(14) E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).
(15) (a) M. J. Kagan and G. D. Lubarsky, *J. Phys. Chem.*, **39**, 837 (1935); (b) E. Koubek and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **25**, 1401 (1963).
(16) Reference 13, pp 350 and 368.
(17) T. G. Traylor, *J. Am. Chem. Soc.*, **86**, 244 (1964).
(18) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, **49**, 6163 (1966).
(19) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).
(20) E. W. Washburn, "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology", Vol. 3, McGraw-Hill, New York, N.Y., 1928, p 207.
(21) Reference 20, p 265.
(22) The labeling experiments of McDowell and Sifniades,[23] which, although suggested tetroxide formation, also indicated a cyclic mechanism, have been explained by an alternative possibility.[5] They were most likely observing methyl radical and formyl radical oxidation rather than acetaldehyde autoxidation.
(23) C. A. McDowell and S. Sifniades, *Can. J. Chem.*, **41**, 300 (1963).
(24) (a) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956); (b) J. A. Howard and J. E. Bennett, *Can. J. Chem.*, **50**, 2374 (1972).
(25) D. Lindsay, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **51**, 870 (1973).
(26) J. E. Bennett and R. Summers, *Can. J. Chem.*, **52**, 1377 (1974).

Thermolysis of Nenitzescu's Hydrocarbon. Kinetic Studies with a Micro-Scale Stirred-Flow Reactor

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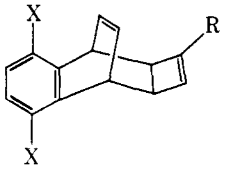
Received December 14, 1974

Abstract: Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**2**) and its *anti*-7,8-benzo derivative **1** equilibrate thermally with the syn-fused tricyclo[6.2.0.0^{2,7}]deca-3,5,9-triene (**8**) and the benzo derivative **13**, respectively. Hydrocarbon **8** cannot undergo disrotatory electrocyclic ring opening to bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**) because of unfavorable transannular interactions in the transition state. Instead, rate-determining homolytic bond fission occurs to give a freely rotating diradical **9** which can reclose to anti-fused tricyclo[6.2.0.0^{2,7}]deca-3,5,9-triene (**16**). Subsequent electrocyclic ring opening to bicyclo-[6.2.0]deca-2,4,6,9-tetraene (**10**) occurs rapidly without interference by transannular steric interactions. Subsequent rearrangement of **10** to *trans*-9,10-dihydronaphthalene explains ultimate formation of 1,2-dihydronaphthalene as the major product. Minor cyclobutene opening to a 1,3-diene in the starting material or the Cope product **8** results in formation of *cis*-9,10-dihydronaphthalene. Labeling studies in the benzo analogs are consistent with the formation of diradical intermediates *after* initial Cope rearrangement. Kinetic studies by the stirred-flow method gave E_a = 46.4 kcal/mol with log A = 15.5 for the formation of 1,2-dihydronaphthalene, and E_a = 40.4 kcal/mol with log A = 12.2 for the appearance of *cis*-9,10-dihydronaphthalene. A technique for performing stirred-flow experiments on milligram scale is described, and its validity is demonstrated by comparison with literature activation parameters for pyrolysis of bicyclo[4.2.2]deca-2,4,7,9-tetraene.

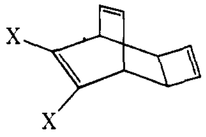
Introduction and Background

The first examples of (CH)$_{10}$ skeletal interconversion were published by Nenitzescu and coworkers.[1] Their paper described the thermal rearrangement of **1a** to 1,4-dimethoxyphenanthrene, and of **2a** into a mixture of esters having the naphthalene skeleton.[2] Several years later, the parent hydrocarbon **2** was prepared.[3] Pyrolysis of **2** was studied by three groups[4-6] and gave varying amounts of 1,2-dihydronaphthalene, *cis*-9,10-dihydronaphthalene, *cis*-1-phenylbutadiene, naphthalene, and minor side products (Table I),[6] depending on reaction conditions.

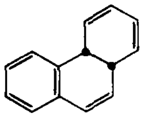
By 1970 other analogous transformations were known including conversion of **1** into 4b,8a-dihydrophenanthrene (**3**)[7,8] and rearrangement of the cyclooctatetraene-diethyl azodicarboxylate adduct into **5**.[9] Mechanisms were suggested involving initial cyclobutene opening to give bicyclo-[4.2.2]deca-2,4,7,9-tetraene intermediates,[7,9] but experiments in our laboratory showed that cyclobutene ring opening is at best a minor side reaction in two cases.[6] Thus, pyrolysis of **2** in a flow system gives 1,2-dihydronaphthalene (84%), while **6** gives *cis*-9,10-dihydronaphthalene (86%) under identical conditions (Table I). Furthermore, 7,8-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (**4**) is too unreactive to be an important intermediate between **1** and **3**.



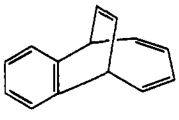
1. X = R = H
1a. X = OCH$_3$; R = H
1b. X = H; R = CH$_3$



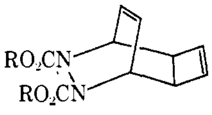
2, X = H
2a, X = CO$_2$CH$_3$

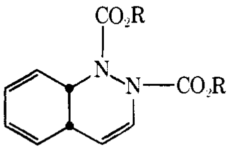


3

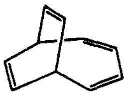


4





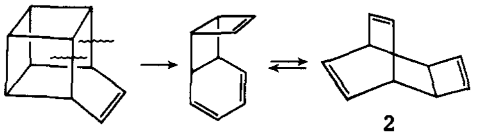
5



6

A clue to the correct mechanism appeared in 1969. Masamune et al. demonstrated the retro-Diels-Alder cleavage of basketene (**7**) to **8** followed by a Cope rearrangement to give **2**.[10] Labeling experiments revealed an equilibrium between **2** and **8** at 180° and ruled out a freely rotating diradical **9** as an intermediate at this temperature. Subsequently, the synthesis of **8** was completed in our laboratory and the facile Cope rearrangement to **2** was confirmed (E_a = 23.5 kcal/mol, log A = 11.5).[11]

In view of the evidence relating **2** and **8**, we proposed that

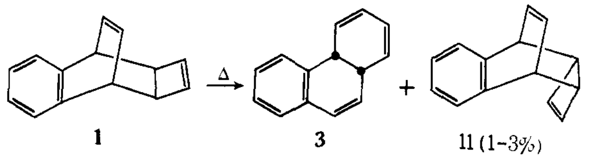

7 8 2


9

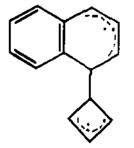
8 is a key intermediate in the rearrangement of **2** into 1,2-dihydronaphthalene, *cis*-9,10-dihydronaphthalene, and *cis*-1-phenylbutadiene.[6] In brief outline, the mechanism involves two principal competing pathways (Scheme I). Path "a" requires cyclohexadiene ring opening to give bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**) which is known to rearrange to *trans*-9,10-dihydronaphthalene.[12] The latter has been identified as a thermal source of both 1,2-dihydronaphthalene and *cis*-1-phenylbutadiene.[13] Path "b" results in symmetry-forbidden cyclobutene opening of **8** to give *cis*-9,10-dihydronaphthalene, which in turn is a thermal source of naphthalene (but *not* of 1,2-dihydronaphthalene or *cis*-1-phenylbutadiene in significant amounts).

In the case of the benzo derivative **1**, a process analogous to path "a" would have to disrupt the aromatic ring, and consequently path "b" predominates. A third path "c", cyclobutene opening in the starting material, can be detected in the benzo series as evidenced by the isolation of **4**. The analogous process may be accessible from **2**, but **6** would not be detected since it is considerably more reactive than **2**.

From the labeling experiments of Masamune et al., there is no doubt that a diradical intermediate **9** is not *required* to interconvert **2** and **8**.[10] However, experiments performed in the benzo series at higher temperatures indicate a more complex situation. For the moment, it is sufficient to note that pyrolysis of **1** at 330° gives a small amount of the syn isomer **11**, apparently resulting from reclosure of a freely rotating diradical such as **12**.[14] This experiment does not clarify the extent to which diradicals are involved, but it obviously raises the question of whether such species might be important in pyrolysis of **2** as well as **1**.

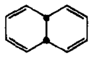
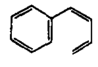
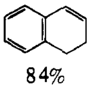
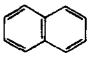


1 3 11 (1-3%)

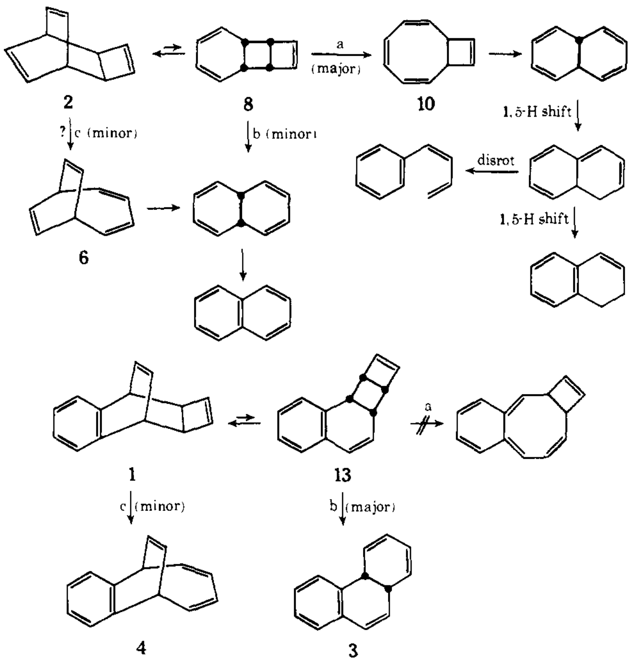

12

Initially, we considered the possibility that the presence of a benzene ring might perturb the tricyclo$[4.2.2.0^{2,5}]$deca-3,7,9-triene skeleton sufficiently to favor diradical formation over the Cope rearrangement. To test this proposition, the Cope intermediate **13** was synthesized from 1,2-naphthoquinone according to Scheme II. Not surprisingly, pyrolysis of **13** between 50 and 80° gives only **1**; no trace of the diradical product **11** can be detected. The activation parameters obtained by monitoring the disappearance of the styrene chromophore of **13** are E_a = 24.2 kcal/mol and log A = 12.3, the same (within experimental error) as the parameters for the Cope rearrangement of **8**.[11] Thus, the presence of a benzene ring does not alter the concerted rearrangement **13** → **1** to any measurable extent below 80°; by microscopic reversibility, the lowest energy path for the reverse reaction must also be concerted.

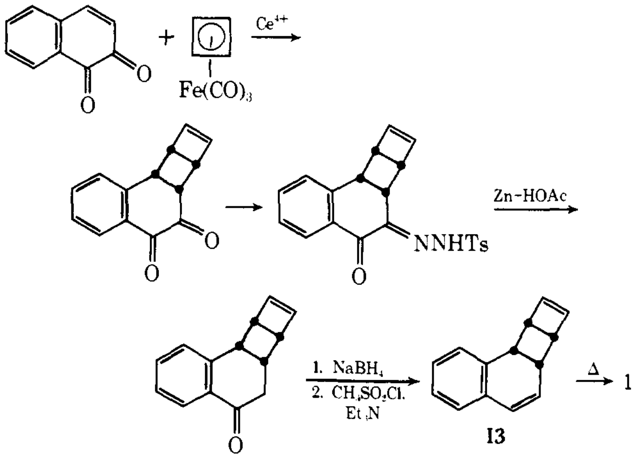
Table I. Pyrolysis in a Tubular Flow System over Pyrex Beads[6]

Starting material				
2 ⟶	7%	8%	84%	1%
6 ⟶	86%	Trace	2%	6%

Scheme I



Scheme II



There is also evidence that diradical cleavage does not become the preferred pathway from **1** to **13** at higher temperatures. If homolytic bond fission of **1** were to become the rate-determining step, then both **1** and **11** should rearrange at comparable rates. However, the anti isomer **1** (which alone has the geometry required for a low-energy Cope rearrangement) reacts at least 180 times faster than does **11**.[14] In fact, all of the products from **11** can be accounted for by initial cyclobutene opening (path "c", Scheme I) because the resulting isomer **4** is somewhat more reactive than **11** and gives the same pyrolysis products.[14] It is logical to conclude that concerted Cope rearrangement is the only significant path from **1** to **13**. Consequently, there must be some other source of the diradical **12** to account for the formation of **11** from **1**.[15] One possibility involves homolytic C–C fission in **13**. By analogy, diradical **9** may be accessible from **8**.

The product studies summarized up to this point do not resolve the following question. Are the diradicals **9** or **12** *required* for any of the principal transformations of **2** or **1**, respectively, or are they formed coincidentally along minor reaction pathways? In principle, the activation parameters for the appearance of the major products from **2** would clarify the situation. However, it is difficult to obtain meaningful kinetic data in any high-temperature reaction which produces 9,10-dihydronaphthalenes. The latter can serve as hydrogen donors to reduce unreacted starting material or other pyrolysis products, resulting in the appearance of naphthalene and $C_{10}H_{12}$ products.[16]

The method of stirred-flow kinetics appeared ideally suited for studying complex reactions such as the pyrolysis of **2**. An efficiently stirred flow reactor reaches a steady-state composition of starting material and products which is characteristic of the reactor volume, temperature, and flow rate.[17] At the steady state, the sum of all processes which form any given product must equal the sum of processes which remove that product from the reactor. For a hypothetical reaction sequence

$$A \xrightarrow{k_a} B \longrightarrow C + D + E$$

material balance in B requires that

$$k_a[A]V = (k_c + k_d + k_e)[B]V + [B]U$$

$[A]$ = steady state concentration of A V = volume of reactor
$[B]$ = steady state concentration of B U = flow rate

$$U/V = k_a[A]/[B] - (k_c + k_d + k_e)$$

Thus, a simple plot of U/V vs. the steady state ratio of starting material to the product in question gives the required rate constant k_a. It is not necessary to consider secondary reactions since their effect is only to alter the intercept and not the slope. Applied to pyrolysis of **2**, a similar argument shows that secondary aromatization of dihydronaphthalenes is immaterial provided that a sufficient concentration of the initial product survives to allow accurate analysis.

Design of a Micro-Scale Stirred-Flow Reactor

One of the limitations of stirred-flow kinetics is the unavoidable consumption of starting material during the time required to establish the characteristic steady state at each flow rate. This difficulty can be minimized by working at very low concentrations of material in the gas stream, but reproducible product analysis becomes increasingly harder. Our pyrolysis apparatus is designed to allow direct injection of the reactor effluent for GLC analysis using a six-port micro-sampling valve. This technique avoids loss of material or alteration of the product mixture during trapping of the effluent gases and other manipulations. Sample concentrations on the order of 10^{-7} M can be measured with acceptable precision using a flame ionization GLC detector.

The sample to be pyrolyzed is introduced into a quartz reactor by passing purified nitrogen through a small chamber which contains a narrow vial (1.5-mm i.d.) of the $(CH)_{10}$ hydrocarbon. The temperature of the chamber is adjusted by means of a circulating constant-temperature water jacket to achieve a convenient sample vapor pressure and a corresponding concentration of starting material in the gas stream. For solid samples, it is desirable to work above the melting point of the substance. In this manner, a constant surface area of the sample (equal to the cross-section of the sample vial) is exposed to the gas stream, and fluctuations in sample concentration are avoided. Efficient mixing within the reactor is provided by the cyclone-like turbulence which results when the sample stream is introduced tangentially at the base of a cone-shaped reactor and is vented at the tip of the cone (see Experimental Section for a diagram).[18]

Under typical conditions, the concentration of hydrocarbons in the gas stream is 10^{-6} M, and flow rates corresponding to 10^{-8} to 10^{-6} mol/hr are maintained. Since each new flow rate requires ca. 0.7–1.5 hr of equilibration time, a rate constant based on duplicate runs at five flow rates can be determined with consumption of less than 1 mg of the $(CH)_{10}$ substrate.

The reactor design was intended to minimize the concentration of sample in the flow system because the $(CH)_{10}$ derivatives under study are nontrivial to prepare. However, we found (rather painfully) that the composition of hydrocarbon vapors at the 10^{-6} M level can be altered remarkably by selective retention (adsorption?) of certain compounds by the sampling valve components, especially in the case of the relatively nonvolatile benzo-$(CH)_{10}$ derivatives.

Ultimately, we found it necessary to flush the sampling loop continuously with carrier gas, with the sampling valve heated at the GLC oven temperature. Just prior to analysis, the reactor effluent is passed into the loop for the shortest time sufficient to displace the carrier gas. The contents of the loop are then injected immediately onto the GLC column for analysis. Any sample retention by the loop using this technique of injection is reflected by GLC peak tailing. Excellent peak shapes are obtained for the $(CH)_{10}$ compounds and for a variety of other substances of similar or lower molecular weight, but tailing becomes apparent for the less volatile benzo-$(CH)_{10}$ compounds (molecular weight = 180). The problem becomes especially severe in analysis of phenanthrene. Under optimum conditions for vapor injection, the phenanthrene peak tails at least 15 min (45 min retention time), while standard syringe injection under the same GLC conditions gives a reasonably Gaussian peak 3 min wide.

Kinetic Studies

To test the validity of data obtained from the stirred-flow reactor, we reexamined the kinetics of two reactions from the literature. A macro-scale stirred-flow technique has been used previously to determine E_a = 50.2 kcal and log A = 14.6 for the retro-Diels–Alder fragmentation of norbornadiene.[19] Our values of E_a = 52.5 kcal and log A = 14.8 are in reasonable agreement.

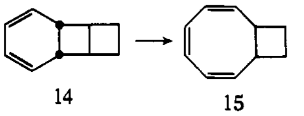
For a more demanding test, we studied the rearrangement of **6** to *cis*-9,10-dihydronaphthalene. Masamune, Seidner, and Nakatsuka have carried out this reaction in a static system by using cyclooctene in the dual role of solvent and hydrogen acceptor to minimize hydrogen transfer from *cis*-9,10-dihydronaphthalene to the starting material.[20] This indirect technique monitors conversion of **6** into naphthalene and gives E_a = 34.9 kcal and log A = 12.33 for disappearance of starting material. Our data yield E_a = 36.6 kcal and log A = 12.4 (255–285°, five temperatures) for the *appearance* of *cis*-9,10-dihydronaphthalene. A total of 4 mg of **6** was consumed in the course of the stirred-flow study.

Having established the practicality of the stirred-flow reactor, we examined the kinetics for rearrangement of **2**. The predominant reaction (91–93% under stirred-flow conditions at 300°), formation of 1,2-dihydronaphthalene, gives excellent first-order plots with E_a = 46.4 kcal/mol and log A = 15.5 in the temperature range 289–330°. Considerably different activation parameters are obtained for the appearance of *cis*-9,10-dihydronaphthalene (3–4% of the product), E_a = 40.4 kcal/mol and log A = 12.2 (309–331°). Under the conditions studied, *cis*-1-phenylbutadiene and naphthalene were present in 2 and 1%, respectively, and could not be integrated with sufficient accuracy to give meaningful rate plots.

Finally, we attempted to determine the kinetics for the rearrangement of **1** under stirred-flow conditions. In contrast to the reaction in a tubular flow system, the stirred-flow experiments invariably gave phenanthrene as the predominant product. It proved impossible to integrate the phenanthrene peak with better than 30% reproducibility under GLC conditions which would separate starting **1** from **3** and **4**. The phenanthrene peak tailed excessively as discussed in the preceding section, and efforts to find a reproducible method for analysis failed. The peak shapes for **3** and **4** were more acceptable, but these products were present in only 5-10% combined relative yield, and accurate integration was not feasible.

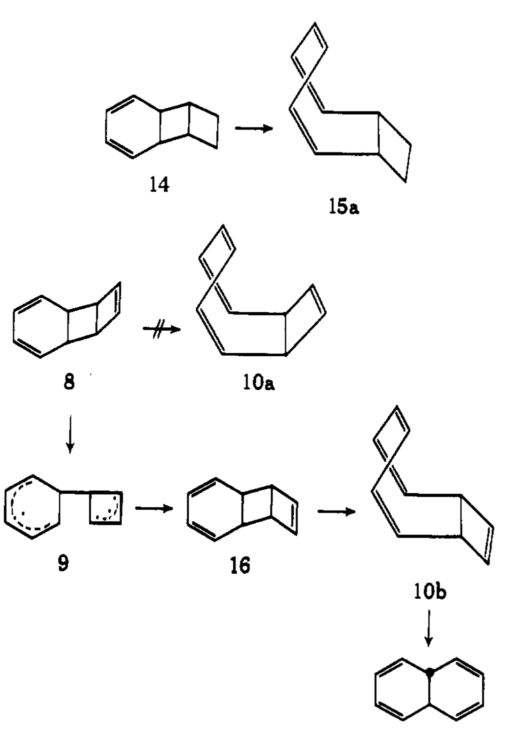
Conclusions

The Arrhenius parameters for appearance of 1,2-dihydronaphthalene from **2** are consistent with rate-determining diradical formation.[21] All available criteria indicate that the first step in Scheme I (interconversion of **2** and **8**) is a concerted process, but the formation of **11** from **1** suggests that diradicals are involved later in the reaction scheme. The only reasonable alternative for the rate-determining step which might require diradical intermediates is the conversion of **8** into **10**. Several apparently analogous reactions are known in which a bicyclo[4.2.0]octadiene opens to a cyclooctatriene derivative with $\Delta E_a = 22 \pm 3$ kcal/mol.[21] The closest analogy, conversion of **14** to **15**, is especially informative.[23] This reaction proceeds readily at 45° ($\Delta F^* = 25.1$ kcal/mol), while the corresponding electrocyclic ring opening of **8** does not take place even at 180°, the temperature required to equilibrate **8** and **2**.[10] The crucial distinction between **8** and **14** is in the geometry of ring fusion. A favorable tub conformation **15a** results from **14** with no steric interference from the cyclobutane ring as the bridgehead carbons rehybridize. In contrast, the tub conformation **10a** which would be formed from **8** suffers severe transannular interactions between cyclobutene and cyclooctatriene carbons. There is good evidence that bicyclo[6.2.0] and bicyclo[6.1.0] derivatives are highly reluctant to adopt analogous conformations.[24] The surprising stability of **8** compared with that of **14** is therefore due to developing steric interactions in the transition state for electrocyclic ring opening to **10**.



Since a low-energy concerted pathway from **8** to **10** is not available, homolytic fission to **9** becomes a feasible alternative. Reclosure of **9** gives the anti-fused isomer **16** which has the correct geometry for facile disrotatory opening to the stable tub **10b**. The activation barrier for rearrangement of **16** to **10** is estimated at 25 kcal/mol (by analogy to **14** → **15**), and the barrier for conversion of **10** into *trans*-9,10-dihydronaphthalene is similar ($\Delta H^* = 25$ kcal/mol).[12] Consequently, these reactions occur rapidly compared with the rate-determining step, formation of the diradical **9**.

Diradical formation from **8** competes very effectively with cyclobutene opening to *cis*-9,10-dihydronaphthalene. Analogous behavior is expected in the benzo series based on the reasonable assumption that radical stabilization in **9** and **12** is comparable, and that rates of cyclobutene opening in **8** and **13** are similar. The appearance of **11** as a minor side product from **1** is an observable consequence of diradical formation with minor reclosure of **12** in the 1,4 sense, while considerable reclosure in the 1,2 sense can be deduced from labeling studies performed by Paquette, Kukla, and Stowell.[25]



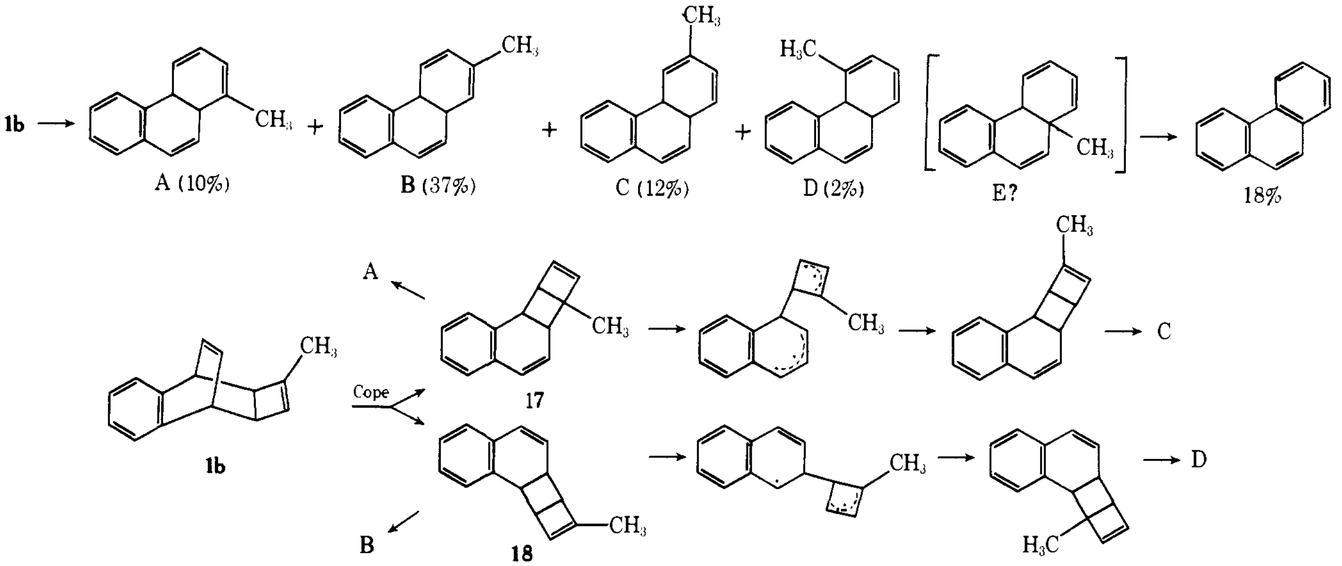
These workers have reported that pyrolysis of **1b** followed by DDQ oxidation gives four isomeric methylphenanthrenes and phenanthrene.[25] The methylphenanthrenes are derived from A, B, C, and D (Scheme III), while phenanthrene is presumed to result from aromatization of a bridgehead methyl isomer such as E.

Only the isomers A and B can be explained if Cope rearrangement followed by cyclobutene opening were the sole reaction paths. Three isomers A, B, and C are expected if diradical cleavage of **1b** were to occur followed by cyclobutene opening. If we invoke diradical cleavage of the two Cope products **17** and **18** at either the benzylic-allylic or allylic-allylic C-C bonds, then all four isomers A, B, C, and D are readily accounted for. Neither diradical mechanism clarifies the source of bridgehead methyl isomers which are plausibly suggested as precursors of phenanthrene.[25] It would be necessary to determine whether A, B, C, and D are stable under the thermolysis conditions before additional speculations are called for. Any high-temperature labeling study of $(CH)_{10}$ derivatives is of course subject to after-the-fact scrambling as demonstrated by Paquette in the degeneracy of *cis*-9,10-dihydronaphthalene.[26]

We do not insist that **1b** must follow the same reaction path as **1**; methyl substitution may well facilitate diradical cleavage in starting material, but the same would also be true for the Cope intermediates **17** or **18**. The only significant point to be made here is that a single rationale explains the behavior of **1** and **1b**. Furthermore, the only difference between **2** and the benzo derivatives is that path "a" is blocked by the presence of a benzene ring.

In their recent review, Scott and Jones considered the possibility that **16** might be the precursor of *cis*-9,10-dihydronaphthalene since the equilibrium concentration of **8** is presumably very low because of reversible Cope rearrangement, while **16** might accumulate.[27] Our kinetic data indicate that this is not the case. The activation parameters for appearance of *cis*-9,10-dihydronaphthalene ($E_a = 40.4$ kcal/mol; log $A = 12.2$) are not compatible with a diradical

Scheme III



pathway but correspond reasonably to thermal cyclobutene → diene rearrangements in fused systems.[28] Either path "b" (rate-determining cyclobutene opening of **8**), or path "c" (rate-determining cyclobutene opening **2** → **6**), or a combination of both may be involved. Path "c" cannot be ruled out because **6** rearranges rapidly to *cis*-9,10-dihydronaphthalene under identical conditions. Furthermore, both "b" and "c" occur in the benzo series with path "b" favored by a factor of ca. 6. There is no reason to suspect different behavior starting from **2**.

A few minor issues remain unresolved. The mechanism by which **4** rearranges to **3** has been the object of interesting rationales, but it is not possible to distinguish among those which are consistent with available data.[6,7] This seems a common (although often overlooked) corollary of rationalization in the $(CH)_{10}$ area and related fields.[29,30]

There is also an ambiguity regarding the high-temperature behavior of *trans*-9,10-dihydronaphthalene. Conversion to *cis*-1-phenylbutadiene was initially proposed by Jones et al.[13b] and was subsequently demonstrated to occur under GLC conditions (235°) by van Tamelen et al.[13a] Masamune and coworkers observed the formation of 1,2-dihydronaphthalene in solution at 115°. at least partly by a second-order process, but their experiment gave no *cis*-1-phenylbutadiene.[13c] Jones et al. isolated *trans*-9,10-dihydronaphthalene, *cis*-1-phenylbutadiene, and 1,2-dihydronaphthalene from a reaction which is believed to generate **10** at ca. 100°.[13b] Attempts in our laboratory to subject *trans*-9,10-dihydronaphthalene[13c] to the same pyrolysis conditions used for rearrangement of **2** gave GLC peaks corresponding to *cis*-1-phenylbutadiene and 1,2-dihydronaphthalene. However, it was impossible to obtain an adequate concentration of *trans*-9,10-dihydronaphthalene in the gas stream for pyrolysis in our apparatus without using a neat sample at room temperature as the source of starting material. Under these conditions, extensive bimolecular decomposition occurred to give naphthalene and tetrahydronaphthalene as reported by Masamune et al.[13c] Thus, the evidence defining *trans*-9,10-dihydronaphthalene as the sole precursor of 1,2-dihydronaphthalene and *cis*-1-phenylbutadiene remains somewhat circumstantial, although there can be no doubt that both reactions do occur in the vapor phase. It is also abundantly clear from our studies that *cis*-9,10-dihydronaphthalene is not a significant thermal precursor of the phenylbutadiene and gives only traces of 1,2-dihydronaphthalene between 270 and 330°.

We shall close with a historical note. In their first papers on $(CH)_{10}$ structures, Nenitzescu and coworkers proposed a highly intuitive rationale for rearrangement of tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene derivatives which was in fact based on the intermediacy of **8**.[3,4] These papers precede the revelation of orbital symmetry concepts by several years, and consequently the mechanistic details suggested by Nenitzescu et al. differed somewhat from Scheme I. Nevertheless, it is interesting that Nenitzescu's imaginative proposal attracted scant notice for more than 10 years until it was found that **8** is indeed the key intermediate in the pyrolysis of **2**.

Experimental Section

Nenitzescu's hydrocarbon **2** was prepared according to the original method.[4] and the benzo analog **1** was made using the procedure of Paquette and Stowell.[7] Bicyclo[4.2.2]decatetraene (**6**) was obtained from bullvalene by palladium chloride catalyzed rearrangement.[31]

Stirred Flow Kinetic Studies Apparatus. The reactor design is illustrated in Figure 1. All heated components were made of quartz, and the reactor was heated with dibasic potassium phosphate for several days, purged with distilled water, and conditioned by a nitrogen stream containing norbornadiene vapors at 300° for several days. The reactor was immersed in the cavity of an insulated aluminum block and covered up to the level of the constricted portion of the outlet tube with iron filings (Figure 2). Inlet and outlet tubes were attached to $^1\!/_{16}$ in. stainless steel tubing using Cajon connectors with minimal dead volume. The volume of the reactor was 18.35 ml.

The aluminum block was heated by a 100-W cartridge heater. Temperature variation of less than ±0.1° was maintained using a proportional temperature controller identical with the oven temperature control system of the Becker Model 409 gas chromatograph (Packard Instruments). The temperature was monitored by a platinum resistance sensor placed in a hole in the aluminum block adjacent to the reactor cavity. Temperatures were determined by a Leeds and Northrup 8693-2 temperature potentiometer and are known to within 0.5°. The temperature within the reactor cavity was monitored continuously by thermocouple leads within the iron filing bath (Figure 2), and also within the thermocouple well at the top of the reactor (Figure 1). Both temperatures were identical within the 0.5° accuracy limits of the potentiometer. In one instance, the outlet tube of a quartz reactor was cut below the 1-mm constriction, and a thermocouple lead was placed directly into the center of the reactor. The temperature inside the reactor under typical nitrogen flow conditions at equilibrium was within 1° of the temperature measured in the normal thermocouple well and did not vary with changes in nitrogen flow rate. The tempera-

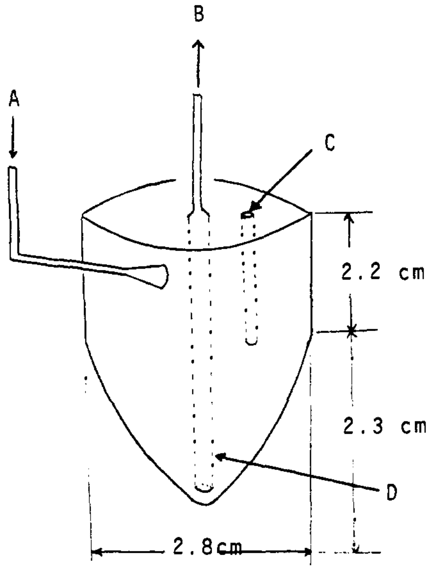


Figure 1. Reactor: (A) 1-mm i.d. quartz connection to sample container; (B) to sampling valve; (C) thermocouple well; (D) quartz outlet tube, 2-mm i.d. inside reactor, 1-mm i.d. outside reactor.

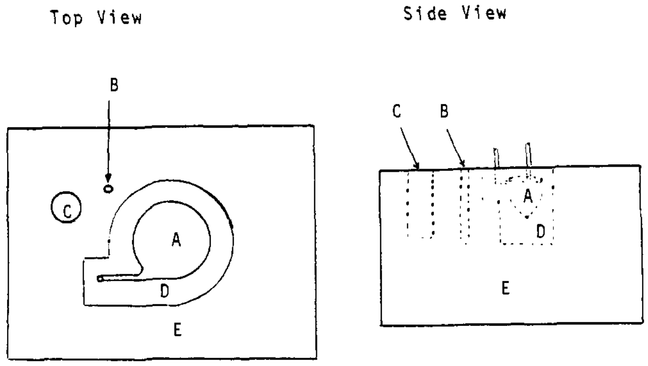


Figure 2. Heating block and reactor: (A) reactor; (B) Pt temperature sensor; (C) 100-W cartridge heater; (D) reactor cavity and iron filings; (E) aluminum block.

ture measured in the reactor cavity was within 3° of the temperature setting of the platinum resistance controller system.

Nitrogen flow through the reactor was controlled with less than 1% fluctuation in flow rate by the flow control system of a dual detector Becker 409 gas chromatograph. One of the two nitrogen lines was used for GLC analysis, while the other was used to provide constant flow through the reactor. Starting material was introduced into the reactor by passing nitrogen into a cavity containing a glass vial (i.d. 1.5 mm, height 1.7 cm) partially filled with hydrocarbon (Figure 3). The sample cavity was machined into a channeled brass block which was heated by circulating water, pumped through a constant-temperature bath. The temperature of the brass block was adjusted to melt the sample in order to maintain a constant cross-section of liquid exposed to the gas stream, and to provide a convenient hydrocarbon vapor pressure (30-50° for $C_{10}H_{10}$ systems). Gas flow was measured by a soap film burret at the reactor outlet and was corrected for ambient pressure and temperature.

The reactor effluent was passed continuously through a six-port sampling valve (Carle #2018) and vented through the buret (Figure 4). A three-way valve was placed in the reactor effluent line just before the sampling valve to permit the effluent to bypass the sampling valve. This is necessary to avoid pressure backup into the reactor during sampling for GLC injection. The GLC carrier gas was passed continuously into the sampling valve using the valve position which inserts the sample loop into the GLC carrier gas line. A ⅛ in. stainless steel sample loop of 5-ml volume was employed. Swagelok connections and $\frac{1}{16}$ in. stainless steel tubing were used throughout the flow system. The sampling valve was mounted inside the gas chromatograph oven and was maintained at the GLC analysis temperature (180° for $C_{10}H_{10}$ compounds). Alternatively, the sampling valve was mounted outside the oven, and the sample was injected onto a cold GLC column which was then heated to 180°. Both methods gave identical product ratios for $(CH)_{10}$ systems, but sharper peaks were obtained in shorter time using the heated sampling valve. Acceptable peak shapes for benzo $(CH)_{10}$ isomers could be achieved only by the heated valve method. A glass sampling loop gave similar results.

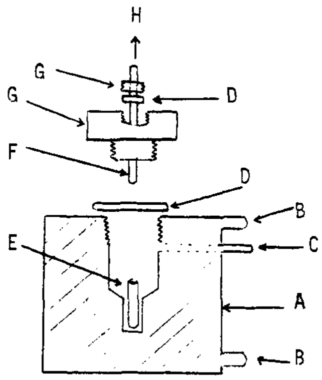


Figure 3. Sample container: (A) channeled brass lock; (B) circulating water bath hose; (C) nitrogen inlet; (D) O-ring; (E) sample vial; (F) height-adjustable $\frac{1}{16}$-in. nitrogen outlet; (G) O-ring compression nut; (H) connect to reactor.

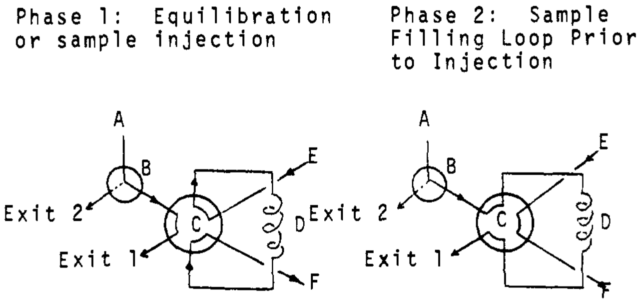


Figure 4. Sampling valve operation: (A) reactor effluent; (B) three-way valve; (C) six-port sampling valve; (D) sampling loop; (E) N_2, carrier gas source; (F) direct connection to GLC column. Exit 2, vent to hood; exit 1, vent to soap film buret.

Each new temperature required 2-3 hr of equilibration time and each flow rate ca. 0.5-1.5 hr. Sample injection using the heated sampling valve was accomplished by scrupulously performing a four-step sequence (refer to Figure 4).

(1) The system is equilibrated in phase 1 with A vented through B and C into exit 1. Just prior to sampling, valve B is switched to vent A through exit 2.

(2) Sampling valve C is switched to phase 2.

(3) As soon as excess GLC pressure (ca. 40 psi) has vented through exit 1, valve B is returned to original position to fill D with reactor effluent.

(4) As soon as sufficient time has passed for reactor effluent flow to displace carrier gas from loop D, valve C is returned to phase 1; the loop contents are thereby injected onto the GLC column.

To minimize sample retention by the sample loop, the maximum time for filling the loop was not allowed to exceed 2 min regardless of effluent flow rate. Efficient injection of all of the sample was evidenced by sharp GLC peaks. Sample retention by the loop gave GLC peaks with nongaussian tailing. Tailing could be minimized by increasing the sampling loop temperature and by reducing the time used to pass reactor effluent into the loop.

Analysis of $(CH)_{10}$ mixtures was performed on 20 ft × ⅛ in. 10% Carbowax—Chrom P at 180° using a flame ionization detector. The relative order of elution was **2** < *cis*-9,10-dihydronaphthalene < *cis*-1-phenylbutadiene < 1,2-dihydronaphthalene <

Table II

Temp, °C	$U/V \times 10^3$	[A]/[B]	k (slope × 10^3)	Correlation coefficient
255.5	2.08	1.52		
	3.66	2.34		
	5.42	3.27	1.93	1.00
	7.19	4.16		
260.5	1.83	0.944		
	2.52	1.09		
	3.60	1.43	3.20	0.999
	5.78	2.11		
269.0	4.51	1.00		
	6.46	1.39		
	7.98	1.67	5.11	1.00
	9.82	2.04		
	12.0	2.47		
277.0	7.92	1.01		
	9.73	1.20		
	12.1	1.49	8.32	0.999
	13.6	1.69		
285.5	10.0	0.610		
	11.5	0.724		
	11.6	0.674		
	13.4	0.865		
	13.7	0.907	13.3	0.993
	16.0	1.05		
	17.9	1.18		

$1/T \times 10^3$	Ln k	
1.892	−6.25	Slope = 18.390
1.874	−5.708	Intercept = 28.65
1.845	−5.277	Correlation coefficient = 0.995
1.818	−4.789	
1.791	−4.320	

E_a = 36.6 kcal/mol
Log A = 12.4

Table III

T, °C	$U/V \times 10^3$	[A]/[B]	[A]/[C]	k (A → B)	k (A → C)
289.5	4.78	1.44			
	6.90	1.79			
	9.32	2.45		3.21×10^{-3}	
	13.5	3.68			
	16.4	4.68			
	21.6	6.58			
300	5.93	0.846			
	7.68	1.15			
	9.81	1.50		6.62×10^{-3}	
	15.5	2.50			
	19.7	2.83			
309	5.41	0.358	5.91	1.40×10^{-2}	1.17×10^{-3}
	7.43	0.496	7.92		
	10.1	0.697	10.8		
	22.2	1.56	20.4		
319	5.21	0.165	2.77		
	6.80	0.204	3.39		
	8.51	0.272	3.79	3.01×10^{-2}	2.46×10^{-3}
	9.64	0.312	4.30		
	12.1	0.380	5.04		
	15.4	0.474	6.28		
	18.9	0.603	7.80		
	22.6	0.737	9.97		
331	5.36	0.069	1.12		
	7.95	0.102	1.42	5.08×10^{-2}	4.14×10^{-3}
	10.8	0.169	2.35		
	16.2	0.266	3.55		
	23.3	0.418	5.34		

$1/T \times 10^3$	Ln k(A → B)	Ln k(A → C)
1.78	−5.74	
1.75	−5.02	
1.72	−4.27	−6.75
1.69	−3.50	−6.01
1.66	−2.98	−5.49
Slope (A → B) = 23,300		Slope (A → C) = 20.300
Intercept +35.8		Intercept +28.0
Correlation coefficient 0.996		Correlation coefficient 0.991
E_a = 46.4 kcal/mol, log A = 15.5		E_a = 40.4 kcal/mol, log A = 12.2

Table IV

T, °C	$k \times 10^5$, sec	
70	70.9	
65	41.5	E_a = 24.2 kcal/mol
60	24.1	Log A = 12.3
55	13.9	
50	7.84	

naphthalene. Product ratios were determined using a disk integrator. Response factors were determined for standard mixtures of the products and differed significantly from unity only in the case of naphthalene. Consequently, the ratios obtained by disk integration were used directly for calculations.

Each kinetic run at a given temperature and flow rate was done in duplicate and reproducibility of ±2% in product ratios could be achieved in general. Reproducibility of ±0.5% was possible by optimizing peak size for each integration. Each change in flow rate was allowed at least 1 hr of equilibration time, although several points were double checked after 30 min of equilibration time and found to give the same product ratios. Flow rates were used in the range of 0.2 ml/sec to 0.02 ml/sec, and the reactor block temperature was adjusted to give convenient (20–80%) conversions within this flow range. Experiments conducted at flow rates >0.5 ml/sec gave erratic plots of U/V vs. product ratios, indicating possible deviations from a steady-state situation in the reactor.

Stirred-Flow Pyrolysis of 6. Product ratios were determined at five temperatures between 255.5 and 285.5° and are reported (Table II) as the ratio [A]/[B] where A = starting material **6**, and B = *cis*-9,10-dihydronaphthalene. The ratio U/V ($\sec^{-1}$) is the flow rate divided by the reactor volume of 18.35 cm^3. Slopes of U/V vs. [A]/[B] were computed using a least-squares routine. Neither the slope nor the correlation coefficient was materially affected by performing the calculation using more than four or five flow points, and excellent straight line plots could be obtained when the flow did not exceed ca. 0.3 ml/sec.

Stirred Flow Pyrolysis of 2. The same techniques were employed as described above except that somewhat higher temperatures were needed (ca. 290–330°); see Table III. Product ratios [A]/[B] correspond to A = **2** and B = 1,2-dihydronaphthalene, while [A]/[C] refers to C = *cis*-9,10-dihydronaphthalene. Accurate values for formation of *cis*-9,10-dihydronaphthalene could not be obtained at the lower temperatures since the substance was not formed in sufficient amount to allow meaningful integration.

Reaction of 1,2-Naphthoquinone with Cyclobutadiene. A solution of 1,2-naphthoquinone (0.9 g) and cyclobutadieneiron tricarbonyl[32] in reagent grade acetone (100 ml) was stirred vigorously, while solid ceric ammonium nitrate (10 g) was added in small portions over 5 min. After addition, the mixture was stirred 3 min, diluted with 4 volumes of brine, and extracted with ether (3 × 70 ml). The combined ether layers were washed once with brine, dried ($MgSO_4$), decolorized with Norit, and evaporated. The product α-diketone was crystallized from ether (two crops, total 0.9 g) as yellow prisms. The product turned dark red upon attempted storage so the crystalline diketone was treated immediately with *p*-toluenesulfonyl hydrazine (0.9 g) in methanol (15 ml). The product monotosylhydrazone crystallized from methanol (two crops, 1.3 g total) as pale-yellow needles (mp 143–145° dec).

3,4-Benzotricyclo[6.2.0.0^{2,7}]deca-3,9-dien-5-one. The crystalline tosylhydrazone (0.1 g) from above was stirred 30 min in glacial acetic acid (8 ml) with zinc dust (1.5 g). Hexane (30 ml) was added, solids were removed by filtration, and the hexane filtrates were extracted with water (30 ml) and sodium carbonate (15 ml, 5%). The hexane layer was dried ($MgSO_4$) and evaporated to yield a colorless oil. Preparative layer chromatography over silica gel using 20% ether–hexane gave two uv-active zones. The less polar zone (R_f 0.8) proved to be the desired benzo-$(CH)_{10}$ hydrocarbon **13** (see below). The more polar zone (R_f 0.3) was identified as 3,4-benzotricyclo[6.2.0.0^{2,7}]deca-3,9-diene-5-one (mp 72–73.5° from hexane) by spectral data: m/e 196 amu; ir (CCl_4) 5.93 μ;

NMR (CCl_4) δ 7.78 (1 H, br d, $J = 7$ Hz), 6.9–7.4 (3 H, m), 6.20 (1 H, t, $J = 2$ Hz), 5.48 (1 H, br t, $J = 2$ Hz), 3.1–3.4 (4 H, m), 2.5 (2 H, ABX, $J_{AB} = 13$, $J_{AX} = 6$, $J_{BX} < 1$ Hz).

An attempt to prepare the monoketone directly from the diketone by zinc reduction failed. No volatile products were obtained, and the reduction mixture was observed to develop an intense violet color which disappeared upon attempted work-up.

3,4-Benzotricyclo[6.2.0.0^{2,7}]deca-3,5,9-triene (13). The ketone from above (0.044 g) was dissolved in methanol (5 ml) at 0° and was stirred with sodium borohydride (0.2 g) for 30 min. The alcohol was extracted with ether (30 ml), the ether layer washed with water (2 × 15 ml), dried ($MgSO_4$), and evaporated. The crude product was dissolved in dry ether (5 ml) at 0°, and methanesulfonyl chloride (0.1 g) was added. Triethylamine (0.15 g, distilled from BaO) was dissolved in dry ether (2 ml) and was added dropwise to the stirred alcohol solution at 0° over 20 min. After addition, the mixture was allowed to warm to 20° for 15 min, solids were removed by filtration, and the filtrate was evaporated. The residue was separated by preparative layer chromatography over silica gel with hexane as eluent. A single uv-active zone was obtained (R_f 0.4), 0.014 g, identified as the hydrocarbon **13** by spectral data: *m/e* 180 amu; uv (methanol) λ_{max} 274 nm (5100), infl 280 (4700), λ_{min} 245 (1700); NMR (CCl_4) δ 6.7–7.1 (4 H, m), 6.0–6.2 (2 H, m), 5.8 (1 H, br s), 5.58 (1 H, d × d, $J = 10, 4$ Hz), 3.2–4.0 (4 H, m).

Rearrangement of 13 to 1. An nmr sample (CCl_4) of **13** was heated overnight at 70°. The signals of **13** disappeared and were replaced by signals of **1**. No other products were present by TLC, GLC, or NMR analysis.

A solution of **13** in spectrograde decalin was prepared in a stoppered uv sample cell (1-cm path). The cell was placed in a heated block inside the sample compartment of a Cary 15 uv instrument. Temperature control was achieved by circulating water through the block and through a constant-temperature bath (Lauda Model NB, temperature accuracy ±0.02°). The reaction was followed by measuring the absorbance at 277 nm in the temperature range 50–70° (see Table IV).

Treatment of data was performed using a computer program (least-squares method) which searched out the optimum infinity absorbances. The infinity absorbances obtained from the program were consistent with the experimental values.

References and Notes

(1) M. Avram, C. D. Nenitzescu, and E. Marica, *Ber.*, **90**, 1857 (1957).

(2) The composition of this mixture has been determined by R. Cookson, J. Hudec, and M. Massden, *Chem. Ind. (London)*, 21 (1961), and also by E. E. van Tamelen and B. C. T. Pappas, *J. Am. Chem. Soc.*, **93**, 6111 (1971).

(3) M. Avram, E. Sliam, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636**, 184 (1960).

(4) C. D. Nenitzescu, M. Avram, I. I. Pogany, G. D. Matescu, and M. Farcasiu, *Acad. Repub. Pop. Rom. Stud. Cercet. Chim.*, **11**, 7 (1973).

(5) W. v. E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966).

(6) E. Vedejs, *Tetrahedron Lett.*, 4963 (1970).

(7) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 2259 (1970).

(8) E. Vedejs and R. A. Shepherd, *Tetrahedron Lett.*, 1863 (1970).

(9) G. Maier, *Chem. Ber.*, **102**, 3310 (1969).

(10) H. H. Westberg, E. N. Cain, and S. Masamune, *J. Am. Chem. Soc.*, **91**, 7512 (1969).

(11) E. Vedejs, *Chem. Commun.*, 536 (1971).

(12) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967).

(13) (a) E. E. van Tamelen, T. L. Burkoth, and R. H. Greeley, *J. Am. Chem. Soc.*, **93**, 6210 (1971); (b) M. Jones, Jr., S. D. Reich, and L. T. Scott, *ibid.*, **92**, 3118 (1970); (c) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968); R. T. Seidner, Ph.D. Dissertation, University of Alberta.

(14) E. Vedejs and E. S. C. Wu, *Tetrahedron Lett.*, 3793 (1973).

(15) An alternative explanation for interconversion of **1** and **11** involves reversible cyclobutene opening and reclosure (path "c" Scheme I). There is no evidence to support this idea since **4** does not give detectable amounts of **11** upon pyrolysis.

(16) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **89**, 4534 (1967).

(17) W. C. Herndon, *J. Chem. Educ.*, **41**, 425 (1964); R. Weston, Jr., and H. A. Schwartz, "Chemical Kinetics", Prentice-Hall, Englewood Cliffs, N.J., 1972.

(18) T. J. Houser and R. B. Bernstein, *J. Am. Chem. Soc.*, **80**, 4439 (1958); C. B. Shepherd and C. E. Lapple, *Ind. Eng. Chem.*, **31**, 972 (1932).

(19) W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86**, 1922 (1964).

(20) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

(21) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 25 (1972).

(22) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, **No. 19**, 3 (1965).

(23) G. Scholes, C. R. Graham, and M. Brookhart, *J. Am. Chem. Soc.*, **96**, 5665 (1974).

(24) W. Grimme, *J. Am. Chem. Soc.*, **94**, 2525 (1972); *ibid.*, **95**, 2381 (1973); A. G. Anastassiou and R. C. Griffith, *ibid.*, **95**, 2379 (1973); and references therein; W. P. Lay and K. MacKenzie, *Chem. Commun.*, 398 (1970); *J. Chem. Soc. C*, 3199 (1971).

(25) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Am. Chem. Soc.*, **94**, 4920 (1972).

(26) L. A. Paquette, *J. Am. Chem. Soc.*, **93**, 7110 (1971).

(27) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(28) H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

(29) In keeping with this philosophy, we suggest that Cope rearrangements of tricyclo[4.2.x.0^{2,5}]-3,7-diene systems deserve more consideration than they have received in the literature.[9] Unprecedented rationales should be viewed with suspicion if a Cope rearrangement followed by cyclobutene opening can explain the products: R. C. DeSelms, *J. Am. Chem. Soc.*, **96**, 1967 (1974).

(30) The possibility that a Cope rearrangement may be involved in the pyrolysis of tricyclo[4.2.1.0^{2,5}]nona-3,7-diene and the related bicyclo-[4.2.1]nona-2,4,7-triene has been considered, but the issue remains unresolved: J. A. Berson, R. B. Boettcher, and J. J. Vollmer, *J. Am. Chem. Soc.*, **93**, 1540 (1971).

(31) E. Vedejs, *J. Am. Chem. Soc.*, **90**, 4751 (1968).

(32) R. Pettit and J. Henery, *Org. Synth.*, **50**, 21 (1970).