Stereochemistry of the Cope Rearrangement and Mechanism of Thermal Aromatization of 3,3'-Bicyclopropenyls

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Abstract: Preparative separation and chemical proof of structure of the *dl*- and *meso*-1,1'-dimethyl-3,3'-bicyclopropenyls (**19**) produced on thermal Cope rearrangement of 1,1'-dimethyl-3,3'-bicyclopropenyl (**18**) have been carried out, and the kinetic distribution of isomeric xylenes formed on thermal aromatization of all three of these bicyclopropenyls has been determined by extrapolation of the time-dependent xylene percentages to 0% conversion. *meso*- and *dl*-**19** interconvert at rates competitive with aromatization, and give rise to similar kinetic xylene distributions; the latter fact suggests strongly that the aromatization passes through an intermediate in which the stereochemical distinction between the two diastereomers of **19** has been lost. The data are most consistent with a mechanism involving initial cleavage of one of the cyclopropene rings, followed by expansion of the other ring, closure to a Dewar benzene, and finally opening of the Dewar intermediate to form aromatic products.

I. Introduction

The rearrangement of 3,3'-bicyclopropenyls (**1**) to benzene derivatives (**2**) is one of the most exothermic unimolecular
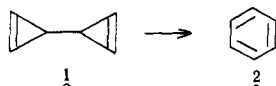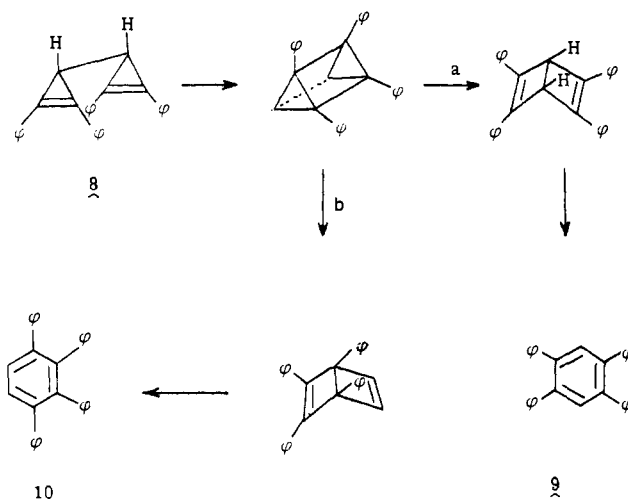

isomerizations known ($\Delta H^\circ_{rxn} = 120$ kcal/mol^2). Its mechanism, however, is not well understood. This rearrangement has been postulated to proceed through Dewar benzene,[3] benzvalene,[4] prismane,[5] diradical,[6] and ionic[3] intermediates, although to date no definitive evidence has been available for distinguishing between these mechanisms.

In 1959, Breslow and Gal[7] first prepared hexaphenylbicyclopropenyl (**4**) by dimerization of triphenylcyclopropenyl radical (**3**) and observed its thermal isomerization to hexaphenylbenzene (**5**). They proposed that the reaction proceeded
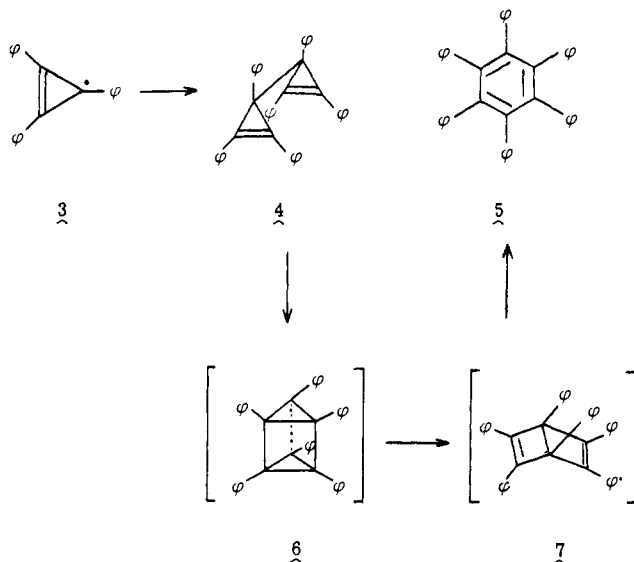

by initial 2 + 2 cyclization to hexaphenylprismane (**6**) followed by rearrangement to hexaphenyl Dewar benzene (**7**). Subsequent isomerization of **7** would then yield **5**. A subsequent study[5] of the isomerization of tetraphenylbicyclopropenyl (**8**) supported this mechanism, although it did not rule out other possibilities. Pyrolysis of **8** was found to give 1,2,4,5-tetraphenylbenzene (**9**) and 1,2,3,4-tetraphenylbenzene (**10**) in a ratio of 10:1 at 135 °C. The product ratio, as well as the ab-


sence of 1,2,4,5-tetraphenylbenzene among the products, was consistent with the prismane mechanism. Isomerization of the proposed tetraphenylprismane by cleavage of the more-substituted cyclopropane bonds (path a) would lead to the less sterically hindered Dewar benzene; thus path a would predominate over path b.

In 1973, Weiss and Andrae[3] observed the formation of a Dewar benzene in the thermal rearrangement of **11**. Pyrolysis of **11** in refluxing dichloromethane for 4 weeks led to benzene
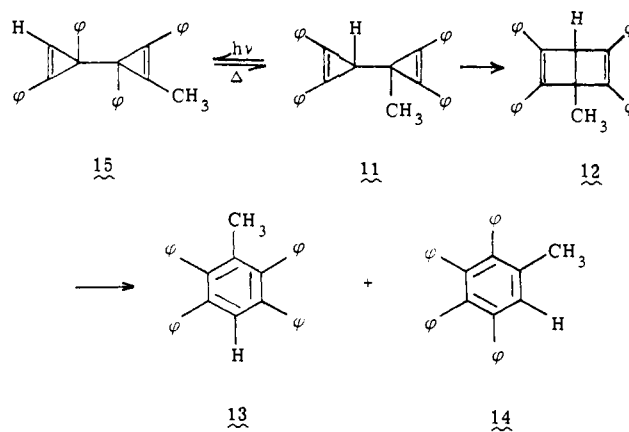

derivatives **13** and **14** as the sole products; however, after 2 weeks of pyrolysis, 9% of the Dewar benzene **12** was observed by NMR.[8] In analogy with experiments on the Ag[1] catalyzed

rearrangements of bicyclopropenyls, Weiss and Andrae suggested that the thermal rearrangement involved initial retrocarbene fission of the cyclopropene ring, followed by ring expansion and closure to give the Dewar benzene, as shown in Scheme I. In 1975 Weiss and Kölbl[6] observed the photo-

Scheme I
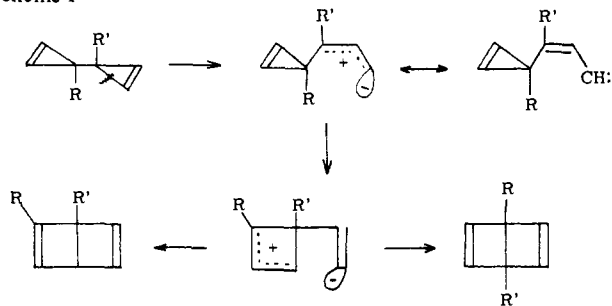
chemical Cope rearrangement of **11** to an isomeric bicyclopropenyl **15**, as well as the thermal Cope rearrangement of **15** to **11**. They postulated that the Cope reaction was a two-step process proceeding through an *anti*-1,4-tricyclohexylene diradical (**16**). This pathway was claimed to be favorable on the basis of an estimate by the authors that **16** has 25 kcal mol^{-1} less strain energy than the pericyclic transition state (**17**). In

16   **17**
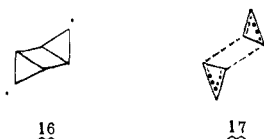
addition to postulating **16** to be an intermediate in the Cope rearrangement, Weiss and Kölbl also argued that **16** could be an intermediate in the aromatization process.[9]

Simultaneously with Weiss and Kölbl's observation of a bicyclopropenyl Cope rearrangement, the Cope rearrangement of 3,3'-dimethyl-3,3'-bicyclopropenyl (**18**) was independently observed by two other research groups. De Wolf, Landheer, and Bickelhaupt[10] observed the rearrangement of **18** to 1,1'-dimethyl-3,3'-bicyclopropenyl (**19**). Two isomers of **19** were

18   **19**
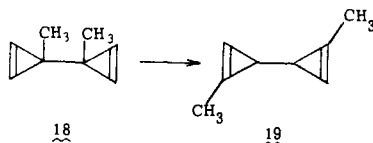
found; these were presumed to be diastereomers, although no attempt was made to determine which was *dl* and which meso. The ratio of the isomeric products was found to vary from 10:1 at 256 °C to 1:1 at 320 °C. In addition further pyrolysis of the mixture of isomers of **19** was found to give a 2:1 ratio of *m*- and *p*-xylene (10% yield). No mechanism for the aromatization was suggested, but in previous studies[4] of the pyrolysis of 3,3'-tetramethylenebicyclopropenyl (**20**) by these authors a benzvalene intermediate had been proposed. This mechanism involved initial retrocarbene fission leading to a vinyl carbene (**21**), which then could add across the double bond of the other ring to yield the benzvalene (**22**). Aromatization of **22** was then assumed to lead to the observed tetralin product (**23**).

20   **21**

22   **23**
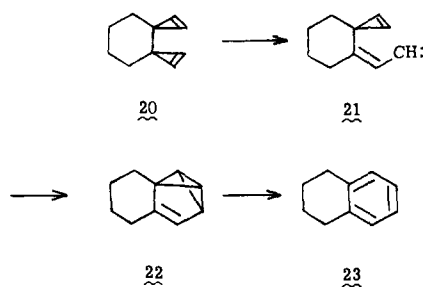
We have also observed the Cope rearrangement of **18** to the two diastereomers of **19** and have previously communicated these results, along with preliminary data on the aromatization study described in this paper.[11] During our study it occurred to us that determination of the ratios of isomeric xylene products formed on thermal aromatization of the two diastereomers of **19** might provide a definitive solution to the aromatization mechanism problem. We therefore set out to preparatively separate and assign the stereochemistries of the diastereomers and carry out the pyrolysis of the pure isomers.

II. Assignment of Stereochemistry to *meso*- and *dl*-19

The stereochemistries of *meso*- and *dl*-19 were determined by chemical correlation with compounds whose configuration could be determined directly (Scheme II). Because our supply

Scheme II
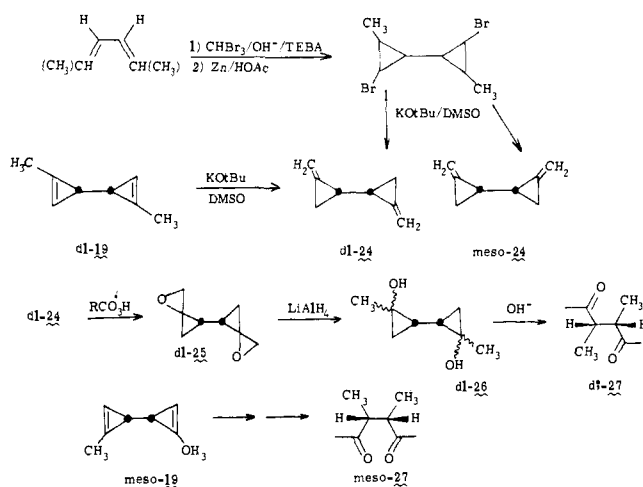
of **19** from the pyrolysis of **18** was very limited, the following method, involving methylenecyclopropanes **24** as relay compounds, was chosen.

First, usable quantities of **24** were prepared independently by addition of CBr_2 to 2,5-hexadiene, followed by reduction with zinc in acetic acid and elimination/isomerization using KO-*t*-Bu/Me$_2$SO. This sequence gave the two diastereomers of **24** in a 1:2 ratio, the minor isomer (which proved to be the meso; vide infra) eluting first from a Carbowax VPC column. A 2:1 mixture of diastereomers **19** was then purified by VPC and converted to the diastereomers **24** by base-catalyzed isomerization, again using KO-*t*-Bu/Me$_2$SO. Analytical VPC showed that this reaction gave a 2:1 mixture of diastereomers **24**. In this case, however, the early-eluting diastereomer of **24** was formed in major amount. The fact that different bismethylenecyclopropane (**24**) diastereomer ratios were obtained from 2,5-hexadiene and **19** shows that equilibration of the diastereomers does not occur in KO-*t*-Bu/Me$_2$SO. We therefore conclude that in the **19** → **24** reaction, the major (early-eluting) diastereomer in the **19** mixture corresponds stereochemically to the minor diastereomer in the **24** mixture.

After attempts at kinetic resolution of the diastereomers of **24** (using both asymmetric hydroboration[12a] and epoxidation with a deficiency of (+)-monoperchamphoric acid[12b]) failed to produce optical activity in either isomer, we decided to correlate the diastereomers of **19** by chemical conversion to *meso*- and *dl*-2,4-hexanediones **27** using the route outlined in Scheme II (for brevity, only the correlation of *dl*-19 is shown in detail). Epoxidation of **24** with *m*-chloroperbenzoic acid gave the mixture of epoxides **25**. These were subjected to ring-opening reduction with LiAlH$_4$, and the cyclopropanols **26** treated with dilute base. Predominant ring cleavage at the

less-substituted carbon, according to precedent,[13] gave diketone **27**. Control experiments showed that *meso-* and *dl-*27 underwent only slight interconversion by epimerization under the reaction conditions. The stereochemistries of *meso-* and *dl-*27 were then assigned through the kinetic resolution[12a] of *dl-*27 by asymmetric hydroboration (see Experimental Section).

III. Mechanistic Considerations

Possible mechanisms for the aromatization process fall into two general groups. The first (group A) postulates some sort of initial bonding interaction between the two cyclopropenyl rings (examples are the concerted double ring expansion and the classical Breslow mechanism), and the other (group B) involves cyclopropene ring bond cleavage as the initial critical step. Comparison of the xylene ratios from pure *meso-* and *dl-*19 allows us to distinguish between these two groups, because (as outlined in detail below) group B mechanisms, involving initial ring bond cleavage, destroy the stereochemical distinction between these diastereomers. Thus if one of the group B mechanisms is operating, we would expect very similar xylene ratios from each. Additionally, as is outlined in detail below, we are able to distinguish among the group A and group B mechanisms by considering additionally the xylene ratios formed from **18**.

(A) Group A Mechanisms. (1) Prismane Mechanism. Initial formation of a prismane from **18**, *dl-*19 and *meso-*19, followed by isomerization to the corresponding Dewar benzenes and aromatization, would predict formation of xylenes as is shown in Scheme III. **18** and *meso-*19 should form the same prismane

Scheme III

18

dl-19

meso-19
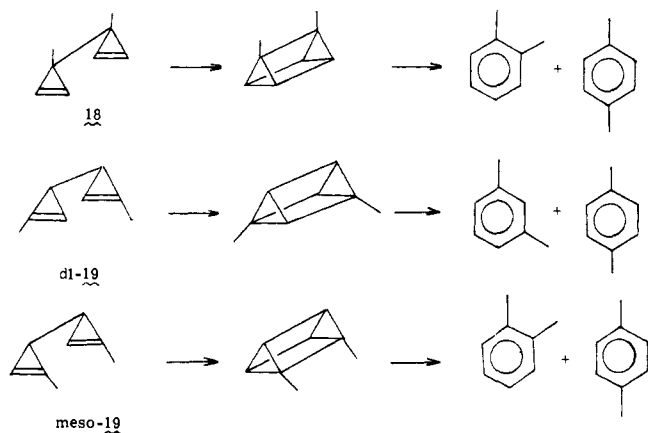
intermediate and thus would give an identical mixture of *o*- and *p*-xylenes, while *dl-*19 would give *m*- and *p*-xylenes.

(2) The Weiss Biradical Mechanisms. The Weiss mechanism involves formation of a common intermediate for the Cope and aromatization processes. The products expected from an *anti-*1,4-tricyclohexylene intermediate are shown in Scheme IV. All three isomers are expected to give a different mixture of xylenes. If, as Weiss suggests, there is an additional pathway for aromatization including "prefulvene" intermediates (e.g., benzvalene), we would still predict substantially different product distributions from each of the isomers.

(3) The Concerted Ring Expansion Mechanism. A mechanism not previously proposed involves concerted ring expansion of both cyclopropenes to give a Dewar benzene directly. As can be seen from Scheme V, in this pathway both **18** and *dl-*19 are predicted to give *p*-xylene exclusively, while *meso-*19 is expected to yield *m*-xylene. Note that there is no pathway for formation of *o*-xylene.

(B) Group B Mechanisms. (1) The Benzvalene Mechanism. The mechanism of de Wolf, Landheer, and Bickelhaupt involves retrocarbene fission of one cyclopropene followed by

Scheme IV

18

dl-19

meso-19

Scheme V

18

dl-19

meso-19
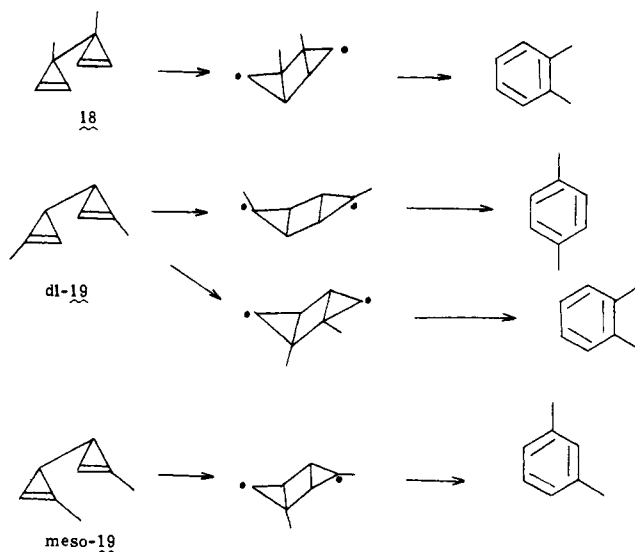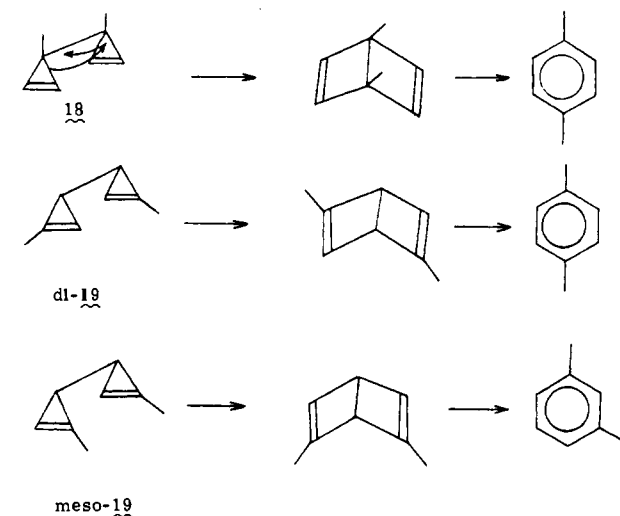
addition of the carbene carbon to the other ring. This benzvalene would then aromatize to give benzene derivatives. The predicted products from our labeled bicyclopropenyls are shown in Scheme VI. Assuming that vinylcyclopropane rearrangement in the benzvalene is slow relative to aromatization, the two diastereomers of **19** are predicted to give the same product distributions, while **18** is predicted to yield exclusively *o*-xylene.
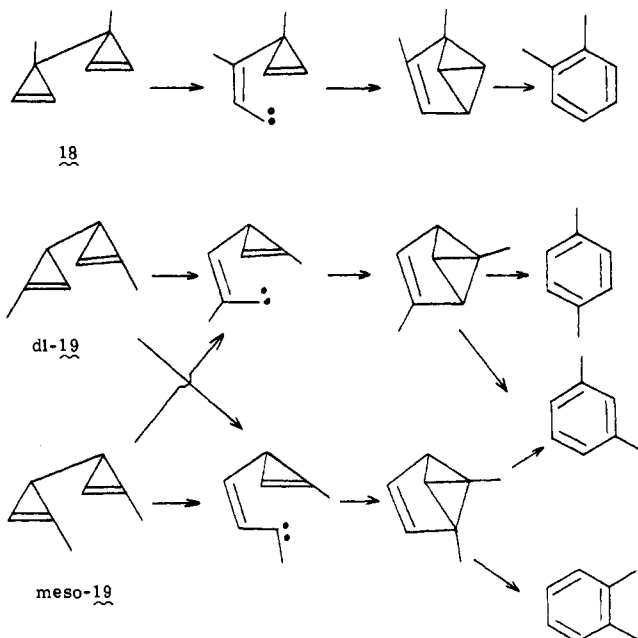
(2) The "Benzvalene-like" Diradical Mechanism. A slight variation on the benzvalene mechanism involves initial ring bond cleavage to give the 1,3-diradical (**28**) followed by ring closure to give the bicyclo[3.1.0]hexenediyl (**29**). Cleavage of the internal cyclopropyl bond yields xylene. As shown in Scheme VII, **18** would yield exclusively *o*-xylene, while *dl-*19 and *meso-*19 would yield a mixture of all three xylenes.

(3) The Weiss "Ag[I]-Type" Mechanism. In their original work Weiss and Andrae proposed the mechanism shown in Scheme I involving a cyclopropenylcarbinyl cation ring expansion. This mechanism predicts that **18** should give both *o*- and *p*-xylenes but no *m*-xylenes, while *dl-*19 and *meso-*19 would yield a mixture of all three xylenes.
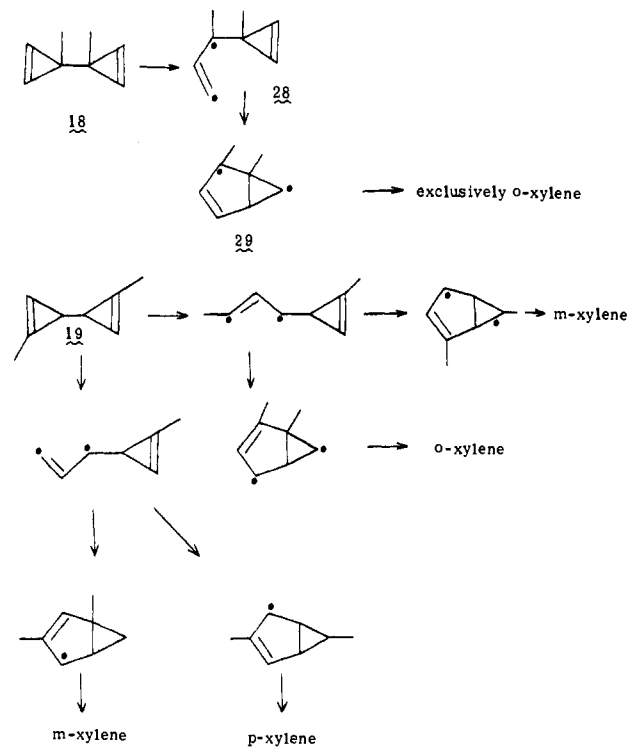
IV. Results

Pyrolyses of 3,3'-dimethyl-3,3'-bicyclopropenyl (**18**) were carried out in both flow and static systems. Under all conditions used, xylenes were the products observed at complete conversion. At earlier reaction times, however, the buildup and dis-

Scheme VI

18

dl-19

meso-19

Scheme VII

18

28

exclusively o-xylene

29

19

m-xylene

o-xylene

m-xylene   p-xylene

appearance of two new products were observed. These compounds were obtained in nearly pure form (>95%) by preparative vapor phase chromatography. The liquid phase used for the separation proved to be crucial. The use of standard "olefin-separation" phases[14a] resulted in decomposition of the bicyclopropenyls and, in at least one case,[14b] resulted in quantitative isomerization to the Dewar benzenes. Hence, the only acceptable phase for VPC analysis of the bicyclopropenyls was the relatively inert SE-30. The sensitivity of the bicyclopropenyls also necessitated the use of glass columns in all VPC work. The stereochemistry of the pure diastereomers was then determined as outlined in section II. When 18 was pyrolyzed in a flow system, the 19 dl/meso ratio was found to vary from 10:1 to 1:1 over a 40 °C temperature range. It appeared that this temperature variation might be due to thermal interconversion of the products dl- and meso-19 under the reaction

Table I. Rate Constants (in s⁻¹, × 10⁵) for Interconversion of Bicyclopropenyls *meso*-19, *dl*-19, and 18 and for their Aromatization at 165.5 °C

Starting material	Product		
	dl-19	*meso*-19	Xylenes
18	15 ± 2	0.12 ± 0.02	2.4 ± 0.2
dl-19		22 ± 2	1.3 ± 0.2
meso-19	20 ± 2		1.7 ± 0.2

Table II. Extrapolated Zero-Time Xylene Distributions Formed in the Gas-Phase Pyrolysis of Dimethylbicyclopropenyls at 165.5 °C

Compd	Xylene isomers, %		
	p	*m*	*o*
dl-19	20 ± 1	72 ± 2	8 ± 3
meso-19	27 ± 2	62 ± 2	11 ± 4
18	26 ± 5	2 ± 2	72 ± 5

conditions. The thermal reactions of all three isomers were therefore examined in more detail using a static pyrolysis system.[15]

Pure samples of 18, *dl*-19, and *meso*-19 were obtained by preparative VPC and pyrolyzed at 165.5 °C. Samples were analyzed at various time intervals ranging from 200 to 5000 s; the data are shown in Figures 1, 2, and 3. Rate constants were determined by computer simulation of concentration vs. time curves using the MS1M4 program.[16] The calculated rate constants are listed in Table I for the interconversion of the dimethylbicyclopropenyls and for their conversion to xylenes. The zero-time xylene distributions were extrapolated from the data shown in Figures 4-6 and are listed in Table II. It was extremely important that the xylene ratios be taken as close as possible to zero time due to two complicating factors. First, in the pyrolysis of 18, the formation of any substantial amount of the Cope products (19) resulted in xylenes formed from both 18 and 19. Second, the aromatization of pure *dl*- and *meso*-19 occurred at a rate competitive with that of interconversion of the diastereomers. With some effort, we were able to analyze accurately for xylene formation at conversions of starting material as low as 1%.

To determine the temperature dependence of the kinetic (zero-time) *dl*/meso ratio, the pyrolysis of 18 was also carried out at 196.5 °C. At both temperatures the *dl*/meso ratio extrapolates to 130 ± 10 at zero time (e.g., Figure 7) and shows no measurable variation with temperature.

V. Discussion

(a) Cope Rearrangement and Bicyclopropenyl Interconversion. The pyrolysis of 3,3'-dimethyl-3,3'-bicyclopropenyl (18) yields both *dl*- and *meso*-1,1'-dimethyl-3,3'-bicyclopropenyl (19) in a ratio of 130 ± 10 at zero time. As shown in Scheme VIII two different transition states are available for the Cope

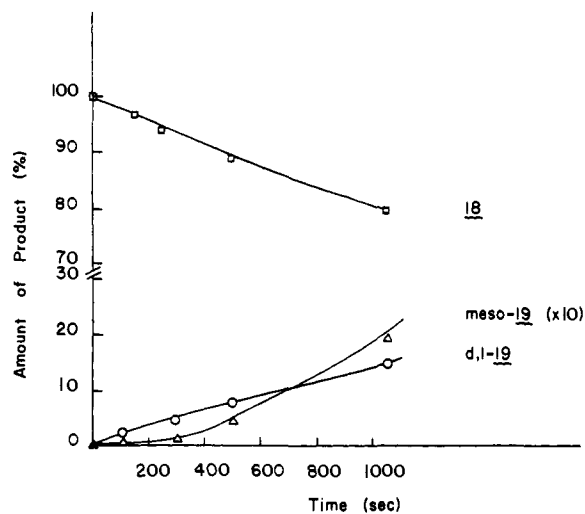Scheme VIII

dl-19

18   meso-19
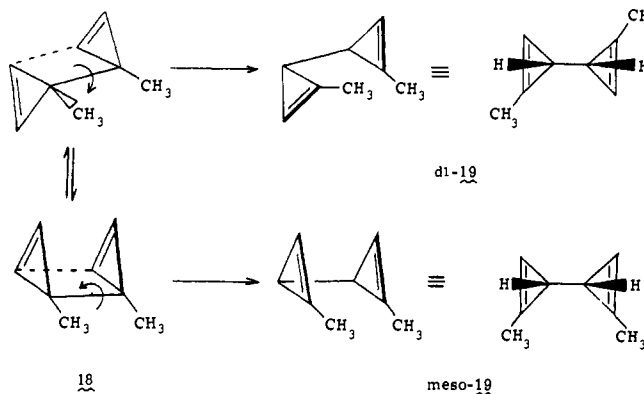
Figure 1. Time dependence of products formed on pyrolysis of 3,3'-dimethyl-3,3'-bicyclopropenyl (**18**) at 165.5 °C. Solid lines are computer-simulated percentages.
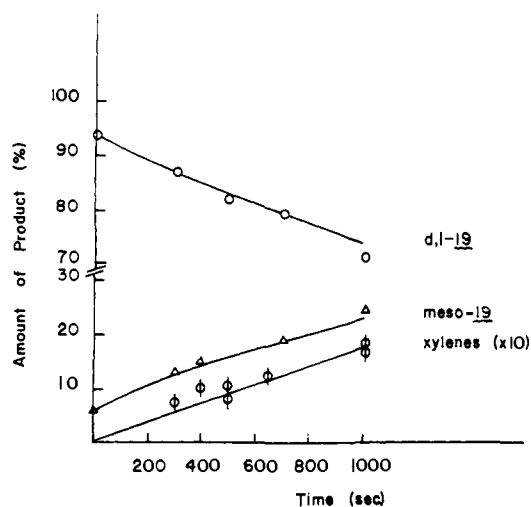

Figure 2. Time dependence of products formed on pyrolysis of *dl*-1,1'-dimethyl-3,3'-bicyclopropenyl (*dl*-**19**) at 165.5 °C. Solid lines are computer-simulated percentages.
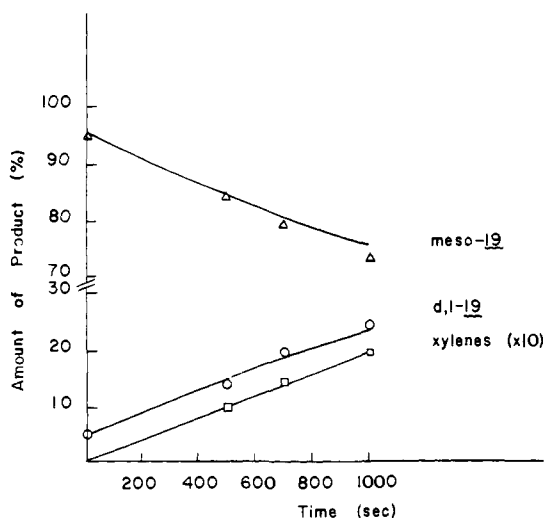

Figure 3. Time dependence of products formed on pyrolysis of *meso*-1,1'-dimethyl-3,3'-bicyclopropenyl (*meso*-**19**) at 165.5 °C. Solid lines are computer-simulated percentages.

rearrangement, with the chair conformer yielding *dl* and the boat giving meso. Goldstein[17] has suggested that the Cope
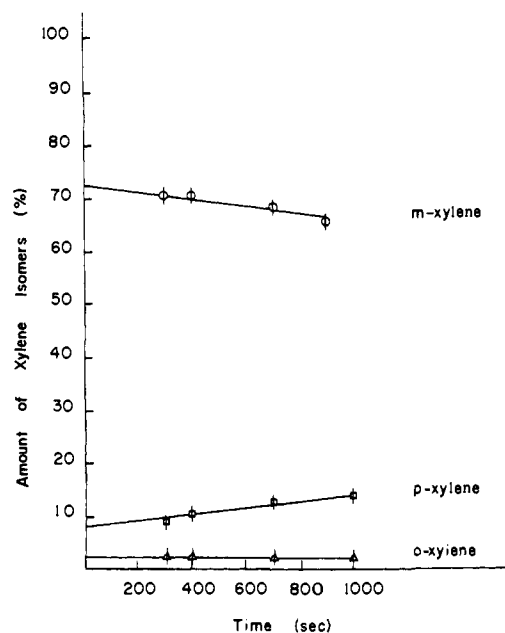

Figure 4. Time dependence of the percentage of each xylene produced on pyrolysis of *dl*-**19** at low percent conversion (165.5 °C).
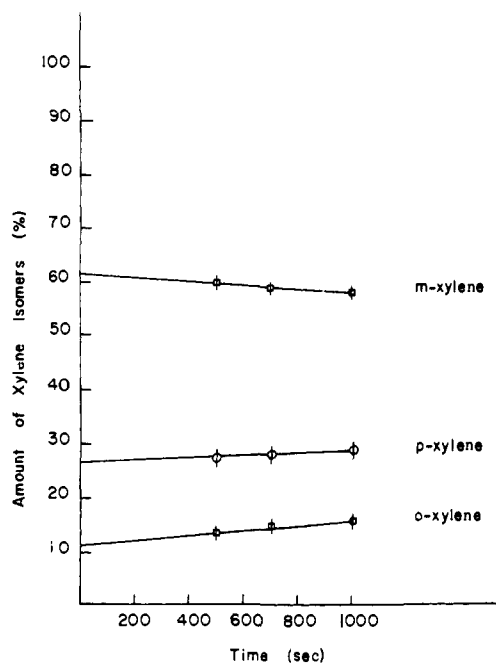

Figure 5. Time dependence of the percentage of each xylene produced on pyrolysis of *meso*-**19** at low percent conversion (165.5 °C).

rearrangement in acyclic systems might be proceeding through other transition states (e.g., twist, plane, and anchor conformers). In the bicyclopropenyl case, however, the rigidity of the system prevents rearrangement through many of the conformations which might be available in more flexible acyclic systems. Additionally the unusual symmetry of the bicyclopropenyl molecule allows the chair and boat conformers to interconvert by a simple rotation rather than a ring flip. Thus it seems likely that the difference in free energy of activation ($\Delta\Delta G^{\ddagger}$) for the formation of *dl*- and *meso*-**19** accurately reflects the free energy difference between the chair and boat transition states. The experimental $\Delta\Delta G^{\ddagger}$ of 4.3 kcal/mol (166 °C) is in good agreement with the $\Delta\Delta G^{\ddagger}$ for the acyclic system (~6 kcal/mol at 498 °C).[18] Our results confirm that the variable *dl*/meso ratios observed by de Wolf, Landheer, and
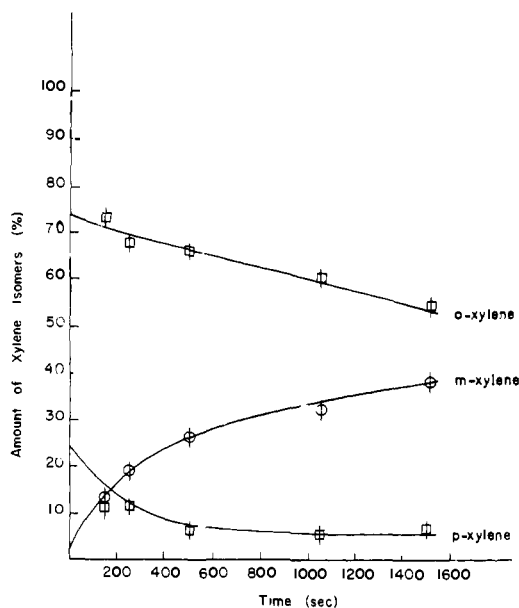
Figure 6. Time dependence of the percentage of each xylene produced on pyrolysis of 18 at low percent conversion (165.5 °C).

Figure 7. Extrapolation to zero time of dl-19/$meso$-19 ratio from pyrolyses of 18 at 165.5 °C.

Bickelhaupt were the result of thermal interconversion of dl- and $meso$-19 at the temperatures required for reaction. In view of this, one might ask whether this interconversion occurs via retro-Cope rearrangement to 18 (Scheme IX). The following

Scheme IX
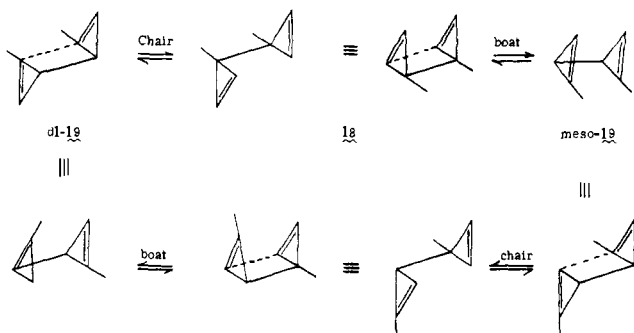
reasoning rules out this possibility. The rate of rearrangement for dl-19 to $meso$-19 is limited by the rates of dl-19 → 18 and 18 → $meso$-19.

$$dl\text{-}19 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} 18 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} meso\text{-}19$$
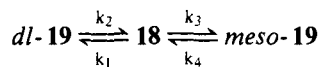
However, the observed rate for the interconversion of dl-19 → $meso$-19 is two orders of magnitude faster than the rate for 18 → $meso$-19. Therefore the reverse Cope rearrangement cannot be operating at a significant rate under our pyrolysis conditions. An additional piece of evidence against interconversion by the reverse Cope rearrangement is our failure to detect any 3,3′-dimethyl-3,3′-bicyclopropenyl or any 1,3′-dimethyl-3,3′-bicyclopropenyl in the pyrolyses of pure dl-19 and $meso$-19.

A reasonable mechanism for the interconversion of dl- and $meso$-19 involves initial ring opening of one cyclopropene followed by bond rotation and ring closure. This mechanism would predict that the rate of interconversion should be approximately the same whether one starts with dl- or $meso$-19. These rates are found to be identical within experimental error (Table I).

(b) Aromatization. The relative rates of formation of each of the xylene isomers from each of the three bicyclopropenyls allows us to distinguish clearly between the various mecha-
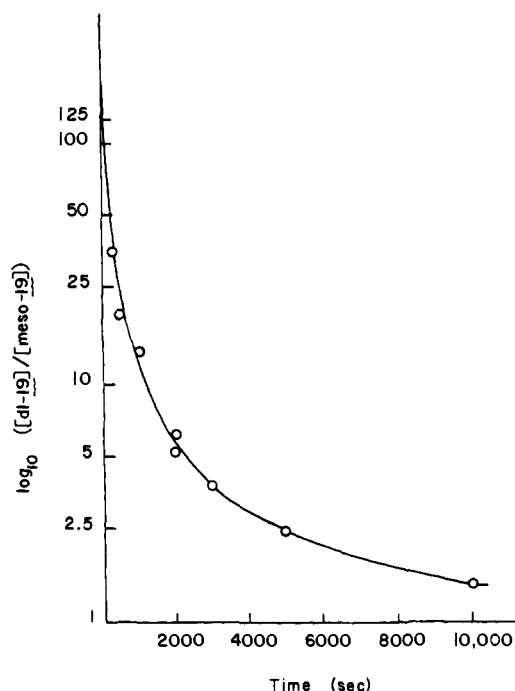
nisms proposed in part III. Our data show that dl- and $meso$-19 yield very similar percentages of xylenes (mostly para and meta), while 18 gives a quite different ratio (mostly ortho). We can therefore rule out all group A pathways—i.e., the prismane mechanism, Weiss' biradical mechanism, and any other pathways which would retain the stereochemical distinctions between dl- and $meso$-19. In addition the benzvalene or "benzvalene-like" diradical mechanism fails to predict accurately the xylene distributions for the three isomers.

The only reasonable mechanism consistent with our observations is the Weiss "Ag[1]-type" mechanism. This involves the zwitterionic form (32) of the ring-opened bicyclopropenyl.
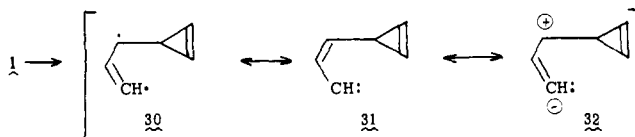
While this species might be important in solution, it is unlikely to play any role in the gas phase due to the greatly unfavorable energy required by charge separation. Recent theoretical calculations[19] indicate that ring opening of a cyclopropene (33) most likely leads to a 1,3-diradical-type state (34), which then
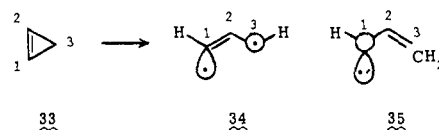
converts to the slightly lower energy "carbene" state (35). When the symmetry of the system is perturbed (for example, by the extra cyclopropene ring in 18) configurations 34 and 35 can mix. Thus it seems likely that the initial ring-opened intermediate formed by ring cleavage in a substituted cyclopropene should have large contributions from configurations resembling 34 and 35, and thus the intermediate should possess significant radical character at carbon 3.

We now propose that 1,2-vinyl migration occurs in 30 to yield a cyclobutenyl radical (36). 1,2-Vinyl shifts of this nature are well-precedented; e.g., the Δ^2-cyclopentenyl methyl radical

30   36

37   38
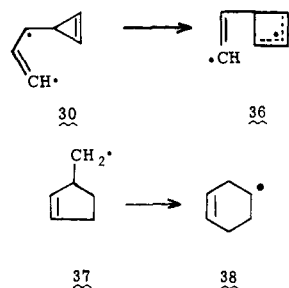
(37) rearranges rapidly[20] to 4-cyclohexenyl radical (38). Ring expansion in **30** should be even more facile than in **37**, since we are not only relieving greater strain in the cyclopropene, but also forming an allylic radical.

This "modified Weiss mechanism" is outlined in detail in Schemes X and XI. This hypothesis accounts for the obser-

Scheme X

o-xylene

p-xylene

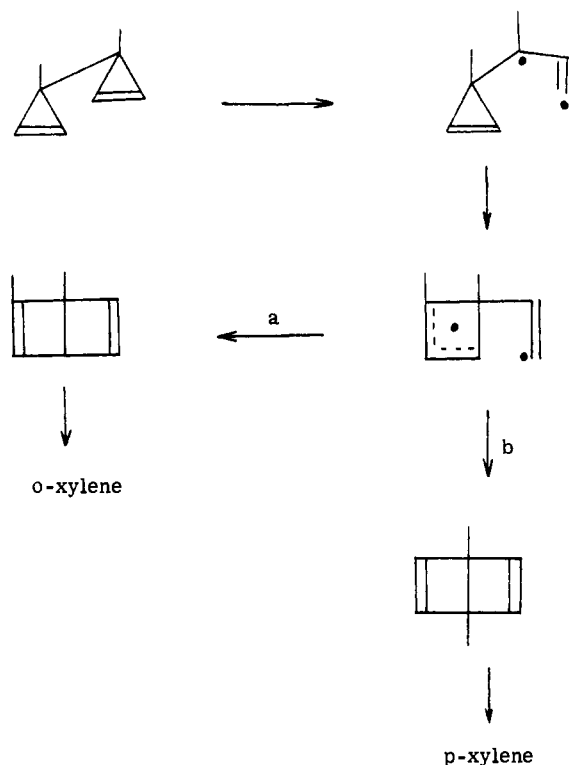vation that, in the case of the pyrolysis of **18**, rearrangement gives both o- and p-xylene but not m-xylene. In addition, since ring closure by path b (Scheme X) involves greater steric hindrance and yields the least substituted double bond, we would expect path a to predominate. Thus, we expect **18** to yield only two xylenes with the major isomer being o-xylene, as is found experimentally. Scheme XI allows us to predict which xylenes should predominate in pyrolysis of dl-**19** and meso-**19**. On a purely statistical basis, we would predict the ratio of o-/m-/p-xylenes to be 1:4:3. Since pathway a involves cleavage of the more substituted cyclopropene bond and thus might be preferred over pathway b, we expect a greater predominance of m-xylene. Experimentally we find a o/m/p ratio of 1:9:2.5 for dl-**19** and 1:6:2.5 for meso-**19**. Thus the xylene ratios from pyrolysis of all three isomers strongly support the mechanism outlined in Schemes X and XI.

The best evidence for this mechanism would, of course, be the direct observation of a Dewar benzene intermediate. Although this has not been possible in the gas-phase reactions due to the low steady concentration of Dewar benzenes (estimated to be $\ll 10^{-6}$), it has been possible to detect spectroscopically the presence of a Dewar benzene in the thermal rearrangement

Scheme XI

m-xylene

p-xylene   o-xylene

p-xylene
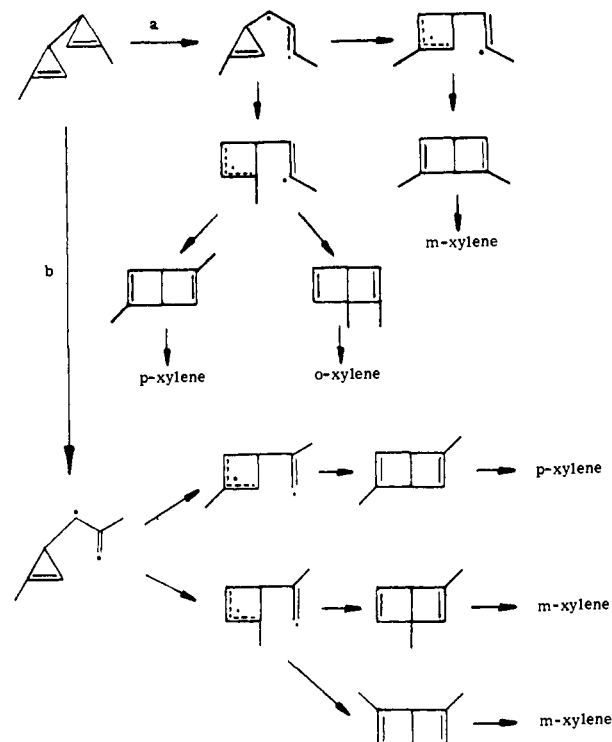
m-xylene

m-xylene

of **18** in solution. In conjunction with Turro and Schuster,[21] we have observed chemiluminescent rearrangement of **18** to xylenes. Furthermore we have shown that the chemiluminescent species is a ground-state intermediate in the rearrangement of **18**. Of the three plausible ground-state intermediates (prismanes, benzvalenes, Dewar benzenes), only Dewar benzenes have been found to chemiluminesce with sufficient intensity to account for the bicyclopropenyl pyrolysis results.

Measurements of the chemiluminescence yields suggest that *at least* 50% of the reaction must be proceeding by way of the Dewar benzene intermediate. Thus this solution data clearly fit the postulated gas-phase mechanisms. While it is always possible for a different mechanism to be operating in the solution chemistry, we feel that the mechanism outlined in Schemes X and XI present by far the most coherent and economical picture of the aromatization of bicyclopropenyls.

VI. Experimental Section

Materials. n-Pentane (reagent grade) was stirred with concentrated sulfuric acid until no further coloration resulted. The pentane was then stirred overnight with 0.5 N KMnO$_4$ in 3 M H$_2$SO$_4$, washed with water and aqueous NaHCO$_3$, and dried over MgSO$_4$. The pentane was distilled from P$_2$O$_5$ through a 1-m distillation column packed with glass helices.[22]

3,3'-Dimethyl-3,3'-bicyclopropenyl was prepared by the method of de Wolf, Landheer, and Bickelhaupt.[23]

trans-1,2-Dimethylcyclohexane was purified by preparative VPC. All bicyclopropenyls were purified just prior to use by preparative VPC on a Varian Aerograph 90-P gas chromatograph using a 20 ft × ¼ in. glass column packed with 30% SE-30 on 60/80 Chromosorb WAW-DMCS. The column temperature was 60-70 °C, the injector temperature 60 °C, and the detector temperature was 80 °C. Other preparative VPC columns used: Column A: 10 ft × ¼ in. glass 15% Carbowax 1500 on 60/80 Chromosorb WAW-DMCS; Column B: 10 ft × ¼ in. glass 5% diethylene glycol succinate (DEGS) on 60/80 Chromosorb WAW-DMCS.

Apparatus. Static pyrolysis of the bicyclopropenyls was carried out in a reactor of 200-ml volume (Figure 8). The reactor was constructed of lead-alkaline glass (Corning 0120) and was joined to a Teflon stopcock A by a length of capillary tubing to minimize dead space. Fused to the capillary tubing and extending into the center of the flask was a thermocouple well. Stopcock A was connected to a vacuum manifold, which included a small coil trap, 14/20 joint B, vacuum
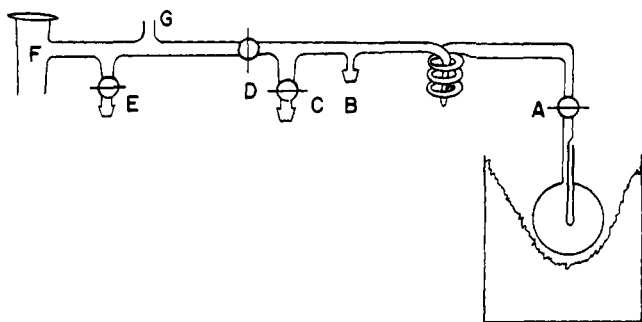
Figure 8. Apparatus for gas-phase kinetics.

stopcock and 14/20 joint C, vacuum stopcock D, vacuum stopcock and 14/20 joint E, and large trap F. System pressure was monitored by a mercury manometer at G.

The reaction flask was immersed in a 6-l. copper beaker containing a high-temperature silicon oil (Lauda Ultra-Therm 330-SCB). Also immersed in the bath was a high-speed Sargent stirrer. Heat was supplied by two 500-W base heaters, one of which was connected to a thermoregulator. The temperature was measured by inserting an iron–constantan thermocouple into the reacter thermocouple well; voltage was read on a Leeds and Northrup millivolt potentiometer (Model 8686). Temperature could be routinely kept constant during a run to better than ±0.2 °C.

The reaction vessel was conditioned by heating bicyclopropenyl **18** in it at 195 °C for 24 h. Rate constants were determined using the following procedure. The entire system was evacuated to less than 0.05 Torr by a Welch pump. An appropriate mixture of bicyclopropenyls and internal standard (*trans*-1,2-dimethylcyclohexane) was degassed at joint C (stopcock A closed). The stopcock to the pump was closed and the mixture allowed to vaporize into the manifold (15–20 Torr). Stopcock C was closed and then degassed pentane was vaporized into the manifold from point E to give a total pressure of ~150 Torr. The Teflon stopcock A was opened and the manifold mixture expanded into the reaction vessel to give a total pressure of 100 Torr. The remaining manifold mixture was condensed, and the system was re-evacuated. After the mixture had been pyrolyzed, stopcocks C and D were closed, and the Teflon stopcock opened momentarily. The material which expanded into the manifold was condensed with liquid nitrogen at point B. The aliquot was removed from the line and stored at −50 °C until analysis.

All analytical VPC was done on either a Hewlett-Packard 5751 gas chromatograph with flame ionization detector or a Perkin Elmer 3920 gas chromatograph. Peak areas were integrated using a Spectro-Physics Autolab System I computing integrator. Two different analytical columns were necessary to determine the *dl*/meso ratio and to determine the *o-/m-/p*-xylene ratios. To measure the relative amounts of **18**, *dl*-**19**, *meso*-**19**, and xylenes, a 20 ft × ¼ in. glass column packed with 30% SE-30 on 60-80 Chromosorb WAW-DMCS was used. This column was temperature programmed with a rise in temperature of 1 °C/min after an initial period of 60 min at 60 °C. VPC analysis of the xylenes required the use of an "internal tandem" 20 ft × ¼ in. glass column packed with 15 ft of 30% SE-30 on Chromosorb WAW (60/80) followed by 5 ft of 5% DC-555 and 5% Bentone-34 on Chromosorb WAW (60/80). This column was usable for separation of xylenes if temperature-programmed at 50 °C for 64 min (to elute the bicyclopropenyls) and then at 1 °C/min to 85 °C. Under these conditions the retention times were: *p*-xylene, 94.4 min; *m*-xylene, 96.9 min; *o*-xylene, 101.0 min.

dl- and *meso*-**2,2′-Bismethylenecyclopropyl**. To a vigorously stirred solution of 2,4-hexadiene (2.9 g, 35.2 mmol, mixture of isomers), bromoform (25.3 g, 100 mmol), triethylbenzylammonium chloride (0.2 g), and ethanol (0.4 ml) was added a 50% aqueous solution of NaOH. The temperature was maintained below 40 °C by means of a water bath. After stirring at room temperature for 20 h, methylene chloride (20 ml) and water (120 ml) were added and the organic layer was separated. The aqueous layer was extracted several times with methylene chloride and the combined organic layers washed with water, dried (MgSO₄), and stripped of solvent. The remaining volatiles were removed under reduced pressure (50 °C (10 mmHg)) and collected in a cold trap. Inspection of the distillate by NMR revealed the presence of bromoform (δ 6.83) and the monodibromocarbene adduct

of 2,4-hexadiene [δ (CCl₄) 5.9–5.0 (m, 2 H, olefinic), 1.75 (d, 3 H, J = 6 Hz), 1.5–1.85 (m, 5 H)]. The dark brown distillation residue solidified upon standing. The solid mass was dissolved in boiling methanol, treated with charcoal, filtered through celite, and cooled. 1,1,1,1′-Tetrabromo-2,2′-dimethyl-3,3′-bicyclopropyl separated as pale yellow crystals, which were separated by suction filtration (4.75 g, 31.7%): NMR (CCl₄) δ 2.1–1.0 (complex multiplet). For large scale preparations the monoadduct and bromoform were recycled through the above reaction sequence. Overall yields of diadduct by this method were typically 50–60%.

A vigorously stirred solution of the tetrabromide (73 g, 0.156 mol) in acetic acid (11) at 80 °C was treated portionwise with zinc dust (96 g, 1.47 mol) over a period of 6 h. The mixture was cooled, filtered, and diluted with water, then extracted with CCl₄, the organic layer washed with water twice, then dried over Na₂SO₄. After removal of solvent under reduced pressure, the residue was vacuum distilled. A total of 22 g (52% yield) of 1,1′-dibromo-2,2′-dimethyl-2,2′-bicyclopropyl was collected at 75–85 °C (2 mm): NMR (CCl₄) δ 2.81 (m, 2 H), 1.4–0.9 (m, 10 H).

To a stirred solution of potassium *tert*-butoxide (12.5 g, 0.11 mol) in Me₂SO (100 ml) at room temperature was added, in one portion, 1,1′-dibromo-2,2′-dimethyl-3,3′-bicyclopropyl (5.0 g, 19 mmol) in Me₂SO (20 ml). The solution immediately turned black. Stirring was maintained at 25 °C for 1 h. Pentane (5 ml) was added and the solution was cautiously treated with water (50 ml) while maintaining the temperature at 5 °C. The layers were separated and the aqueous portion extracted three times with pentane. The combined pentane extracts were washed twice with water then dried over Na₂SO₄. The dark brown solution was transferred under vacuum (0.5 mmHg) through a 0 °C trap and into a −196 °C trap. A black intractable residue remained in the pot. The 0 °C trap served to isolate mono-dehydrohalogenation products, usually present in very small amounts. The contents of the −196 °C trap were carefully reduced in volume (3–4 cm³) by distillation through a Vigreux column (pot temperature 40 °C). Analysis of the concentrated pentane solution by VPC (5 ft × ¼ in. 30% SE-30, Chrom W-AW-DMCS, 45 °C, 100 cm³/min) revealed the presence of two new major products (retention times 13 and 16.5 min). The first eluting peak(s) (unstable to GC conditions), exhibiting absorption at δ (CDCl₃) 6.5 (br s), 1.5–1.2 (m), 1.2–0.9 (m), was not characterized. The last peak to elute exhibited spectroscopic properties consistent with 2,2′-bismethylenecyclopropyl [NMR (CCl₄) δ 5.3 (finely split s, 4 H), 1.65 (m, 2 H), 1.0 (br m, 4 H); IR 3075, 3050, 2980, 2975, 1780, 1750, 890 cm⁻¹]. The two diastereomers could then be separated on column B at 40 °C; their A-60-A NMR spectra were essentially identical.

Base-Catalyzed Isomerization of 1,1′-Dimethyl-3,3′-bicyclopropenyl (19). A dimethyl sulfoxide (Me₂SO) solution of a mixture of diastereomers of *meso*- and *dl*-1,1′-dimethyl-3,3′-bicyclopropenyl (**19**) (3.5 mg, VPC purified, diastereomer ratio 2:1) was added at room temperature to a stirred solution of Me₂SO (3 ml) and potassium *tert*-butoxide (50 mg) under a nitrogen atmosphere. After stirring at room temperature for 1.5 h, cyclohexane (1 ml) was added and the solution was cautiously treated with water (5 ml). The layers were separated and the organic phase dried (Na₂SO₄). VPC analysis (column A, 40 °C) revealed the presence of two product peaks with retention times identical with those of an authentic mixture of diastereomers of 2,2′-bismethylenecyclopropane. The ratio of diastereomers was found to be 0.43:1 (in order of elution, meso/*dl*). The products from the isomerization were isolated by preparative GC and were found to have IR spectra identical with those of *authentic* samples of **24** prepared as described above.

Conversion of the Isomeric Bismethylenecyclopropanes to 3,4-Dimethyl-2,5-hexanedione. The individual diastereomers of bismethylenecyclopropane were isolated by preparative VPC (column A, 40 °C). To a solution of *m*-chloroperbenzoic acid (0.145 g, 0.84 mmol) in dry methylene chloride (8 ml) was added a methylene chloride solution (1 ml) of *meso*-**24** (32.1 mg, 0.303 mmol). The solution was stirred at room temperature for 45 h. Bisoxaspiropentane (**25**) [NMR (CCl₄) δ 2.95 (s, 4 H) 1.5–0.58 (br complex m, 6 h)] was isolated by trap to trap distillation (−41 °C), and then without further purification dissolved in pure ether (5 ml) and added over a period of 15 min to an ether suspension (9 ml) of lithium aluminum hydride (0.03 g, 0.79 mmol). The reaction was allowed to stir for 20 min at room temperature and then quenched with 0.2 N NaOH (0.3 ml). The resulting mixture was decanted and the remaining precipitate triturated with ether. The combined ether portions were washed with dilute

NH$_4$Cl and water until neutral then dried over Na$_2$SO$_4$. The elapsed time between addition of NaOH to neutralization was 7.5 min. After concentration of the sample, analysis was performed by VPC. The resulting chromatogram revealed the presence of three C$_8$ diketone isomers, 3,4-dimethyl-2,5-hexanedione (73%), 3-methyl-2,6-hepta-nedione (22%), and 2,7-octanedione (5%) in addition to several un-identified peaks at shorter and longer retention times than those of the diketones. The 3,4-dimethyl-2,5-hexanediones consisted of a mixture of diastereomers of meso (94%) and *dl* (6%).

The identical procedure starting with isomer *dl*-24 gave the following 3,4-dimethyl-2,5-hexanedione diastereomer distribution: meso (12%), *dl* (88%). This establishes the major Cope isomer from pyrolysis of 18 to be *dl*-19.

Kinetic Resolution of 3,4-Dimethyl-2,5-hexanedione (27). The α-pinene/diborane complex was prepared from α-pinene (1.5 g, 11 mmol), NaBH$_4$ (0.175 g, 4.6 mmol), and boron trifluoride etherate (0.79 g, 5.57 mmol) in diglyme (5 ml) according to the procedure of Brown and Zweifel.[12a] To a stirred suspension of the complex at 0 °C was added a chilled solution of 27 (mixture of diastereomers, 2.34 g, 16.5 mmol) in diglyme (3 ml) over 5 min. Stirring was maintained for 1.5 h. Pentane (15 ml) and water (50 ml) were cautiously added and the layers separated. The aqueous phase was extracted with pentane (twice) and the combined organic layers washed with brine and dried over Na$_2$SO$_4$. Solvent was removed and the residue distilled (95 °C (2 mmHg)). The individual diastereomers were isolated by preparative VPC (column A). The first eluting diastereomer exhibited a specific rotation of $[\alpha]_{365}^{20}$ +2.51° and was shown to be pure by VPC on several columns and by NMR. The later eluting diastereomer also exhibited optical activity, but was shown by VPC and NMR to contain a significant amount of an unidentified impurity. The sample was repurified by preparative VPC (Column B) and shown to be racemic. All of the observed optical activity was found to reside in the impurity.

References and Notes

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(2) Estimated using standard group equivalent values and a cyclopropene strain energy of 54 kcal/mol; cf. S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
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(8) From the experimental data given, it is not clear whether 12 is in fact an intermediate on the major pathway or merely a side reaction product.
(9) The authors did not correlate this proposed diradical intermediate with their previous observations of Dewar benzene formation.[3]
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(14) (a) The following phases were tried: 1,2,3-tris(2-cyanoethoxy)propane (TCEP); β,β-oxydipropionitrilephenyl acetonitrile, Carbowax 20M, diethylene glycol succinate; (b) TCEP.
(15) The bicyclopropenyls are relatively sensitive compounds, and care must be taken to ensure that one is observing reproducible, gas-phase reactions. In order to eliminate surface-catalyzed reactions, we employed a reaction flask constructed of lead–potash glass,[15a] and conditioned it by pyrolyzing samples of 18 for extended periods of time. Furthermore, pyrolyses of *meso*- and *dl*-19 were carried out repetitively to ensure that we were obtaining reproducible product formation data, and pyrolyses at different total pressures (30–400 mm using both N$_2$ and pentane as inert diluent gas) showed that the data were pressure independent; (a) W. von E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973).
(16) Developed by D. L. Bunker and F. Houle, University of California, Irvine, Calif., and available from the Quantum Chemistry Program Exchange (Program No. 293). This is an interactive program which operates in a different way from the conventional (e.g., Runge–Kutta) numerical integration methods. A limited but adequate number of molecules of the various species involved in the reaction is selected and used to typify the course of events in the much larger system that contains it. Each reaction in the mechanism is assigned a probability based on the rate constant associated with it, and one reaction event at a time is selected randomly, on the basis of these correctly weighted probabilities. After every selection of a reaction, the numbers of the species involved are updated as well as the time.
 In modeling the bicyclopropenyl rearrangement kinetics, rate constants used in the initial trial were estimated from the beginning slopes of concentration vs. time plots. Reaction path degeneracy is included in each rate constant; i.e., rate constants are defined for overall conversion of one compound to another, regardless of mechanism, with no assumptions made as to how many independent paths might exist for a given process. When a good visual fit of the model to concentration vs. time plots was obtained, the rate constants were varied separately (and also in compensating directions) to get an estimate of how sensitive the model was to changes in these values. The error limits recorded represent maximum errors estimated using this procedure.
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