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(17) Of course, for sufficiently long chains, C_{elf} becomes smaller than C_{min} even in the dynamic model of the reaction. This, however, does not affect our argument.

Thermal Isomerization Reactions of *cis*-9,10-Dihydronaphthalene Derivatives

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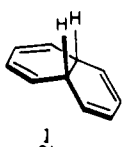
Abstract: *cis*-9,10-Dihydronaphthalene-*2,3-d*$_2$ (**37**) rearranges upon heating in the gas phase (510°, contact time ~1 sec) to return the starting tetraene frame carrying near statistical distribution of the isotopic label at all positions. The propensity for degenerate behavior in **37** thereby established, the response of the 9,10-dicarbomethoxy (**3**) and 9,10-dimethyl derivatives (**26**) to thermal activation was also studied. When heated in dimethoxyethane solution at 80° (19 hr), **3** afforded predominantly 1,5- and 1,9-dicarbomethoxy-*cis*-9,10-dihydronaphthalene (**12** and **13**). Hydrocarbon **26** behaved analogously, giving rise to the structurally isomerized (but with retention of the *cis*-9,10-dihydronaphthalene framework) 1,5- and 1,9-dimethyl isomers **29** and **30**. The consequences of heating each of these six compounds at higher temperatures were also studied. Quite complex product mixtures were seen. Considerably more elucidative were the kinetic data for rearrangement of **3** and **26**. From the findings that both compounds isomerize with comparable activation parameters ($E_a \approx 26$ kcal/mol; log $A \approx 12$; $\Delta H^{\ddagger} \approx 25$ kcal/mol; and $\Delta S^{\ddagger} \approx -4$ eu), the conclusion is reached that comparable reaction pathways are followed in the two cases. The possible involvement of intramolecular Diels–Alder and Cope rearrangement pathways could be readily discounted. Rather, conclusions are reached that passage to 1,9 products proceeds via [1,5]suprafacial migration of one of four identical trigonal α carbons, while conversion to the 1,5 isomers involves transient intervention of *cis*[5]-cyclodecapentaene intermediates. The agreement between the present data and past findings with prototypical reaction channels of these types is discussed.

Degenerate rearrangement reactions occupy a unique position among the myriad types of thermal isomerization. That certain molecules can suffer appreciable levels of bond cleavage only to possess the latent capability for interchange of their constituent atoms and ultimate reconstruction of the starting frames merits recognition as a fascinating reactivity pattern. Since the much publicized demonstration of this behavior in bullvalene,[1] several additional examples of related fluxional isomerism have been uncovered. In the main, the $(CH)_n$ class of hydrocarbons has been primarily responsible for developments in this field. For example, the capacity for degenerate isomerization is now recognized for bicyclo[4.2.2]decatetraene,[2] snoutene,[3] hypostrophene,[4] cyclooctatetraene,[5] semibullvalene,[6] and lumibullvalene.[7]

Within this group of compounds, the mechanisms which allow for attainment of degeneracy are recognized to vary widely, but some pathways, such as that followed by *cis*-9,10-dihydronaphthalene (**1**), have remained elusive.[8] As a direct consequence of the possibility that thermal activation of **1** may result in valence isomerization to *cis*[5]-cyclodecapentaene (**2**), there has been a strong undercurrent of interest in this system for some time.[9] All attempts to achieve disrotatory thermal ring expansion of **1**,[10] its 9,10-dicarbomethoxy derivative,[11] and 12-oxa[4.4.3]propellatetraene[12] to such 10π-electron systems have failed. With Masamune's recent successful low-temperature synthesis of **2**[13] has come the realization that the lability of [10]annulenes precludes their isolation from thermolysis reactions. However, their transient formation under these conditions is not discounted and it was of interest to examine closely this question.



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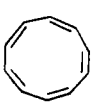

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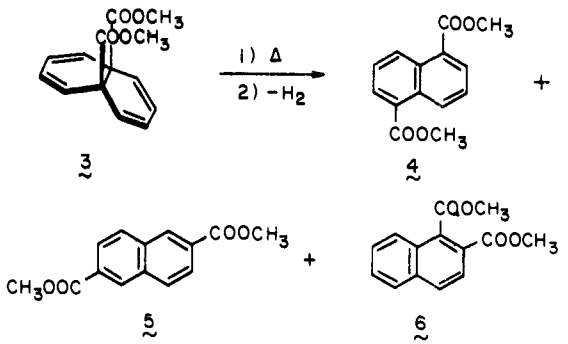
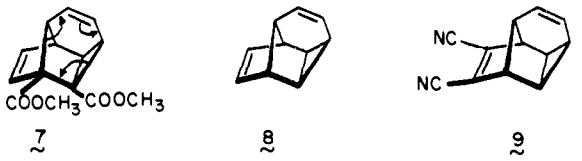
Prior to the start of this investigation, van Tamelen and Pappas had reported in 1963 that heating of dilute carbon tetrachloride solutions of **1** for 10–15 min at 150–220° resulted in quantitative conversion to naphthalene.[10] Under these conditions, therefore, aromatization with liberation of hydrogen is kinetically dominant. In view of the exceptional hydrogen transfer properties of **1**,[14] the absence of disproportionation products is rather surprising.

A year later, Vogel, Meckel, and Grimme[11] considered the possibility that replacement of the sp^3-bound hydrogens in **1** by carbomethoxyl groups as in **3** would preclude dehydrogenation and [1,5]sigmatropic hydrogen shifting from competing with the desired isomerization. These investigators noted that when **3** was heated at 90° for 2 hr and the resulting mixture of rearranged diesters directly dehydrogenated at 150°, diesters **4**–**6** were isolated together with other unidentified products. The formation of **4** and **5** was taken as an indication of the transient intervention of an unstable [10]annulene. On the other hand, the isolation of **6** has been widely interpreted[9a,c] as the probable result of intramolecular ($_{\pi}4_s + {}_{\pi}2_s$) addition to give **7** followed by retrograde Diels–Alder ring opening in the opposite direction.



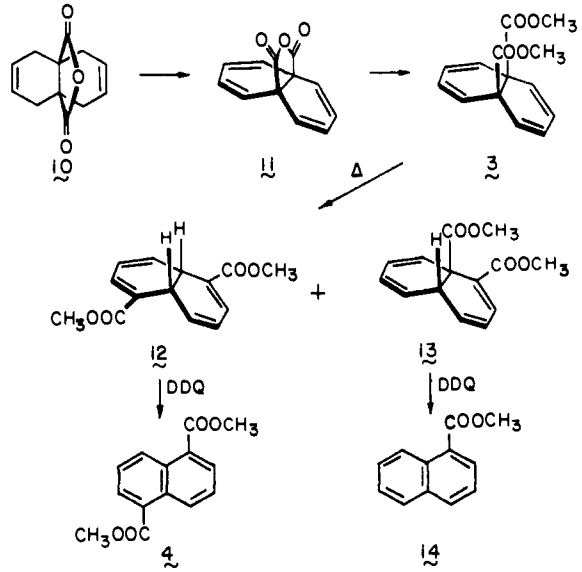
The facile thermal isomerizations of parent tetracyclic diene **8** to **1**[15] and dinitrile **9** to 1,2-dicyanonaphthalene[16] have been cited as mechanistic analogy.



Eventually, attention was turned to the behavior of **1** in a flow system. At 390°, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and naphthalene are formed.[1b,17] However, it was not until the behavior of the 2,3-dideuterio derivative of **1** was examined that rather indiscriminate scrambling of the isotopic label prior to aromatization was revealed.[8] The capability of **1** for degenerate valence isomerism was thereby made evident.

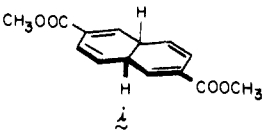
Product Studies

***cis*-9,10-Dicarbomethoxy-9,10-dihydronaphthalene (3).** The synthesis of **3** began with the readily available anhydride **10**[18] and was effected by sequential twofold allylic bromination with *N*-bromosuccinimide, dehydrobromination with quinoline, and two-step esterification according to the procedure originally devised by Vogel.[11] Thermal rearrangement of **3** in dimethoxyethane solution at 80° for 19 hr was observed to give rise to the two new dihydronapthalene diesters **12** and **13** in addition to much lesser amounts of aromatic products. Careful chromatography on silica gel permitted separation of these tetraenes. The more rapidly eluted component was identified as 1,5-dicarbomethoxy derivative **12** on the basis of its ^{1}H NMR, ir, and uv spectra (see Experimental Section) and its conversion exclusively to



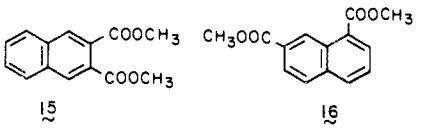
4[19] when dehydrogenated with DDQ in dimethoxyethane at 50°. Product identity in the case of **13** likewise followed from the emergent spectral features and its clean aromatization to methyl α-naphthoate (**14**) upon exposure to DDQ. Additionally, the properties of **12** and **13** are in reasonable agreement with data previously reported by Meckel.[20]

The problem of defining unequivocally the cis stereochemistry of **12** and **13** persists. Although the uv spectra of **1** (λ_{max} 248 nm (ϵ 4072))[1b] and *trans*-9,10-dihydronaphthalene (λ_{max} 276 nm (ϵ 3850))[21] do differ widely, direct extrapolation to such dicarbomethoxy derivatives is fraught with serious limitations.[22] NMR methods are likewise unsatisfactory. Diester **12** as well as its trans isomer are sym-



metrical molecules; ^{13}C measurements are consequently not capable of resolving the issue. A further complication lies in the fact that the signal due to the sp^3-bound protons in **12** is overlapped partially by the intense methoxyl singlet. Detailed analysis of this portion of the spectrum is thereby precluded in the absence of suitable deuterium substitution. However, in view of the experimental findings relating **26** to **29** and **30** (vide infra) where stereochemistry is no longer equivocal, the ring junctures in **12** and **13** are assigned cis by analogy. This matter is understandably of crucial mechanistic consequence and the assumption that **3** and **26** rearrange by identical pathways may seem unjustified to the reader. However, the great similarity in the kinetic behavior of these two systems (vide infra) should substantially lessen the arbitrariness of this direct comparison.

When both **12** and **13** were individually warmed to 80° for 7 hr in sealed NMR tubes (tetrachloroethylene solution), only minor proton spectral changes were noted. Extension of the heating period to 24 hr, followed by treatment of the solutions with DDQ at 50°, resulted in formation of those product mixtures detailed in Table I. These reactions are of course indicative of the proclivity of such 9,10-dihydronaphthalene diesters to further skeletal rearrangement. From the product composition data, it follows that **12** (30% of **4** isolated) is approximately twice as reactive as **13** (62% of **14** obtained), barring the incursion of undetectable degenerate isomerizations. In either case, the energy barrier which requires surmounting is necessarily larger than that facing **3**.



As concerns the behavior of **12**, a preference is seen for a return to vicinal placement of the two carbomethoxyl groups although now at C_1,C_2 (20% of **6**) rather than at C_1,C_9 (trace of **14**). During passage to **5** (5%), the substituents have remained on diametrically opposite corners of the naphthalene core. Conversion to **16** (13%), on the other hand, results perhaps from a more deep-seated realignment of these groups. In the case of **13**, the pattern is dismayingly simple, the two carbomethoxy functions remaining attached to adjacent carbon centers during conversion both to **6** (23%) and **15** (15%).

In the 1,5-dicarbomethoxy-9,10-dihydronaphthalene experiments, an apparently homogeneous substance was also produced in appreciable amounts (32%). On the basis of the ^{1}H NMR spectrum ($\delta_{TMS}^{CDCl_3}$ 7.6 (br s), 7.2 (m), 3.8 (s),

Table I. Isomerization–Dehydrogenation Studies of 12 and 13 at 80° ($Cl_2C{=}CCl_2$ Solution)[a]

Diester	Naphthalene products, %						
	1-$COOCH_3$ (14)	1,5-$(COOCH_3)_2$ (4)	1,2-$(COOCH_3)_2$ (6)	2,3-$(COOCH_3)_2$ (15)	2,6-$(COOCH_3)_2$ (5)	1,7-$(COOCH_3)_2$ (16)	Unknown(s), %
12	Trace	29.8	20.1	Trace	4.8	13.2	32
13	61.5	Trace	22.8	14.9	...	...	...

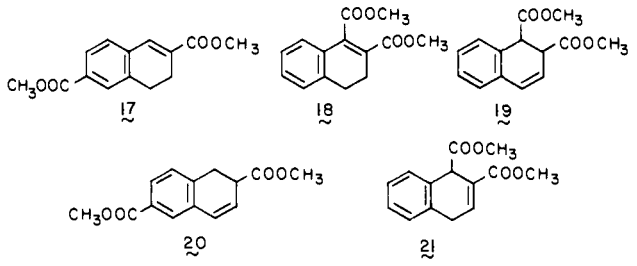
[a] Data obtained by manual integration of VPC traces from duplicate runs. The per cent composition figures are average values.

Table II. Isomerization–Dehydrogenation Studies of 3, 12, and 13 at 100° (Dioxane Solution) and 150° (Diglyme Solution)[a]

Diester	Temp, °C	Naphthalene products, %						
		1-$COOCH_3$ (14)	1,5-$(COOCH_3)_2$ (4)	1,2-$(COOCH_3)_2$ (6)	2,3-$(COOCH_3)_2$ (15)	2,6-$(COOCH_3)_2$ (5)	1,7-$(COOCH_3)_2$ (16)	Unknown(s) %
3	100	25.0	10.8	20.6	26.6	3.2	6.9	6.5
	150	2.7	6.9	28.0	29.6	9.2	3.1	20.2
12	100	3.1	36.8	10.6	13.5	12.6	24.2	...
	150	15.3	26.7	20.8	11.1	9.2	9.8	7.1
13	100	17.4	6.7	26.7	42.9	...	...	6.3
	150	35.9	5.1	22.5	25.3	...	...	11.2

[a] Data obtained by manual integration of VPC traces from duplicate runs. The per cent composition figures are average values.

and 2.84–4.0 (br m)), its structure was recognized not to be that of a fully aromatized naphthalene derivative. The possibility was considered that the isomerization and subsequent dehydrogenation of **12** had given rise to **17**,[10] **18**,[23] or **19**,[23] but these diesters proved to be quite different in their ^1H NMR features, nor does the compound appear to be **20**[24] or **21**.[25] At this point, structural assignment to the unknown has not been pursued further because of its difficult accessibility.



Although thermal activation of **3**, **12**, and **13** at still more elevated temperatures was expected to promote yet more extensive rearrangement, their isomerization behavior at 100° (dioxane solution) and 150° (in diglyme) was examined to determine if the available reaction manifolds were entirely overlapping. As before, dehydrogenation with DDQ was effected at 50° prior to product analysis by VPC. The results are summarized in Table II.

***cis*-9,10-Dimethyl-9,10-dihydronaphthalene (26).** Preparation of hydrocarbon **26** began with conversion of readily available dimesylate **22** to diiodide **23** by reaction with sodium iodide in hexamethylphosphoramide. Lithium aluminum hydride reduction of **23** in dimethoxyethane solution gave in 74% yield a semisolid distillate which was shown by VPC to consist of **24**[26] and **25**[27] in a 9:1 ratio. Separation was effected only after conversion to the respective dienes **26** and **27**. Interestingly, a sequence involving bromination of **24** with pyridinium hydrobromide perbromide and dehydrohalogenation of **28** with anhydrous lithium chloride and lithium carbonate in hexamethylphosphoramide provided not **26**, but chiefly *cis*-1,5-dimethyl-9,10-dihydronaphthalene (**29**, 10%) admixed with lesser amounts of **27**, **32**, and an unidentified monobromide. Skeletal rearrangement could be effectively deterred, however, by sequential use of *N*-bromosuccinimide and potassium *tert*-butoxide (in tetrahydrofuran). The ^1H NMR spectrum of **26** is characterized by an AA'BB' multiplet of area 8 centered at δ 6.52 and a six-proton singlet at 1.03. Its catalytic reduction provided *cis*-9,10-dimethyldecalin exclusively. The features of the ^1H NMR spectrum of **29** are equally revealing, with absorptions appearing in the olefinic (δ 5.91 (dd, 2), 5.66 (d, 2), and 5.25 (d, 2)), doubly allylic (3.04 (m, 2)), and methyl regions (1.83 (s, 6)). The electronic spectra of both **26** ($\lambda_{max}^{isooctane}$ 244 nm (ϵ 5575)) and **29** ($\lambda_{max}^{isooctane}$ 250 nm (ϵ 6470)) are so similar to that of *cis*-9,10-dihydronapthalene (vide supra) that the likelihood of trans ring fusion in either compound can be dismissed with certainty. The ready DDQ dehydrogenation of **29** to 1,5-dimethylnaphthalene (**32**) serves as added proof of structure.

At 80° in tetrachloroethylene solution, **26** was quantitatively isomerized to a mixture of **29** (53.5%) and **30** (46.5%) which could be separated by VPC methods at 80° using a 2 ft 7.5% SE-30 column. The more rapidly eluted component was assigned the *cis*-1,9-dimethyl structure on the basis of its spectra and dehydrogenation chiefly to 1-methylnaphthalene (**31**). This isomer shows ^1H NMR signals due to 7 olefinic protons (δ 5.22–5.96), one doubly allylic hydrogen (2.92), and two distinctly different methyl groups (1.66 and 1.17). According to the uv ($\lambda_{max}^{isooctane}$ 240 (ϵ 3910) and 246 nm (3920)), a cis juncture is likewise present in **30**. Suitable control experiments showed **29** and **30** to be stable to the reaction conditions.

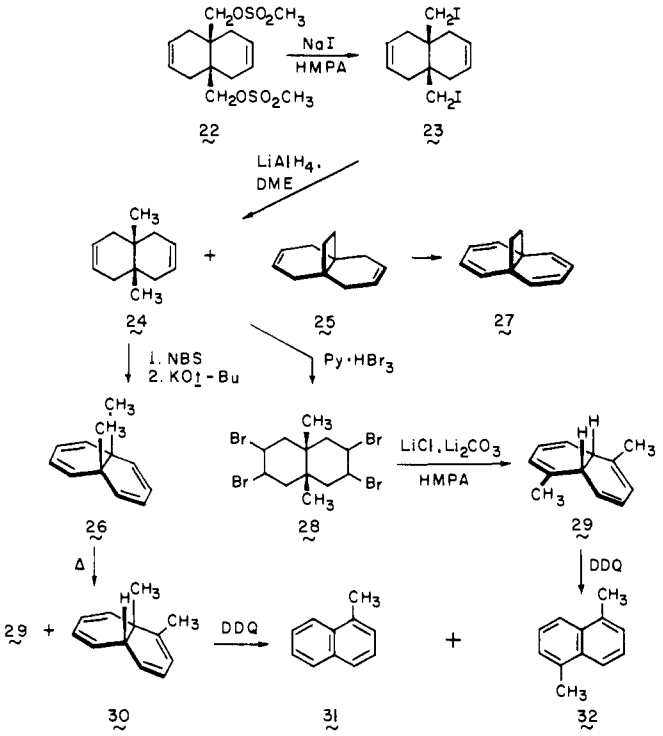
The gas phase pyrolysis of **29** at several temperatures was investigated briefly. In these experiments, the pyrolysate was dehydrogenated directly to facilitate product analysis since all of the dimethylnaphthalenes were available for comparison. The levels of monomethylnaphthalene(s) were not assayed. The data which are summarized in Table III reveal an initial dominance of 1,5-dimethylnaphthalene (**32**) in the mixture, as anticipated from the prior isolation of **29**. As the level of heat input was increased, the relative concentrations of 1,7- and 2,6-dimethylnaphthalenes are seen to increase at the expense of **32**; significantly, 1,2-dimethylnaphthalene formation was not observed.

***cis*-9,10-Dihydronaphthalene-2,3-d_2 (37).** Fundamentally at issue in this study was the question of whether one or more of several possible carbon scrambling schemes operate upon thermal activation of the *cis*-9,10-dihydronaphthalene ring system prior to, or competitive with, disproportionation schemes. The preceding investigations reveal convincingly that skeletal rearrangement with reconstruction of the *cis*-

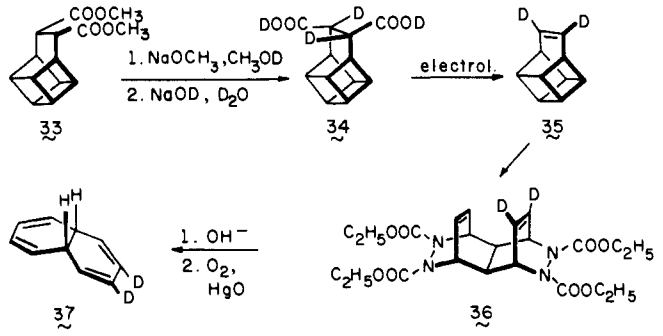
Table III. Vapor Phase Thermolyses of 29[a]

Per cent conversion	T, °C	Dimethylnaphthalenes,[b] rel % 1,5-	1,7-	2,6-	2,3-
15.3	250	84.7	10.8	2.8	1.7
40.1	280	59.9	29.4	5.8	4.8
65.9	310	34.1	51.2	11.2	3.5

[a] Contact time of 1–2 sec. [b] Produced upon DDQ oxidation of the pyrolysates in dimethoxyethane solution at 50°; analysis was performed by planimeter tracing of unweighted VPC peaks.



9,10-dihydronaphthalene frame does indeed occur when the 9- and 10-positions carry a pair of methyl or carbomethoxy groups. It now remained to examine the behavior of the parent molecule, the assessment by van Tamelen and Pappas[10] that this molecule exhibits "no overt tendency for cyclodecapentaene formation" notwithstanding. The present approach was to label **1** specifically with deuterium and to search for degenerate rearrangement in the form of isotopic migration. A doubly deuterated substrate of high isotopic purity was desired and a convenient synthesis of the 2,3-d_2 derivative (**37**) was realized by adaptation of a method modeled after certain of Shen's recent findings.[28]



This procedure required 9,10-dideuteriobasketene (**35**) which we prepared by treating diester **33**[29] first with a catalytic quantity of sodium methoxide in CH_3OD and then with NaOD in D_2O, followed by electrolytic bisdecarboxylation of trans diacid **34** as previously outlined.[30] The deuterium content of **35** was >98% d_2 by ^1H NMR analysis. Cycloaddition of diethyl azodicarboxylate to **35** gave **36**, the deuterium labeling pattern in which was clearly evident from its ^1H NMR spectrum: δ 5.8–6.5 (m, 2), 4.5–5.1 (m, 4), 4.23 (q, 8), 2.93 (br s, 2), and 1.25 (t, 12). Hydrolysis–decarboxylation of **36** under a carefully deoxygenated nitrogen atmosphere and subsequent oxidation of the derived hydrazine afforded **37** having >98% d_2 content (manual integration, expanded scale 100-MHz ^1H NMR spectra). Such samples display three multiplets at approximately δ 5.81 (2.0 H), 5.42 (4.0 H), and 3.25 (2.0 H).[31]

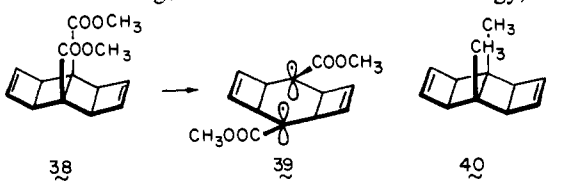
Under conditions where **37** was slowly introduced via the gas phase (510°, 30 mm N_2, contact time ~1 sec) into the packed quartz tube and subsequently repurified by VPC,[32] the tetraene had undergone extensive scrambling of its deuterium labels. Such was revealed by the ^1H NMR spectrum which now showed a proton composition of 3.4 H, 3.3 H, and 1.4 H, respectively. The average experimental error of ±0.3 H can be construed to mean that the theoretical random ratio of 3.2:3.2:1.6 had probably been realized.[33]

Kinetic Results

The isomerizations of **3** and **26** were studied kinetically. Good first-order plots were obtained for the disappearance of both reactants and were reproducible when duplicate runs were made. The rate constants and activation parameters are listed in Table IV. Although dimethyl derivative **26** is seen to rearrange approximately 14 times faster than diester **3** at 71.1°, the values of k_1 determined at three temperatures show the two compounds to differ insignificantly in their E_A, log A, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ terms.

cis-9,10-Dicarbomethoxy-9,10-dihydronaphthalene (**3**) rearranged smoothly to give a distribution of **12** (25.7%) and **13** (74.3%) which remained invariant during the period of rearrangement and was seemingly independent of temperature. Factoring k_1 for the disappearance of **3** by these percentage values provided quantitative data for the rates of appearance of these 9,10-dihydronaphthalenes (**12**, $k_{71.1°} = 0.36 \times 10^{-5}$ sec^{-1}, $k_{81.2°} = 1.04 \times 10^{-5}$ sec^{-1}, $k_{91.0°} = 2.96 \times 10^{-5}$ sec^{-1}, $E_A = 26.1$ kcal/mol, log $A = 11.2$; **13**, $k_{71.1°} = 1.03 \times 10^{-5}$ sec^{-1}, $k_{81.2°} = 3.02 \times 10^{-5}$ sec^{-1}, $k_{91.0°} = 8.54$ sec^{-1}, $E_A = 26.4$ kcal/mol, log $A = 11.8$). These computations assume that we are not dealing with two consecutive first-order reactions of the type **3** → **12** → **13** or **3** → **13** → **12**. However, the constancy of the percentage composition and the demonstrated stability of both **12** and **13** to the rearrangement conditions do not allow for this possibility. Rather, all indications are that **12** and **13** result directly from **3** at very similar rates.

The kinetic behavior of **3** is strikingly similar to that of diester **38** which had been determined in perchlorobutadiene solution at 50–80°.[22] On the basis of the activation parameters for ring opening in **38** ($E_A = 24.5$ kcal/mol, log $A = 12.0$, $\Delta H^\ddagger = 23.8$ kcal/mol, and $\Delta S^\ddagger = -5.8$ cal/(deg mol)), Martin and Hekman favored that unimolecular decomposition pathway involving homolytic cleavage of the central bond and generation of **39**.[34] From analogy, initial



disrotation of one of the cyclobutene rings is expected to be more energy demanding ($E_A \geq 27$ kcal/mol and log $A \approx 14$).[35]

cis-9,10-Dimethyl-9,10-dihydronaphthalene (**26**) was shown to give rise only to **29** and **30** whose relative percent-

Table IV. Rate Constants and Activation Parameters for Thermal Rearrangement of 3 and 26 ($Cl_2C{=}CCl_2$–CH_3COCH_3, 3:2)[a]

Compd	Temp, °C	$10^5 k_1$, sec^{-1}	E_a, kcal/mol	log A, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)
3	71.1	1.39 ± 0.06				
		1.38 ± 0.05				
	81.2	4.07 ± 0.11	26.7 ± 0.7	12.1 ± 0.4	25.7 ± 0.4	−6.3 ± 1.2
		4.04 ± 0.14				
	91.0	11.50 ± 0.50				
		11.50 ± 0.49				
26	51.0	1.77 ± 0.10				
		1.76 ± 0.08				
	61.3	5.62 ± 0.21	26.0 ± 0.8	12.8 ± 0.6	25.4 ± 0.5	−2.1 ± 1.6
		5.65 ± 0.12				
	71.1	18.90 ± 1.10				
		18.70 ± 0.91				

[a] For **26**, VPC analysis was employed. In the case of 3, ^{1}H NMR methods were utilized and the acetone solvent was d_6.

ages (53.5 vs. 46.5) also remained constant with time at the three temperatures studied. As previously discussed, both **29** and **30** are unreactive to the conditions of rearrangement. Factoring as before is seen to provide k_1 values for the appearance of these hydrocarbons which are approximately half those given for **26** in Table IV. Expectedly, all three sets of activation parameters are comparable.

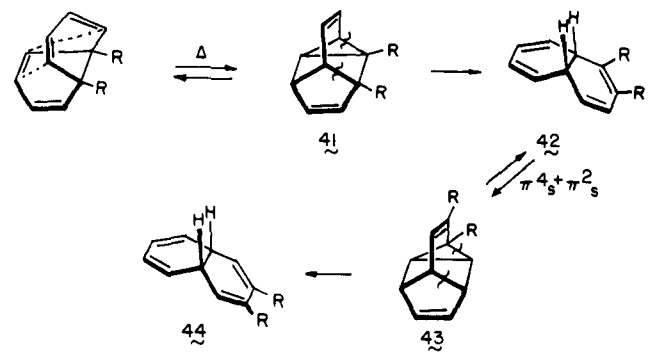
Recently, **40** was reported to have a half-life of 20 min at 145°.[36] No additional kinetic data were provided. Suitable extrapolation of our data for **26** to this temperature leads to an estimate of $t_{1/2}$ = 4–5 sec! Judging from this comparison, we see that **26** is some 250-fold more reactive than **40** despite the appreciably higher level of ring strain in the latter.

Discussion

With the capability of *cis*-9,10-dihydronaphthalenes for thermal skeletal isomerization presently established, the question now arises as to how these rearrangements take place. Since those experiments conducted at more elevated temperatures reveal that several mechanistic pathways likely operate concomitantly in dismayingly complex fashion under these conditions, the present discussion will consequently be focused on those rearrangement steps which initially take place at the lower temperatures. As a working hypothesis, we have assumed that bond relocation might occur by one or more of four symmetry-allowed processes from among the group: (a) intramolecular Diels–Alder cycloaddition, followed by ($_\sigma 2_s + {}_\sigma 2_s + {}_\pi 2_s$) retrogression; (b) Cope rearrangement; (c) [1,5]sigmatropic shifting of one or more trigonal ring carbon centers; and (d) disrotatory ring opening with formation of a *cis*^{5}-cyclodecapentaene and subsequent disrotatory reclosure of this transient intermediate in an alternative sense. Distinctions between these schemes are now possible since the present experimental findings do not satisfy certain of the conditions individually required by these four options.

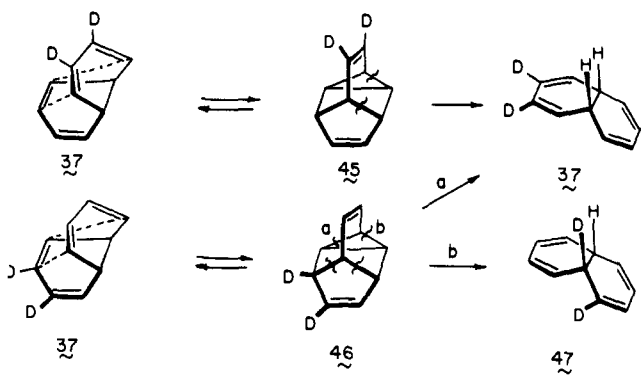
According to the first alternative, thermal activation of a 9,10-disubstituted *cis*-9,10-dihydronaphthalene could trigger intramolecular ($_\pi 4_s + {}_\pi 2_s$) bonding in which an olefinic linkage in one of the cyclohexadiene rings is required to play a dienophilic role (Scheme I). As previously noted,[15-17] the new diene arising in this manner (**41**) can ring open under retro-Diels–Alder control, a process which leads inescapably to **42**, the precursor to 1,2-disubstituted naphthalene derivatives. Repetition of this particular pathway with **42** leads via **43** ultimately to **44**. However, neither 1,2- nor 2,3-disubstituted naphthalenes are encountered upon thermal rearrangement–dehydrogenation of **3** or **26**. Since these isomers appear at more elevated temperatures, we are of the opinion that **42** and **44**, if formed, would be stable to the reaction conditions. However, this point has not yet been assessed directly by experiment. Importantly, access to 1,5- and 2,6-substitution plans cannot be gained readily in this reaction manifold.

Scheme I



A further disclaimer against this mechanism is found in the behavior of dideuterio compound **37**. Incursion of ($_\pi 4_s + {}_\pi 2_s$) bonding can lead directly to **45** and **46** (Scheme II),

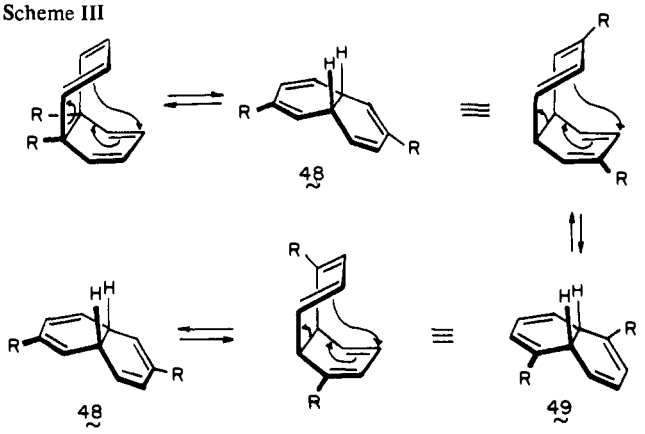
Scheme II



subsequent six-electron reorganization in which would provide *cis*-9,10-dihydronaphthalenes **37** and **47** in an approximate ratio of 2:1. Although deuterium isotope effects have been ignored in this assessment, such influences clearly will not result in major alteration of this isomer partitioning, but the data for thermal rearrangement of **37** are consistent with a near statistical distribution of isotopic label. Consequently, Scheme II is too discriminating in favor of the 2,3-d_2 isomer (**37**). Criteria for adoption of this mechanism have therefore again not been met and we discount the likelihood of its operation at the temperatures specified.

Alternatively, the *cis*-9,10-dihydronaphthalenes could be experiencing symmetry-allowed [3.3]sigmatropic shifting (Scheme III). Such Cope rearrangements have the effect of distributing the substituents at C_9 and C_{10} to positions 2,6 and 1,5 in a manner which does not allow for formation of

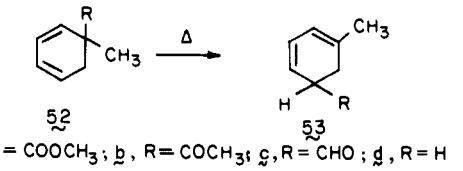
Scheme III



other isomers, i.e., 9,10 ⇄ 2,6 ⇄ 1,5. 2,6-Isomer **48** is a requisite intermediate, but no evidence for this species has been uncovered. Furthermore, **12** has been found to exhibit little tendency for interconversion with its 9,10- and 2,6-isomers (Table I) as expected of these relationships. Although such Cope rearrangements would have the effect of extensively distributing the deuterium label in **37** as early as one reaction half-life into the cycle, we surmise that it is nonoperative. The reason for the absence of this pathway as a low energy process very likely arises from the fact that [3.3]sigmatropic shifting in this fashion necessarily occurs in an "antara-antara" manner,[37] for which bona fide examples are lacking despite a seemingly adequate search.[38]

When the data for thermal activation of **3** and **26** are closely examined, a decided preference for initial isomerization to 1,9- and 1,5-isomers is witnessed. While formation of the 1,9-disubstituted products is the result of continued vicinal positioning of the pair of R groups, conversion to the 1,5 series necessitates separation of these markers by six carbons and placement at diametrically opposite positions on the *cis*-9,10-dihydronaphthalene frame. These changes cannot be plausibly accounted for in terms of a single reaction channel; rather, bifurcate reactivity involving mechanistic categories (c) and (d) best fits the observations without the need for special assumptions.

Suprafacial [1,5] migration of one of the four equivalent trigonal α-carbons in **3** or **26** leads directly to a 1,9-disubstituted 9,10-dihydronaphthalene of correct stereochemistry (cis ring fusion; Scheme IV). That this rearrangement proceeds to the exclusion of possible competitive migration by the angular carbomethoxy or methyl groups requires that vinyl carbon possess inherently better latent migratory capability in this particular structural situation. Although prior examples of comparable vinyl carbon migration are indeed few,[39] several investigations have observed related isomerization reactions requiring intramolecular sigmatropic rearrangement of carbomethoxy,[40,41] formyl,[41] acetyl,[41] phenyl,[42] cyano,[43] and alkyl groups.[44] Particularly informative is the kinetic analysis by Schiess and Fünfschilling of the rearrangements of 1-methylcyclohexadienes **52** to the isomeric dienes **53** in the temperature range of 150–360°.[41] Their findings reveal formyl (E_A = 31.0 kcal/mol; log A = 11.5) to migrate faster than hydrogen (E_A = 35.2 kcal/mol; log A = 11.2) by more than two orders of magnitude, acetyl (E_A = 35.9 kcal/mol; log A = 12.1) to possess comparable migratory ability, and carbomethoxy (E_A = 40.8 kcal/mol; log A = 11.8) to be approximately 70-fold slower than H. Most importantly, all four R groups migrate with greater facility than methyl. In their study of the thermal reorganization of substituted indenes, Miller and coworkers noted the preference order H > C_6H_5 > CH_3 to be operative in those [1,5]sigmatropic shifts which prevailed.[42] Though additional work is required to expand on this presently limited view, the evidence currently available underscores the greater migratory capability of trigonal carbon centers relative to their sp^3-hybridized counterparts. That 9,10-disubstituted *cis*-9,10-dihydronaphthalenes would selectively undergo preferential α-carbon migration as shown in Scheme IV need therefore not be considered enigmatic or demanding of special interpretation.



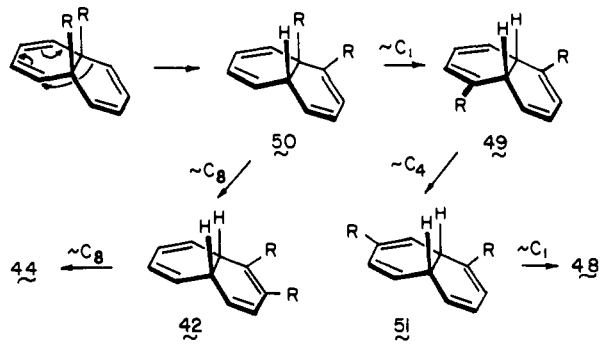
52 **53**

a, R = $COOCH_3$; **b**, R = $COCH_3$; **c**, R = CHO; **d**, R = H

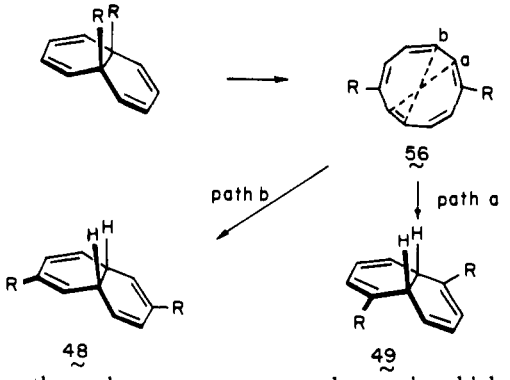
The Arrhenius parameters for appearance of **13** and **30** ($E_A \approx$ 26 kcal/mol; log A = 11–12) are consistent with rate-determining [1,5]sigmatropic shifting. In the 9,10-disubstituted series, this reaction channel is expected to be specifically facilitated due to strain relief (removal of 9,10 interaction) and the stabilizing effect resulting from positioning of one R group at C_1. Continued rearrangement of intermediate **50** by migration of either C_1 or C_8 (see Scheme IV) should not be as favorable because the steric driving force is lacking. The data now available bear this out.

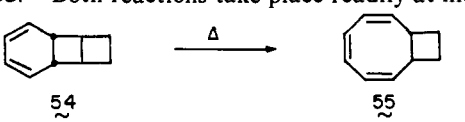
Whereas the sigmatropic pathway results in retention of the vicinal relationship of the R groups, electrocyclic disrotatory ring opening leading to *cis*[5]-cyclodecapentaene intermediates serves appropriately to maintain these substituents in a diametrically opposed relationship (Scheme V). Several apparently analogous processes are known in which a fused cyclohexadiene ring opens to an all-cis triene. Close analogies are found in the conversion of *cis*-bicyclo[4.2.0]octadiene to *cis*[3]-1,3,5-cyclooctatriene[45] and in the conversion of **54** to **55**.[46] Both reactions take place readily at moderate

Scheme IV



Scheme V

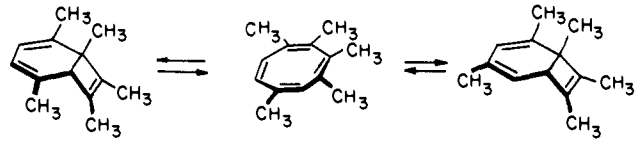




54 **55**

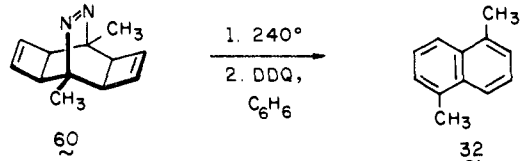
temperatures and are characterized by activation enthalpies (26.6 and 25.1 kcal/mol, respectively) entirely comparable to those determined herein for formation of **12** and **29**. Biradical alternatives seem less attractive and appear unnecessary, although it is recognized that methyl and carbomethoxy substituents provide quite comparable stabilization (3 vs. 4 kcal/mol)[47] to odd-electron centers.

Serious consideration of intermediate **56** demands rationalization of its preferred disrotatory electrocyclization to **49** rather than **48**. Firstly, there exists ample evidence to support the concept that ring closure of **56** should proceed more readily than its formation.[48] Most relevant is the finding by Masamune that closure of parent hydrocarbon **2** to give **1** proceeds with $\Delta H^{\ddagger} = 20$ kcal/mol ($\Delta S^{\ddagger} = -3$ eu).[13] Arguments for selective positioning of the R groups at C_1 and C_5 originate chiefly from thermodynamic considerations; however, it remains entirely possible that kinetic control factors operate in the same direction. Information on this last point is indeed scanty. In their study of the kinetics of electrocyclic ring closure in alkyl 1,3,5-hexatrienes, Spangler and coworkers observed that substitution at the 3 position enhances the cyclization rate, whereas placement of the same group at the 1 position has a marginal effect.[49] Unfortunately, the consequences of C_2 substitution were not examined. Along other lines, Photis has observed that 1,2,3,4,6-pentamethylcyclooctatetraene (**57**) undergoes valence tautomerism preferentially to **58** rather than **59**.[50] The two bicyclic trienes differ only in relative po-



58 57 59

sitioning of the fifth methyl group located on the conjugated diene moiety and consequently have comparable structural strain. As with **49**, however, the substituent prefers bonding to the terminus of the conjugated π system where direct interaction can operate. Cross conjugation as in **48** and **59** is certain to be less effective for stabilization purposes. It is especially noteworthy that thermal extrusion of nitrogen from tetracyclic azo compound **60** leads after dehydrogenation to a single product identified as 1,5-dimeth-



60 32

ylnaphthalene.[34] In this instance, central bond cleavage is demanded by the cheletropic reaction.

One of the striking observations in this study is the great similarity in the rates and activation parameters for sigmatropic and electrocyclic rearrangement in **3** and **26**. Apparently, the special structural features of the *cis*-9,10-dihydronaphthalene ring system, coupled with the steric consequences resulting from 9,10-disubstitution, facilitate competitive incursion of this pair of reaction channels.

In conclusion, we point out that the precise responses of dideuterio compound **37** to thermal activation need not mirror exactly those of **3** and **26**. [1,5]Sigmatropic hydrogen migration will, of course, gain importance, but this phenomenon is very probably irrelevant to the degeneracy question since return to *cis*-9,10-dihydronaphthalene after the onset of aromatization is quite unlikely.[51] Rather, as judged from the thermal responses of **12**, **13**, **29**, and **30**, a relative decrease in the capability of **37** to follow mechanism (c) is anticipated. Such circumstantial evidence leads to postulation of transient *cis*[5]-cyclodecapentaene intervention as the principal reaction channel for isomerization in **1**. In any event, *cis*-9,10-dihydronaphthalene clearly does not deserve the rather unflattering position it has held in recent times as the "thermodynanic sink" on the $(CH)_{10}$ energy surface but should now command the degree of sustained fascination generally accorded other molecules capable of degenerate rearrangement behavior.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. The ^{1}H NMR spectra were determined with Varian A-60A and Jeolco MH-100 instruments and apparent splittings are given in all cases. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

9,10-Dihydronaphthalene-9,10-dicarboxylic Acid Anhydride (11). A mixture of $\Delta^{2,6}$-hexalin-9,10-dicarboxylic acid anhydride (**10**)[18] (25 g, 0.12 mol), *N*-bromosuccinimide (50 g, 0.28 mol), and (0.2–0.3 g) benzoyl peroxide in 100 ml of carbon tetrachloride was heated at reflux for 1 hr with stirring. The mixture was cooled, the insoluble succinimide separated by filtration, and the solvent evaporated to leave a viscous yellow oil. This material was dissolved in 100 ml of quinoline and the solution stirred at 145° for 15 min. The mixture was poured onto ice (250 g) and hydrochloric acid (50 ml) and extracted with ether (3 × 175 ml). The combined organic layers were washed with 10% sodium thiosulfate, 10% hydrochloric acid, and saturated sodium bicarbonate solutions before drying and concentration. The residual brown oil was chromatographed on silica gel (elution with hexane–ether (3:1)) to give 4.7 g (19%) of colorless crystals, mp 74–75° (lit.[11] mp 74–75°), whose ^{1}H NMR spectrum was identical with that previously reported.

***cis*-9,10-Dicarbomethoxy-9,10-dihydronaphthalene (3).** A solution of 8.0 g (40 mmol) of **11** in 200 ml of methanol was heated at 45° with stirring for 44 hr, cooled, and evaporated to leave 9.3 g (100%) of monoacid ester: $\delta_{TMS}^{CDCl_3}$ 5.4–6.0 (m, 8, olefinic) and 3.60 (s, 3, methoxyl).

This substance was slowly added to an ethereal solution of diazomethane (0.4 mol) which after 2 hr at room temperature was treated with formic acid (to neutrality) and evaporated. The pasty white solid was recrystallized from ether–hexane to furnish 6.3 g (64%) of white needles, mp 102.5–104° (lit.[11] mp 103–104°), whose ^{1}H NMR was the same as that reported; $\lambda_{max}^{isooctane}$ 256 nm (ϵ 6850).

Thermal Rearrangement of 3 in Dimethoxyethane Solution (80°). A magnetically stirred solution of **3** (2.0 g, 8.13 mmol) in dry dimethoxyethane (20 ml) was heated at reflux for 19 hr, cooled, and evaporated in vacuo. This mixture was chromatographed on silica gel (300 g). Elution with dichloromethane at a rate of 75 ml/hr gave the following results (50-ml fractions): fractions 18–33, 270 mg, recovered **3** and minor aromatics; fractions 34–45, 520 mg, pure **12**; fractions 46–54, 380 mg, mixture of **12** and **13**; fractions 55–81, 600 mg, pure **13**. The total weight of 1700 mg represents an 89% recovery.

For **12**: $\nu_{max}^{CCl_4}$ 1730, 1710, and 1280 cm^{-1}; $\lambda_{max}^{isooctane}$ 275 (ϵ 7390), 240 (4110), and 232 nm (3900); $\delta_{TMS}^{CDCl_3}$ 7.1 (d, J = 5.5 Hz, 2), 5.6–6.3 (m, 4), 2.7–4.2 (m, 2), and 3.80 (s, 6), calcd for $C_{14}H_{14}O_4$ *m/e* 246.0892, found 246.0895.

For **13**: $\nu_{max}^{CCl_4}$ 1750, 1720, 1235, and 910 cm^{-1}; $\lambda_{max}^{isooctane}$ 283 sh (ϵ 4190), 257 (7720), and 252 nm (7890); $\delta_{TMS}^{CDCl_3}$ 7.1 (d, J = 5.5 Hz, 1), 5.5–6.2 (m, 6), 3.72, 3.69 (s, 3 each), and 3.5–4.0 (m, 1); calcd for $C_{14}H_{14}O_4$ *m/e* 246.0892, found 246.0895.

When both **12** and **13** were individually sealed in NMR tubes (tetrachloroethylene solutions) and heated at 80° for 7 hr, only minor spectral changes were noted.

Dehydrogenation of 12. A solution of **12** (63 mg, 0.25 mmol) in 10 ml of dimethoxyethane was treated with 300 mg (1.3 mmol) of 2,3-dichloro-2,3-dicyanobenzoquinone (DDQ) and heated with stirring at 50° under nitrogen for 24 hr. Chromatography on alumina (dichloromethane elution) led to the isolation of **4** contaminated with residual **12**. Repetition of the process for an additional 24 hr gave only **4**, mp 117–118° (lit.[52] mp 119°), whose ir and ^{1}H

NMR spectra were superimposable upon those of an authentic sample.[19]

Dehydrogenation of 13. A 187-mg sample (0.75 mmol) of **13** was heated with 500 mg (2.2 mmol) of DDQ and 10 ml of dimethoxyethane under nitrogen at 50° for 24 hr. Purification by chromatography on alumina (dichloromethane elution) and VPC purification afforded monoester **14**[53] accompanied by small quantities of 1,2- and 2,3-dicarbomethoxynaphthalenes.

Thermal Rearrangement of 12 and 13 in Tetrachloroethylene Solution at 80°. Samples of **12** and **13** dissolved in tetrachloroethylene were heated in sealed NMR tubes for 24 hr at 80°. Treatment of the thermolysates with DDQ in the predescribed manner at 50° followed by quantitative VPC analysis on a 12 ft × 0.25 in. column packed with 15% QF-1 on Chromosorb W provided the data summarized in Table I.

Thermal Rearrangement of 3, 12, and 13 at 100° and 150°. A magnetically stirred solution of 50 mg (0.2 mmol) of a given dihydro diester in 10 ml of dry dioxane (for the 100° experiments) or 10 ml of purified diglyme (for the runs at 150°) was heated for 24 hr under an argon atmosphere. The solution was cooled to 50°, DDQ (150 mg, 0.6 mmol) was added, and the mixture was stirred at this temperature for 24 hr. Purification was achieved by filtration through a short column of alumina. Product composition data (Table II) were obtained by comparison of VPC retention times with those of authentic samples and by manual planimeter integration of the traces (minimum of at least two runs).

***cis*-9,10-Bis(iodomethyl)-$\Delta^{2,6}$-hexalin (23).** A mixture of 25 g (0.072 mol) of dimesylate **22**[18b,54] and 107 g (0.71 mol) of sodium iodide in 175 ml of dry hexamethylphosphoramide was heated at 130–135° with stirring for 3 days. The black solution was cooled, treated with water (500 ml), and extracted with ethyl acetate (5 × 300 ml). The combined organic layers were washed with water (1.5 l.), followed by 10% sodium thiosulfate, 10% hydrochloric acid, 10% sodium bicarbonate, and saturated salt solution, before drying. Removal of solvent under reduced pressure and recrystallization of the residue from 95% ethanol afforded 22.0 g (74%) of white needles, mp 95–99° (lit. mp 97–98°,[26] 99°[27]).

***cis*-9,10-Dimethylhexalin (24).** A solution of 20.2 g (0.05 mol) of unpurified **23** in 100 ml of dimethoxyethane was introduced dropwise into a magnetically stirred slurry of lithium aluminum hydride (5.7 g, 0.15 mol) in the same solvent (200 ml) and the mixture was kept at reflux for 3 days. The contents were cooled, and water was carefully added to destroy excess hydride before pouring into 500 ml of cold 10% hydrochloric acid. Extraction with petroleum ether (3 × 500 ml), washing of the combined organic layers with water (600 ml) and brine (500 ml), drying, and concentration by distillation through an 18-in. Vigreux column at atmospheric pressure followed by vacuum distillation yielded 5.9 g (74%) of a semisolid distillate, bp 98–110° (13 mm). VPC analysis (6 ft 10% XF-1150 on Chromosorb G at 130°) showed this material to be composed of 90% **24** and 10% of **25**. For **24**: ν_{max}^{neat} 3100–2900, 1450, 1435, 1240, and 1030 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.55 (m, 4, olefinic), 1.83 (m, 8, methylene), and 0.9 (s, 6, methyl). This spectrum compares well with that previously described by Scott.[26]

***cis*-9,10-Dimethyl-9,10-dihydronaphthalene (26).** A mixture of *N*-bromosuccinimide (1.18 g, 6.7 mmol), hydrocarbons **24** and **25** (90:10) (500 mg, 3.1 mmol), carbon tetrachloride (10 ml), and a few grains of AIBN was heated on a steam bath at reflux for 1 hr. The cooled mixture was rid of succinimide by filtration and the filtrate was concentrated on a rotary evaporator to leave a pale yellow oil (quantitative): $\delta_{TMS}^{CDCl_3}$ 5.6 (m, 4), 4.8 (br m, 2), 2.1 (m, 4), 0.9–1.4 (series of methyl singlets, total area 6); a singlet at 2.65 due to the ethano bridged impurity was also clearly evident.

This oil was dissolved in 15 ml of tetrahydrofuran and the solution was transferred to a 25-ml three-necked round-bottom flask equipped with a mechanical stirrer, condenser, and nitrogen inlet. After cooling to −78°, potassium *tert*-butoxide (3.36 g, 31 mmol) was added in one portion and the mixture was alowed to stir at room temperature for 16 hr. The contents were poured into 250 ml of ice water and extracted with pentane (3 × 200 ml). The combined organic layers were washed with water (2 × 400 ml), saturated sodium bicarbonate (400 ml), and brine solutions (400 ml), dried, filtered, and evaporated to leave a yellow oil. Preparative VPC purification (6 ft × 0.25 in. 5% SE-30 n Chromosorb G at 85°) furnished 46 mg (9.2%) of **26** and 10 mg (2%) of **27**. For **26**: $\lambda_{max}^{isooctane}$ 244 nm (ϵ 5575); $\delta_{TMS}^{CDCl_3}$ 6.52 (AA'BB', 8, olefinic) and 1.03 (s, 6, methyls); calcd for $C_{12}H_{14}$ *m/e* 158.1097, found 158.1095.

The ^1H NMR spectrum of **27** was identical with that reported.[27]

Catalytic Hydrogenation of 26. A 10-mg sample of **26** in 5 ml of ether was hydrogenated at 1 atm over 10% palladium on carbon (50 mg) for 1 hr. The solution was filtered and evaporated to give a clear camphoraceous semisolid whose ^1H NMR spectrum was identical with that of the known *cis*-9,10-dimethyldecalin.[26] Analogous catalytic reduction of diene **24** produced the same saturated hydrocarbon.

***cis*-1,5-Dimethyl-9,10-dihydronaphthalene (29).** To a mechanically stirred solution of dienes **24** and **25** (90:10) (3.0 g, 0.018 mol) in 60 ml of acetic acid was added 23.7 g (0.07 mol) of freshly prepared pyridinium hydrobromide perbromide and the mixture was stirred at room temperature for 1 hr. Water (500 ml) was added and the mixture was extracted with ether (2 × 200 ml). The combined organic layers were washed with 10% sodium hydroxide solution (500 ml) and water (500 ml), dried, and evaporated. After vacuum drying, there remained 8.22 g (91%) of powdery white tetrabromide mixture which was used without further purification.

A 1.0-g (2.1 mmol) sample of tetrabromide was dissolved in 25 ml of hexamethylphosphoramide. To this solution was added 0.9 g (21 mmol) of anhydrous lithium chloride and 1.55 g (21 mmol) of dry lithium carbonate, and the mixture was heated at 90° for 5 hr. After cooling, water (150 ml) and pentane (150 ml) were introduced, and the organic phase was washed with water (3 × 300 ml) and brine (200 ml), dried, and concentrated. The residual yellow oil consisted of four components; these were separated in a pure state by preparative VPC on 5% SF-96 at 115° (Chromosorb G). The initial hydrocarbon to elute was **29** (100 mg, 10%): $\delta_{TMS}^{CDCl_3}$ 5.91 (dd, 2), 5.66 (d, 2), 5.25 (d, 2), 3.04 (m, 2), and 1.83 (s, 6); $\lambda_{max}^{isooctane}$ 250 (ϵ 6470) and 277 sh nm (2130); calcd for $C_{12}H_{14}$ *m/e* 158.1097, found 158.1095.

The second fraction (80 mg, 8%) was identified as **27** on the basis of its ^1H NMR spectrum.[27]

The third component (19.2 mg, 1.9%) was shown to be 1,5-dimethylnaphthalene (**32**) by direct comparison with an authentic sample.

The final product was a monobromide (*m/e* 238) which remains unidentified (58 mg, 5.8%).

Thermal Rearrangement of 26 in Tetrachloroethylene Solution (80°). A 40-mg (0.25 mmol) sample of **26** dissolved in 0.5 ml of tetrachloroethylene was sealed under vacuum in a Pyrex tube. The tube was immersed in a preheated (80°) oil bath for 5 hr. The components of the product mixture were isolated by preparative VPC (2 ft × 0.25 in. 7.5% SE-30 on Chromosorb P) at 80°. There was obtained 14 mg (34%) of **29** which proved identical with the above sample and 9 mg (23%) of **30**: $\delta_{TMS}^{CDCl_3}$ 5.22–5.96 (m, 7, olefinic), 2.92 (m, 1), 1.66 (d, 3, methyl), and 1.17 (s, 3, methyl); $\lambda_{max}^{isooctane}$ 240 (ϵ 3910) and 246 nm (3920); calcd for $C_{12}H_{14}$ *m/e* 158.1095, found 158.1097.

Dehydrogenation of 29 and 30. A solution of 4 mg of the hydrocarbon in 2 ml of dry dimethoxyethane was treated with 15 mg of DDQ and heated at 50° for 24 hr. After chromatography on a short alumina column (dichloromethane elution) and careful solvent evaporation, product analysis was achieved by VPC methods (12 ft × 0.25 in. 5% Carbowax 20 M–1% potassium hydroxide at 140°). While **29** gave 1,5-dimethylnaphthalene (**32**) as the only detectable volatile, **30** yielded an 80:20 mixture of α-methylnaphthalene (**31**) and (**32**).

Vapor Phase Pyrolysis of 29. In a typical experiment, 10 mg of **29** was passed through a quartz tube packed with quartz chips in the vapor phase with a nitrogen stream at 30 mm pressure and the pyrolysate (5–8 mg) was collected in a trap cooled with Dry Ice–isopropyl alcohol. This material was dissolved in 1 ml of dimethoxymethane and dehydrogenated with DDQ (25 mg) as before (20 hr at 50°). After passage of this solution through a short alumina column (dichloromethane elution), product analysis was conducted on a 12 ft × 0.25 in. VPC column packed with Carbowax 20M–1% KOH on Chromosorb G at 140°. The breakdown on the levels of dimethylnaphthalenes formed is given in Table III.

***trans*-Basketane-*9,10-d*$_2$-9,10-dicarboxylic Acid-*d*$_2$ (34).** To 100 ml of methanol-*O-d* in which a pea of metallic sodium had been dissolved was added 14.97 g (0.06 mol) of cis diester **33**[29] and the solution was heated at reflux for 16 hr with protection from atmospheric moisture. The solvent was removed in vacuo and the resi-

due was treated with 50 ml of 10% NaOD in D_2O. After 24 hr of heating, the alkaline solution was cooled and neutralized with D_2SO_4 in D_2O. There was isolated 11.5 g (85.6%) of **34**, mp 226–228°.

Basketene-*9,10-d*$_2$ (35). A solution of 1.40 g of **34** in 90 ml of pyridine and 10 ml of water containing 1.4 ml of triethylamine was subjected to electrolysis in a water-jacketed cell equipped with platinum electrodes. Oxidative decarboxylation was allowed to proceed for 10 hr at 10–23°: initial current 0.5 A, final current 0.1 A. The dark solution was diluted with 250 ml of water and extracted with five 7-ml portions of pentane. The combined pentane extracts from four such runs were washed with dilute hydrochloric acid, dried, and evaporated through a Vigreux column. Molecular distillation of the residue afforded 310 mg of pure **35**.[30]

Cycloaddition of Diethyl Azodicarboxylate to 35. A solution of 310 mg (2.35 mmol) of **35** and 1.04 g (6.0 mmol) of diethyl azodicarboxylate in 7 ml of carbon tetrachloride was refluxed for 9 days. The solution was evaporated and the residual oil was chromatographed on silica gel. Recrystallization of the appropriate combined fractions from ethanol furnished 416 mg (40.5%) of adduct **36**: mp 188–190°; $\delta_{TMS}^{CDCl_3}$ 5.8–6.5 (m, 2, olefinic), 4.5–5.1 (m, 4, >C*H*N<), 4.23 (q, 8, -OCH_2-), 2.93 (br s, 2, methine), and 1.25 (t, 12, methyl).

Hydrolysis–Oxidation of 36. A mixture of 416 mg of adduct and 500 mg of potassium hydroxide in 2 ml of water and 4 ml of methanol was heated at reflux under carefully deoxygenated nitrogen for 4 hr. After cooling, dichloromethane (15 ml) and water (10 ml) were added, and oxygen was bubbled through this mixture (magnetic stirring) for 40 min. The organic layer was separated, dried, filtered, and concentrated by careful distillation through a packed Vigreux column at atmospheric pressure. A sample of **37** was purified by preparative VPC (10% SE-30 on Chromosorb W) at 115° for ^{1}H NMR purposes: $\delta_{TMS}^{CHCl_3}$ 5.81 (m, 2.0), 5.42 (m, 4.0), and 3.25 (m, 2.0). The estimated isotopic purity is 98 ± 2% d_2.

The water layer was treated with yellow mercuric oxide and subsequently extracted with dichloromethane. After similar processing, the solution was concentrated and combined with the above sample, yield 25 mg.

Vapor Phase Pyrolysis of 37. A 12-mg sample of **37** was slowly introduced into the heated quartz tube utilized before (510°) and the pyrolysate was subjected to VPC purification (10% SE-30 on Chromosorb W) at 115°. There was isolated 2 mg of *cis*-9,10-dihydronaphthalene, the ^{1}H NMR spectrum of which was recorded with CAT amplification at 100 MHz: $\delta_{TMS}^{CDCl_3}$ 5.81 (m, 3.4), 5.42 (m, 3.3), and 3.25 (m, 1.4).

Kinetic Determinations. A standard solution was prepared by dissolving 3.00 g (12.4 mmol) of **3** in 25 ml of 3:2 tetrachloroethylene-acetone-d_6 (0.49 *M*). Aliquots (200 μl) were transferred via syringe to 13 × 0.5 Pyrex tubes which had previously been treated with dilute aqueous nitric acid, dilute aqueous ammonium hydroxide, water, and acetone before drying at 75°. The sample tubes were sealed under a vacuum of 30 mm. For each run ten tubes were immersed in an oil bath thermostated at the appropriate temperature. At various suitable time intervals, a tube was removed, immediately immersed in ice water, and stored at −10° for short periods until ^{1}H NMR analysis was possible.

Progress of the reaction was monitored by manual integration of the ester peaks of **12** (δ 3.80) and **13** (3.72 only; the 3.67 singlet falls under that due to **3**) relative to that of **3** (3.65) on expanded spectra recorded at 60 MHz. The per cent of **3** present at a given time was calculated according to the following equation:

$$\%\ \mathbf{3} = [\mathbf{3}]/([\mathbf{3}] + [\mathbf{12}] + [\mathbf{13}]) =$$

(area of 3.65 singlet − area of 3.72 singlet)/total area

Interestingly, that ratio of **12**:**13** remained invariant at 25.7:74.3 in all runs. The percentage of **3** was plotted vs. time, and the resulting data were analyzed by the method of least squares. A tabulation of these findings is given in Table IV.

For the dimethyl example, a standard solution was prepared by dissolving 46 mg of **26** and 40 mg of *n*-decane in 10 ml of 3:2 tetrachloroethylene-acetone. Sealed tubes were prepared as before (100-μl aliquots). In this instance, progress of the rearrangement was monitored by flame ionization VPC (2 ft 5% SE-30 on Chromosorb G) at 65°. Again, the ratio of **29** to **30** remained invariant at 53.5:46.5 from run to run. The kinetic data are summarized in Table IV.

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(32) Small quantities of naphthalene, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene were also produced during the pyrolysis. Appropriate control experiments with **37** indicated clearly that no deuterium scrambling was operative under the VPC conditions employed.

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ii

Benzotropyl + Benzene ⇌ Tropyl + Naphthalene[1]

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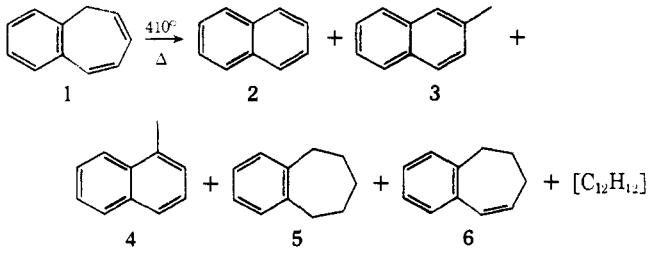
Abstract: Pyrolysis (400°) of 1,2-benzotropilidene (**1**) has been shown to produce naphthalene (**2**), 2-methylnaphthalene (**3**), 1-methylnaphthalene (**4**), benzocycloheptene (**5**), and benzocycloheptadiene (**6**). The formation of naphthalene was shown not to involve extrusion of methylene, even though in the presence of benzene toluene was produced, but did involve free radicals. Initiation by di-*tert*-butyl nitroxide at 300° produced naphthalene and, in the presence of benzene, toluene. It was also shown that the thermal rearrangement of tropilidene (**11**) to produce benzene gives methylnaphthalene when naphthalene is present. Di-*tert*-butyl nitroxide also was a good initiator for this free radical reaction and, when it was run at 300°, 1,2-benzotropilidene was a product. The observation that bitropyl produced products similar to tropilidene or tropilidene plus nitroxide suggests the tropyl radical is involved. By analogy, the benzotropyl radical is implicated in the benzotropilidene reaction. The free radicals (**9** and **10**) produced by the addition of the benzyl radical to naphthalene and by the α-naphthylmethyl radical to benzene were shown not to be intermediates in the reaction of benzotropilidene with benzene to produce naphthalene and toluene. As a result of these data the mechanism shown in Scheme I is postulated for the above reactions. The central feature of this mechanistic pathway is the reversible reaction shown in reaction 1.

Our interest in the thermal hydrogen rearrangement reactions of benzotropilidenes[3,4] has led us to discover a heretofore unrecognized reaction of 1,2-benzotropilidene. As we recently reported[5] the pyrolysis (gas phase, evacuated Pyrex ampoule) of 1,2-benzotropilidene (**1**) at 410° results in the formation of naphthalene (**2**, 14% relative, 12% absolute), 2-methylnaphthalene (**3**, 18% relative), 1-methylnaphthalene (**4**, 50% relative), benzocycloheptene (**5**, ca. 1% relative), and 1,2-benzocyclohepta-1,3-diene (**6**, 17% relative).[6] In addition, low voltage mass spectroscopic analysis of the crude pyrolysate indicated an ion at *m/e* 156 corresponding to $C_{12}H_{12}$.



Product identification was straightforward. Naphthalene, the methylnaphthalenes, and benzocycloheptene were compared spectrally to authentic samples. The low voltage mass spectrum of **6**[7] showed the parent at *m/e* 144 and the NMR spectrum showed the following resonances which were consistent with **6**: τ 8.11 (m, 2, CH_2), 7.75 (m, 2, CH_2), 7.24 (m, 2, CH_2), 4.16 (dt, 1, J = 12.5 and 4 Hz, -CH=C*H*CH$_2$-), 3.50 (dt, 1, J = 12.5 and 2 Hz, Ar-C*H*=CH), and 2.82 (m, 4, Ar*H*). In addition, the reduction of benzotropylium fluoborate with lithium aluminum hydride produced some **6** among the products.[8,9]

Control experiments demonstrated that the methylnaphthalenes were not converted to naphthalene under the reaction conditions.

We also looked for dimers among the products by heating a 200 mg sample at 360° for 2 hr and chromatographing the pyrolysate over alumina. A yellow oil (34 mg) was obtained (after the monomeric fraction had been eluted) which could not be crystallized. The NMR spectrum of this material was consistent with a "dimer", more properly a dihydrodimer or mixture of isomeric dihydrodimers of methylnaphthalene and benzocycloheptene: τ 2.1-3.1 (m, 10, Ar-*H*), 6.9-8.8 (m, 9, CH_2 and C*H*), and 7.4 ppm (s, 3, CH_3Ar). In addition the uv spectrum resembled that of naphthalene: uv max [$(C_2H_5)_2O$] 222 (log ϵ 4.08), 258