate of cycloreversion at least by 10^{16}.[3b] The observed dramatic rate enhancement has been attributed to the formation of resonance-stabilized and weakly basic anions from more strongly basic anionic adducts. Similar oxyanion accelerations have been reported in other types of thermal pericyclic reactions.[4-6] To account for such substituent effects on the rates of pericyclic reactions, Carpenter[7] has recently proposed a comprehensive theoretical model and predicted that [4 + 2] cycloreversion would also be accelerated by anionic, cationic, and possibly radical substituents on the 2π component. In connection with other objectives we have decided to examine if the temperatures required for cycloreversion of 9,10-dihydro-9,10-ethanoanthracenes, which are typically 200 °C or above, could be substantially lowered by introduction of such substit-

† Contribution No. 3004.

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(2) Sauer, J.; Sustmann, R. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 779 and references therein.
(3) (a) Grimme, W.; Neukam, W. *Tetrahedron Lett.* **1978**, 2201. (b) Papies, O.; Grimme, W. *Ibid.* **1980**, 2799.
(4) For oxyanion acceleration of [3,3] sigmatropic shifts see: (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774. (c) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3319.
(5) For oxyanion acceleration of [1,3] sigmatropic shifts see: (a) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, 846. (b) Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050. (c) Wilson, S. R.; Mao, T. M.; Jernberg, K. M.; Ezmirly, S. T. *Tetrahedron Lett.* **1977**, 2559. (d) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 1241.
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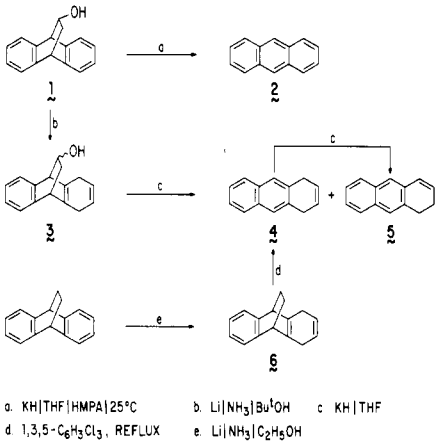
Table I. Oxyanion-Assisted Cycloreversion of 11-Hydroxy-9,10-dihydro- and -1,4,9,10-tetrahydro-9,10-ethanoanthracene

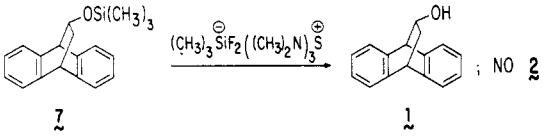
compd	base: MH	base: equiv	medium	temp, °C	time, h	product (yield, %)
1	KH	1.10	THF/HMPA	25	66	2 (60)
1	KH	1.15	THF	25	17	2 (10), 1 (90)
1	KH	2.22	dioxane	101	3	2a (79), 2 (5)
1	NaH	4.62	dioxane	101	3	2 (53), 1 (30)
3	KH	2.63	THF	25	18	5 (69)[a]

[a] 1,4-Dihydroanthracene (4) is detected by NMR at shorter reaction periods.

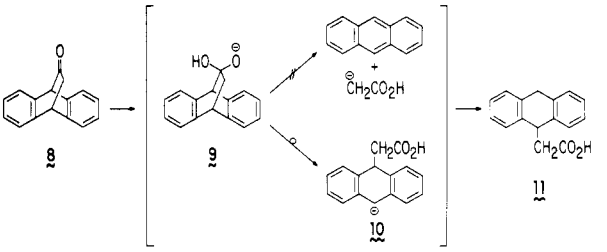
Scheme I



Scheme II



Scheme III



uents on the ethano-bridge, i.e., the 2π component of the system.

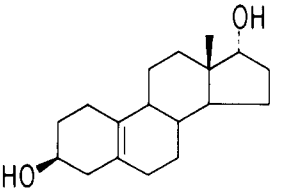
Results

Oxyanions. We find that 11-hydroxy-9,10-dihydro-9,10-ethanoanthracene (1)[8a] yields anthracene (2) in high yield upon treatment with an equivalent amount of potassium hydride in THF/HMPA at room temperature, although it cycloreverts thermally only at temperatures above 200 °C.[8b] The reaction can be carried out also in the absence of HMPA or even by using NaH. However, the cycloreversion is slower under these conditions, and refluxing dioxane is needed to effect the reaction, particularly with NaH. At higher temperatures and with excess KH further reduction of 2 to 9,10-dihydroanthracene (2a) is observed to some extent. These results are summarized in Table I and Scheme I. The 1,4-dihydro derivative (3) prepared by lithium/liquid ammonia reduction of 1 undergoes even more facile debridging than 1. Treatment of 3 with KH in THF (see Table I) both in the presence and absence of HMPA yields 1,4- and 1,2-dihydroanthracenes (4[9a] and 5). The ratio, 4/5, depends on the reaction conditions, and prolonged reaction times yield almost exclusively 5. Independent experiments demonstrate that 4 isomerizes to 5 under the reaction conditions. Authentic 4 was prepared by a retro-Diels–Alder reaction of 6[9b] in boiling 1,3,5-trichlorobenzene.

The trimethylsilyl ether 7 (Scheme II) regenerates 1 upon treatment with tris(dimethylamino)sulfonium trimethyldifluorosilicate[10] (an anhydrous fluoride ion source) or tetra-*n*-butylammonium fluoride, and no cycloreversion products are formed. Similarly, saponification of 11-acetoxy-9,10-dihydro-9,10-ethanoanthracene[8a] affords 1 without debridging. The 11-alkoxide is apparently quenched by proton transfer from the sulfonium ion or adventitious (or solvent) water more efficiently than undergoing retro-Diels–Alder reaction.

It is interesting to note that the 11-oxo derivative (8) is reported[11] to give 9,10-dihydroanthracene-9-acetic acid (11) as the only product when 8 is heated under reflux with ethanolic KOH or alkaline ethylene glycol (Scheme III). The presumed oxyanion intermediate 9 does not apparently cyclorevert to 2 but rearranges to the anion 10 by one-bond cleavage.

The oxyanion acceleration discussed above as well as those reported by others[3-6] suggest a maximal rate acceleration of thermal electrocyclic reactions may be obtained by ion-pair dissociation. However, Pillai et al.[12] have recently reported that *endo*- but not *exo*-bicyclo[2.2.1]-hept-5-en-2-ol cycloreverts upon treatment with anhydrous magnesium bromide in the presence of a trace of sodium hydroxide, phenylmagnesium bromide, or sodium hydride all in refluxing ether. In this cycloreversion intramolecular participation of oxygen-bound metal ion to the double bond is claimed to be important.[12] In our hands, the potassium salt generated from *endo*- and *exo*-bicyclo-[2.2.2]hept-5-en-2-ol (12) and KH has yielded neither cyclopentadiene nor its derivatives in refluxing ether or THF,



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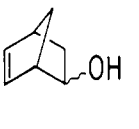

12

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(9) (a) Rigaudy, J.; Cuong, N. K. *C. R. Hebd. Seances Acad. Sci.* **1959**, *248*, 262. (b) Rabideau, P. W.; Jessup, D. W.; Ponder, J. W.; Beekman, G. F. *J. Org. Chem.* **1979**, *44*, 4594.
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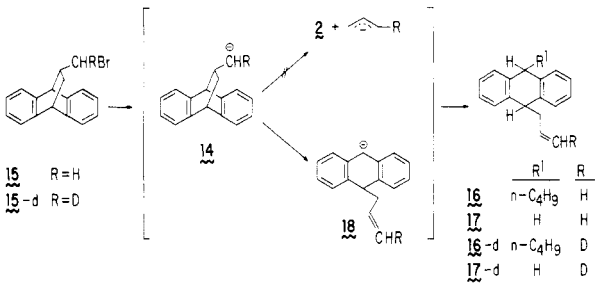
Scheme IV

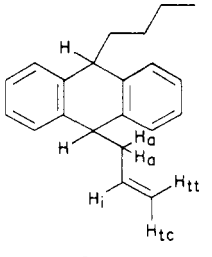


although some starting alcohol is consumed. A simple cyclohexen-4-ol derivative, **13**,[13] as the potassium salt does not yield the expected diene up to 100 °C.

Carbanions. To compare the oxyanions with a carbanion, we have generated the 11-carbanion **14** from the bromomethyl derivative **15**[14] by lithium exchange with an equivalent amount of *n*-butyllithium in *n*-hexane at −74 °C and found the dihydroanthracene derivatives **16** and **17** as the only identifiable products (Scheme IV). The butylated product (**16**) undoubtedly comes from the anion **18** by quenching with in situ generated *n*-butyl bromide. The anion **18**, however, could arise from either one-bond cleavage of **14** or cycloreversion of **14** followed by recombination of allyl anion with anthracene.

To distinguish between the two possibilities we have prepared monodeuterated bromide **15**-*d* by the sequence shown in Scheme V. Sodium tetradeuterioborate reduction of aldehyde **19** gives **20**-*d* bearing a diastereotopic proton at C-13. The NMR spectrum ($CDCl_3$, 360 MHz) shows two doublets in the methylene region at δ 3.29 (J = 6.05 Hz) and 2.94 (J = 9.46 Hz). Integration reveals 96–98% deuterium incorporation and diastereotopic excess of deuterium of 2.41 ± 0.09 to 1.00 in favor of the doublet at δ 3.29, supporting diastereotopic preference for hydride attack from the top side of the aldehyde conformer depicted by structure **19**. NMR analysis of the methylene region of bromide **15**-*d* prepared by treatment of **20**-*d* with triphenylphosphine dibromide in refluxing acetonitrile shows that the deuterium in **20**-*d* is completely retained (96–98% *d*) in **15**-*d* and that two doublets at δ 3.05 (J = 6.21 Hz) and 2.77 (J = 9.86 Hz) are in the ratio of 1.00:2.14 ± 0.05, indicating 88 ± 5% inversion of configuration in the substitution.

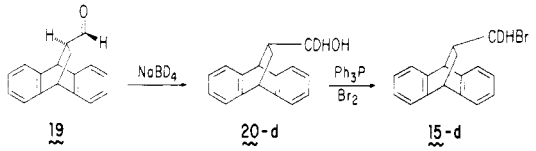
Treatment of **15**-*d* (98% *d* at C-13) with *n*-butyllithium under a variety of conditions gives rise to mixtures of **16**-*d* and **17**-*d*. The NMR analysis of **16**-*d* discussed below conclusively shows all deuterium is located in the terminal vinyl positions. The internal vinyl proton H_i (see structure **16**) resonates at δ 6.00–5.82, integrates for 1.0 H, and



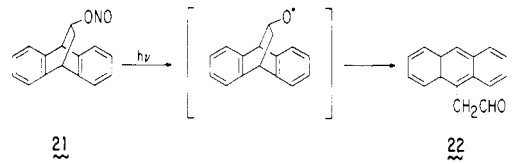
16

represents an immobile internal standard for deuterium

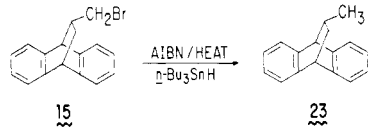
Scheme V



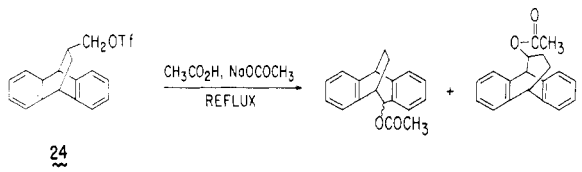
Scheme VI



Scheme VII



Scheme VIII



incorporation at other positions. The allylic protons H_a (δ 2.53) integrate as 2.00 ± 0.04 H. The terminal vinyl proton resonances H_{tc} (cis to H_i) and H_{tt} (trans to H_i) appear at δ 5.04 (J = 10.1 Hz) and 4.96 (J = 17 Hz), respectively, integrating in toto as 1.04 ± 0.03 H. The deuterium is equally distributed at both H_{tc} and H_{tt}. Thus, the carbanion **14** does not undergo cycloreversion but ring opens by a one-bond cleavage process.

Radicals. To probe the effects of oxy–radical center participation, we have prepared and photolyzed ethanoanthracene 11-nitrite **21** (Scheme VI). The major product obtained after chromatography is **22**, and no anthracene could be detected. Similarly, the alkoxy radicals generated from 3-cyclohexenols are reported to undergo one-bond cleavage.[15]

The corresponding carbon radical generated from **15** with azobis(isobutyronitrile) (AIBN) in the presence of tri-*n*-butyltin hydride gives the 11-methyl derivative **23** (Scheme VII). No evidence for either oxy or carbon radical acceleration of the cycloreversion could be observed.

Carbocation. Cristol et al.[16] have reported earlier that solvolysis of triflate **24** (Tf = trifluoromethanesulfonate) gives the Wagner–Meerwein (Scheme VIII). We have confirmed these results and failed to detect traces of ring-opened products.

Discussion

It is well recognized that the frontier molecular orbital theory is valuable in predicting regiochemistry of the [4 + 2] cycloaddition.[2] The transition state of the reaction then must reflect the properties of the 4π and 2π components or, in other words, must be edductlike. A corollary to this is that the transition state of the [4 + 2] cycloreversion, even a highly exothermic one, is late along the reaction pathway and is productlike.[3] The results pres-

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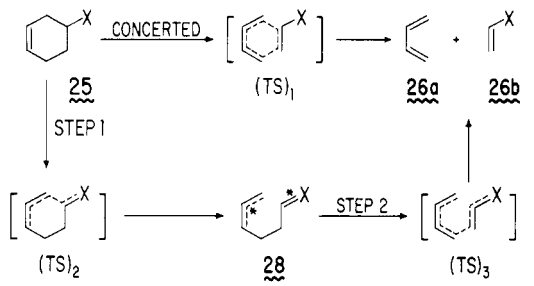
Table II. Hückel π-Electron Energies and the Relative Activation Energies in β Units

	25 → 26[7]			25 → 28		28 → 26		
	R	$(TS)_1$	Δ	$(TS)_2$	Δ	R	$(TS)_3$	Δ
pol	2.000	8.721	−0.721	5.464	−0.992	4.828	8.055	+0.933
con	4.000	10.424	−0.424	6.988	−0.516	5.656	9.518	+0.299
0	2.000	8.000	0.000	4.472	0.000	2.828	6.988	0.000

Scheme IX



ented in this paper are in complete agreement with this prediction, in that a retro-Diels–Alder reaction occurs only if the substrate is capable of fragmenting into an aromatic nucleus and a highly resonance stabilized enolate anion as the 4π and 2π components, respectively. In these cases (1 and 3) the ease with which the cycloreversion proceeds reflects the resonance stabilization (REPE)[17] of the aromatic nucleus. Compound 3 that generates naphthalene (REPE = 0.055 β) debridges more readily than 1 which generates anthracene (REPE = 0.047 β). Compounds 12 and 13, which would yield a butadiene fragment (REPE = 0.000 β) do not undergo cycloreversion.

Generation of an anthracene nucleus alone is not sufficient, and the thermodynamic stability of the potential 2π fragment is also important. In contrast to the resonance stabilized enolate anion, $[CH_2{=}{=}CH{=}{=}O]^-$, the allylic anionic, radical, or cationic moiety and the acetic acid enolate ($^-CH_2COOH$) do not offer sufficient driving force to lead to cycloreversion.

Carpenter[7] has proposed a simple model for predicting the effect of substituents on the rates of retro-Diels–Alder reactions and other thermal pericyclic reactions. Unfortunately, however, the analysis does not address the problem if the rates of nonconcerted and stepwise processes, e.g., stepwise [2 + 4] cycloreversion, would be affected by substituents. Thus, we have expaned Carpenter's analysis of concerted [2 + 4] cycloreversion involving the model transition state $(TS)_1$ to the stepwise process involving transition states $(TS)_2$ and $(TS)_3$ for polar (pol), conjugating (con), and no substituent (0) as shown in Scheme IX. The Hückel π-electron energies are calculated for the model transition states $(TS)_2$ and $(TS)_3$, 1-X-butadiene and 1-X-hexatriene, respectively. Table II summarizes the results together with Carpenter's results for the concerted process. The Hückel energy of the reactant (R) for the latter and step 1 is the same. The Δ value represents the relative "activation energies" with respect to an arbitrary zero for the unsubstituted case, and a negative Δ value indicates[7] a higher rate relative to the unsubstituted reference. Although this analysis does not reveal preference between the concerted (**25→26**) and the one bond cleavage process (**25→28**), it predicts that both processes are accelerated by the substituents. However, the second step (**28→26**) of the stepwise cycloreversion is retarded by substitution; the reverse process (**26→28**) is also predicted to be retarded.

On the basis of the results discussed, we conclude that the cycloreversion assisted by an oxyanion is a concerted process and occurs only if both 4π and 2π fragments are highly resonance stabilized. In cases where this condition is not met, other reactions can occur, including the Wagner–Meerwein rearrangement and ring opening to yield the resonance-stabilized dihydroanthryl moiety. Finally, once the latter is generated, it does not undergo the second bond cleavage leading to cycloreversion.

Experimental Section

General Procedures. All melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 double-beam Acculab 8 spectrometer. Unless otherwise indicated, NMR spectra were obtained on a Varian HR-220 or EM-390 spectrometer, and chemical shifts are reported from tetramethylsilane and were recorded for $CDCl_3$ solutions.

11-Hydroxy-9,10-dihydro-9,10-ethanoanthracene (1). A solution of 10 g (37.88 mmol) of 11-acetoxy-9,10-dihydroanthracene[8a] in 100 mL of methanol and 100 mL of dimethoxyethane was stirred with 50 mL of 2 N sodium hydroxide for 30 min at room temperature. Most of the methanol and dimethoxyethane were removed on a rotary evaporator, and the aqueous layer was extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and concentrated. The white powder so obtained (6.80 g, 81%) was recrystallized from 1:1 ether/petroleum ether (bp 40–60 °C); mp 143–145 °C (lit.[8a] mp 142–143 °C).

Retro-Diels–Alder Reaction of the Potassium Alcoholate of 1 in THF and HMPA. A mixture of 0.100 g (0.45 mmol) of 1 and 0.020 g (0.50 mmol) of potassium hydride was stirred at room temperature in 7 mL of anhydrous THF and 3 mL of HMPA for 66 h. Water (~50 mL) was added, and the mixture was extracted with low-boiling petroleum ether. Concentration and filtration through silica gel with petroleum ether yielded 0.049 g (60%) of anthracene identified by its characteristic NMR spectrum and melting point.

Retro-Diels–Alder Reaction of the Potassium Alcoholate of 1 in THF Alone. A mixture of the alcohol (0.330 g, 1.49 mmol) and 0.0685 g (1.71 mmol) of mineral oil free potassium hydride in THF was stirred at room temperature for 17 h. Water (10 mL) was added, and the product (>95%) was identified as unreacted alcohol contaminated with traces of anthracene (10%) as determined by NMR spectroscopy.

Retro-Diels–Alder Reaction of the Potassium Alcoholate of 1 in Refluxing Dioxane in the Presence of Excess Potassium Hydride. To a suspension of ~1 mL of a 20% suspension of potassium hydride in mineral oil (5 mmol) in 10 mL of dioxane was added 0.500 g (2.25 mmol) of 1. The mixture was brought to reflux and maintained at that temperature for 3 h. The product, 0.320 g (79%) of 9,10-dihydroanthracene, was filtered through a silica gel (80 g) column and analyzed by NMR spectroscopy: mp 106–108 °C (lit. 108–110 °C); ^1H NMR ($CDCl_3$/Me_4Si) δ 7.10 (m, 8 H), 3.80 (s, 4 H). The crude product contained 5% anthracene as an impurity.

Repetition of the experiment with less than 1 equiv of KH with respect to the alcohol yielded only anthracene and none of the reduction product.

Reduction of Anthracene with Potassium Hydride in Refluxing Dioxane. A mixture of 0.500 g (2.81 mmol) of anthracene and excess potassium hydride (1 mL of a 20% suspension in mineral oil) in 20 mL of dioxane was stirred for 2 h. The mixture was cooled, and the precipitated solid was filtered off and identified as unreacted starting material (0.380 g, 2.13 mmol). The filtrate was concentrated and chromatographed on silica with petroleum ether as the solvent. The 0.080 g (0.45 mmol) of product

(17) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.
(18) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480. Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

so obtained was identified by NMR spectroscopy and GC as a mixture (2:3) of anthracene and dihydroanthracene.

Retro-Diels–Alder Reaction of the Sodium Alcoholate of 1 in Refluxing Dioxane. A mixture of 0.200 g (0.90 mmol) of 1 and 0.100 g (4.16 mmol) of sodium hydride in 10 mL of dioxane was refluxed for 3 h. Addition to excess water, extraction with pentane, and chromatography of the product yielded 0.080 g (53%) of anthracene and 0.060 g (30%) of the starting material. No dihydroanthracene was detected under these conditions.

Preparation of 11-(Trimethylsiloxy)-9,10-ethano-9,10-dihydroanthracene (7). To a mixture of 0.3109 g (1.39 mmol) of 1 in 5 mL of methylene chloride and 0.90 mL (5.17 mmol) of ethyldiisopropylamine at 0 °C was added 0.60 mL (4.73 mmol) of chlorotrimethylsilane. The mixture was stirred at 0 °C for 2 h and added to 100 mL of hexane and 10 mL of saturated sodium bicarbonate. The hexane solution was washed with saturated potassium hydrogen phosphate solution and water. Drying, concentration, and removal of last traces of solvent on a high-vacuum pump yielded an oily residue which subsequently solidified: yield 0.312 g (76%); ^{1}H NMR δ 7.10 (m, 8 H), 4.10 (m, 3 H), 2.10 (m, 1 H), 1.30 (m, 1 H), 0.05 (s, 9 H).

Generation of Tris(dimethylamino)sulfonium 9,10-Dihydro-9,10-ethanoanthracen-11-olate from 11-(Trimethylsiloxy)-9,10-ethano-9,10-dihydroanthracene and Fluoride Ion. To a mixture of 0.400 g (1.45 mmol) of tris(dimethylamino)-sulfonium difluorotrimethylsilicate (TASF)[10] and 0.270 g (0.92 mmol) of the silyl ether 7 was added 15 mL of anhydrous THF. The mixture was stirred at room temperature for 24 h. A check of TLC on silica with 10% ether/hexane as the solvent indicated absence of anthracene. The mixture was further refluxed for 5 h and then poured into excess water and hexane. Extraction with hexane and concentration yielded 0.196 g (96%) of a solid identified as 1, resulting from simple *O*-silyl cleavage of the starting ether. No trace of anthracene was detected.

Preparation of 11-Hydroxy-1,4,9,10-tetrahydro-9,10-ethanoanthracene (3). Anhydrous ammonia (150 mL) was collected in a three-necked flask fitted with a dry ice condenser, a serum stopper, and a gas inlet. A solution of 1.10 g (4.95 mmol) of 1 in 100 mL of anhydrous THF was slowly added to ammonia. When the mixture warmed up to −30 °C, 0.150 g (21.7 mmol) of freshly cut lithium wire was added, and the mixture was stirred for 20 min. Excess (15 mL) *tert*-butyl alcohol was added, excess THF was removed on a rotary evaporator, and the product was extracted with two 75-mL portions of methylene chloride. The combined methylene chloride layers were washed with water and concentrated. One recrystallization from ether/hexane yielded a mixture of alcohols enriched in starting alcohol. The second crop containing predominantly the reduction product 3 was further purified by medium-pressure chromatography with 25% ether/petroleum ether on silica gel. The desired product (0.649 g, 59%) was probably a mixture of isomeric alcohols 3 (exo and endo), mp 142.5–145 °C. Attempted separation of the two via chromatography was not successful. This mixture was used for subsequent reactions: ^{1}H NMR δ 7.10 (m, 4 H), 5.70 (s, 2 H), 4.10 (br m, 1 H), 3.75 and 3.80 (2 d, J = 4 Hz, together 1 H), 3.55 (t, J = 3 Hz, 1 H), 2.93 and 2.80 (2 s, together 4 H) 2.03 (ddd, J = 13, 8, 3 Hz, 1 H), 1.57 (br s, 1 H, exchanged with D_2O), 1.30 (dt, J = 13, 3 Hz, 1 H); HRMS, m/e 224.1217 (M^+; calcd for $C_{16}H_{16}O$, 224.1201), ($M^+ - H_2O$; calcd 206.1082); 180.0937 ($M^+ - C_2H_4O$; calcd 180.0938).

Retro-Diels–Alder Reaction of the Potassium Alcoholate of 3 in THF at Room Temperature. To 0.058 g (1.45 mmol) of mineral oil free potassium hydride in 10 mL of anhydrous THF was added 0.124 g (0.55 mmol) of 3, and the mixture was stirred under nitrogen for 18 h. Water (10 mL) was added. Extraction of the product with petroleum ether followed by chromatography on silica gel yielded 0.068 g (69%) of a white solid identified as 1,2-dihydroanthracene by comparison of spectral properties with those of a sample prepared as follows.

Preparation of 1,2- and 1,4-Dihydroanthracenes (4 and 5) from 1,4,9,10-Tetrahydro-9,10-ethanoanthracene. A solution of 0.500 g (2.40 mmol) of 6[9b] in 5 g 1,3,5-trichlorobenzene was refluxed for 18 h. Hexane (20 mL) was added and the precipitated solid removed. The remaining hexane solution was concentrated and chromatographed on silica gel with hexane as the solvent. The white solid containing traces of anthracene was identified as 1,4-dihydroanthracene: 0.120 g (28%); ^{1}H NMR δ 7.30 (m, 6 H), 5.90 (br s, 2 H), 3.50 (s, 4 H).

A mixture of 0.048 g (1.20 mmol) of mineral oil free potassium hydride and 0.058 g (0.32 mmol) of 1,4-dihydroanthracene in 5 mL of anhydrous THF was stirred under nitrogen for 17 h at room temperature. Chromatography on silica gel with hexane yielded the 0.041 g (71%) of product identical in all respects with the product (1,2-dihydroanthracene[9a]) obtained via retro-Diels–Alder reaction of the alcoholate of 3: ^{1}H NMR δ 7.75 (m, 2 H), 7.40 (m, 4 H), 6.68 (d, J = 10 Hz, 1 H), 6.20 (dd, J = 10, 4 Hz, 1 H), 3.00 (t, J = 8 Hz, 2 H), 2.45 (m, 2 H).

Preparation and Photolysis of 9,10-Ethano-9,10-dihydroanthran-11-yl Nitrite (21). To a solution of 1.25 g (5.63 mmol) of 1 in 20 mL of anhydrous pyridine was added slowly 0.95 mL (20.55 mm) of nitrosyl chloride collected in a separate cold trap. After stirring for 2 h, 10 mL of water and 30 mL of hexane were added. The hexane layer was separated, and the aqueous layer repeatedly extracted with three 40-mL portions of hexane. The combined organic layer was washed with ice cold sulfuric acid and water. The yellow oil (95%) so obtained was recrystallized from hexane/ether: mp 91–97 °C dec; ^{1}H NMR δ 7.20 (m, 8 H, aromatic), 5.70 (ddd, J = 9, 3, 3 Hz, 1 H, HC–ONO), 4.50 (d, J = 3 H, 1 H, bridgehead β to ONO), 4.20 (dd, J = 3, 3 Hz, 1 H, other bridgehead methine), 2.35 (ddd, J = 13, 9, 3 Hz, anti H on carbon β to ONO), 1.55 (ddd, J = 13, 3, 3 Hz, 1 H, syn H on carbon β to ONO); IR(CCl_4) 1660 cm^{-1} (strong).

A solution of 0.200 g (0.80 mmol) of the nitrite in 20 mL of benzene was degassed and photolyzed in Rayonet photolysis equipment with a Hanovia medium-pressure lamp for 66 min. A check of TLC (1:1 ether/hexane, silica) indicated a number of products including uncoverted starting material. The reaction was optimized for the maximum amount of the highly fluorescent spot by varying the photolysis time alone. This spot was isolated by preparative TLC (0.040 g, 23%) and identified as (9-anthranyl)acetaldehyde (22): ^{1}H NMR δ 9.80 (t, J = 2.70 Hz, 1 H, aldehyde H), 8.00–7.60 (m, 9 H, aromatic), 4.65 (d, J = 2.70 Hz, 2 H, CH_2CHO); IR (KBr) 1720 cm^{-1}; HRMS, m/e 220.0884 (M^+; calcd for $C_{16}H_{22}O$ 220.0868); 191.0843 (M^+ – CHO; calcd 191.0860).

Preparation of 11-(Bromomethyl)-9,10-ethano-9,10-dihydroanthracene (15). The bromide 15 was prepared from the corresponding alcohol[19] 20 using the triphenylphosphine bromine method.[20]

Reactions of 11-(Bromomethyl)-9,10-ethano-9,10-dihydroanthracene (15) with *n*-Butyllithium. A 3 g (10 mmol) solution of 15 in 30 mL of dry THF was cooled to −74 °C (dry ice–acetone bath) under nitrogen and treated over 5 min with 7.0 mL (11.2 mmol) of 1.6 M *n*-butyllithium in *n*-hexane. An immediate red color appeared and persisted. After 10 min, the mixture was quenched at −74 °C by addition of 0.60 mL (10 mmol) of acetic acid dissolved in 10 mL of THF, during which the mixture became pale yellow. After warming to room temperature, the reaction mixture was poured into 50 mL of water and extracted twice (50 mL each) with methylene chloride, and the organics were dried (Na_2SO_4) and concentrated. The residue (3.05 g) was analyzed by NMR and found to contain 15 (69%) and 9-propenyl-9,10-dihydroanthracene (17, 31%).

A similar run at +25 or −15 °C gave only 17: IR (neat) 1635 (m), 910 (s), 750 (s) cm^{-1}; ^{1}H NMR δ 7.4–6.95 (m, 8 H), 6.0–5.4 (m, 1 H), 5.1–4.7 (m, 2 H), 4.2–3.85 (m, 3 H), 2.7–2.3 (m, 2 H). Anal.: C, H.

An identical reaction (25 °C) was quenched with 1.4 mL (11 mmol) of chlorotrimethylsilane to provide 9-propenyl-10-(trimethylsilyl)-9,10-dihydroanthracene as an oil: 78% IR (neat) 1645 (m), 910 (m), 838 (s), 775 (m), 755 (s) cm^{-1}; ^{1}H NMR (CCl_4 + 2% CH_2Cl_2) δ 6.95 (m, 8 H), 6.0–5.4 (m, 1 H), 5.04–4.7 (m, 2 H), 3.84 (t, J = 10 Hz, 1 H), 3.72 (s, 1 H), 2.30 (m, 2 H), 0.08 (s, 9 H); HRMS, δ 292.1619 (M^+, calcd for $C_{20}H_{24}Si$, 292.1646). Anal.: C, H.

A moderate delay between *n*-butyllithium addition and quenching results in formation of mixtures of 17 and the self-quenching product 9-*n*-butyl-10-propenyl-9,10-dihydroanthracene

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(20) Horner, L.; Oediger, H.; Hoffmann, H. *Justus Liebigs Ann. Chem.* **1959**, *626*, 26.

(16): IR (neat) 1632 (m), 908 (s), 751 (s) cm^{-1}; ^1H NMR δ 7.2–7.05 (m, 8 H), 6.0–5.5 (m, 1 H), 5.1–4.8 (m, 2 H), 3.96 (t, J = 7.5 Hz, 1 H), 3.86 (t, J = 7.5 Hz, 1 H), 2.53 (t, J = 7.0, 2 H), 1.4–1.1 (m, 6 H), 0.88 (t, J = 7.1 Hz, 3 H). Anal.: C, H. Identical material was obtained by addition of *n*-BuLi to anthracene followed by anion trapping with allyl bromide.

Deuterated Precursors. Monodeuterio bromide **15**-*d* was prepared by the sequence shown in Scheme V. The aldehyde **19** was obtained via oxalyl chloride–dimethyl sulfoxide oxidation[18] of perprotio alcohol **20**. The aldehyde **19** exhibited the following properties: mp 72–74 °C; IR (Nujol) 2700 (m), 1710 (s) cm^{-1}; ^1H NMR δ 9.39 (d, J = 1.7 Hz, 1 H), 7.32–7.00 (m, 8 H), 4.67 (d, J = 2.50 Hz, 1 H), 4.39 (t, J = 2.70 Hz, 1 H), 2.75 (m, 1 H), 2.09 (m, 1 H), 1.97 (m, 1 H). Anal.: C, H.

Reduction of 5.00 g (21.40 mmol) **19** with 0.498 g (11.91 mmol) of sodium tetradeuteroborate in 50 mL of ethanol at room temperature afforded **20**-*d*: 98% yield; mp 101–103 °C; IR (Nujol) 3400 (br), 2130 (w, C–D) cm^{-1}; HRMS, m/e 237.1259 (M^+; calcd for $C_{17}H_{15}DO$ 237.1264). The ^1H NMR spectrum ($CDCl_3$, 360 MHz) of **20**-*d* showed inter alia two doublets in the methylene region: δ 3.29 (J = 6.05 Hz) and 2.94 (J = 9.46 Hz), respectively (1 H).

Deuterio alcohol **20**-*d* was converted to bromide **15**-*d* in 84% yield by heating a mixture of 3.555 g (15 mmol) of **20**-*d* and triphenylphosphine dibromide [from triphenylphosphine (3.93 g, 15 mmol) and bromine (0.768 mL, 15 mmol)] in 40 mL of acetonitrile at reflux for 4 h. When the mixture cooled, bromide **15**-*d* separated as white needles; yield 3.78 g (84%) in three crops: mp 125–127 °C; ^1H NMR (inter alia) δ 3.05 (d, J = 6.21 Hz), 2.77 (d, J = 9.86 Hz), in a ratio of 1.00:2.14 (±0.05); HRMS 299.0413 (M^+; calcd for $C_{17}H_{14}DBr$, 299.0420).

Reaction of Bromide 15-*d* with *n*-Butyllithium. A solution of 0.600 g (2.00 mmol) of **15**-*d* in 15 mL of dry THF under nitrogen was treated at room temperature with 0.60 mL (1.28 mmol, 0.64 equiv) of 2.14 M *n*-butyllithium in hexane. The red solution was allowed to stand 30 min, during which time the color dissipated to yellow. Quenching (saturated NH_4Cl) followed by an aqueous methylene chloride workup yielded 630 mg of a pale yellow oil on concentration. NMR analysis revealed the presence of starting material (0.359 g, 60%) and 9-*n*-butyl-10-propenyl-3-*d*-9,10-dihydroanthracene (**16**-*d*; 0.222 g, 40%). A portion of the mixture was purified by preparative TLC (200-μm micron silica gel) with *n*-hexane elution: R_f 0.40 (**16**-*d*), 0.19 (**15**-*d*). NMR analysis of recovered **16**-*d* showed that the diastereotopic excess of deuterium is unaltered during reaction. The ^1H NMR spectrum ($CDCl_3$, 360 MHz) of the product indicates that all deuterium is located in the terminal vinyl positions (see Results).

Reduction of 15 with Tri-*n*-butyltin Hydride. A mixture of 2.99 g (10 mmol) of **15**, 2.91 g (10 mmol) of tri-*n*-butyltin hydride, and 0.035 g (2 mol %) azobis(isobutyronitrile) (AIBN) was heated in 50 mL of benzene under nitrogen at 80 °C for 2 h. Concentration provided 5.84 g of a mixture of white solid and a pale yellow oil. trituration with cold ethanol and filtration gave a mixture of 1.10 g (2.6 mmol) of recovered **15** and 11-methyl-9,10-ethano-9,10-dihydroanthracene (**23**). The mother liquors were concentrated, and 4.30 g of the residue was chromatographed on 75 g silica. Elution with petroleum ether afforded 1.27 g of **23** (cuts 6–9), and later fractions (cuts 11–18) gave some more **15**, making the material balance nearly quantitative. Compound **23** (76% total yield) was identical in all respects with an authentic sample.[21] No ring-opened compounds were detected in the reaction products.

Registry No. **1**, 1521-59-1; **1**·K, 84332-54-7; **2**, 120-12-7; **3**, 84332-55-8; **3**·K, 84332-56-9; **4**, 5910-32-7; **5**, 58746-82-0; **6**, 71870-46-7; **15**, 42166-01-8; **15**-d_1, 84332-62-7; **16**, 84332-61-6; **16**-d_1, 84332-63-8; **17**, 84332-59-2; **19**, 7673-68-9; **20**-d_1, 35964-05-7; **21**, 84332-57-0; **22**, 84332-58-1; **23**, 32363-36-3; TASF, 59218-87-0; 9-propenyl-10-(trimethylsilyl)-9,10-dihydroanthracene, 84332-60-5.

(21) Panker, V. D.; Dirlam, J. P.; Eberson, L. *Acta Chem. Scand.* **1971**, *25*, 341.

Synthesis of (*Z*,*Z*)-11,13-Hexadecadienal, a Principal Component of Navel Orangeworm (*Pamyelois transitella*) Pheromone

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This report outlines a commercial synthetic process for (*Z*,*Z*)-11,13-hexadecadienal (navel orangeworm pheromone). The synthetic scheme which is employed introduces the stereochemically labile conjugated diene moiety at a late stage in the synthesis, thereby avoiding complications during the purification of intermediates. In addition, the aldehyde function is generated through a Grignard reaction sequence, obviating the generally accepted techniques which are usually unsuitable for commercial preparations. We have also observed the first reported selective inclusion by urea of a conjugated (*Z*,*Z*)-diene as a means of mild purification of labile dienic pheromone intermediates.

As the first pheromone discovered to contain a *Z*,*Z* conjugated diene moiety, the navel orangeworm pheromone presents some unique challenges from a synthetic standpoint. Sonnet and Heath[1] followed the straightforward synthetic approach of generating the conjugated diene system through dialkylborane reduction of the appropriate diyne obtained from Cadiot–Chodkiewicz[2] coupling of the proper acetylenes as outlined in Scheme I.

This synthesis suffers from two weaknesses. It utilizes chromium oxidation[3] to generate the aldehyde, and 2 equiv of expensive dicyclohexylborane are necessary to reduce the diyne to the (*Z*,*Z*)-diene.

Results and Discussion

In our continuing search for a more convenient and cost-effective approach to the generation of the (*Z*,*Z*)-diene functionality, we found that dialkylborane reduction of the appropriate (*Z*)-enyne would afford the desired diene, thus requiring only half the expensive dialkylborane reagent

(1) Sonnet, P. E.; Heath, R. R. *J. Chem. Ecol.* **1980**, *6* (1), 221–8.
(2) Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, [13] 2, 819.

(3) In a commercial reaction sequence, chromium oxidations where possible are to be avoided due to the disposal problems that accompany such processes.

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