endoperoxides, we intend to clarify whether these processes are not only controlled by simple selection rules, but also by other factors.

6. Summary. In Figure 3 the results of the photolysis and thermolysis[5] of PO, as well as the photooxidation[4] of HCD, are compiled in one diagram. Here the reaction paths of the photoreversible and photochromic system

$$HCD + O_2 \underset{UV/\Delta}{\overset{vis}{\rightleftharpoons}} PO$$

are reported. The construction of this scheme thereby follows the state correlation diagram envisaged by Kearns and Khan.[17-19] The state diagrams of PO and the pair, HCD-O_2, are depicted on a linear scale on the left- and right-hand sides of Figure 3, respectively. The observed reactions are characterized by continuous arrows. Initial and product states are connected by full lines. The enthalpies of activation of thermolysis and of photooxidation, $\Delta H_T^{\ddagger}$ and $\Delta H_P^{\ddagger}$, are given, as well as the difference in enthalpies between HCD and PO, ΔH_0. The wavelike arrows represent radiationless deactivation processes and the dashed arrow the absorption process.

Acknowledgment. The financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes

(1) H.-D. Brauer, W. Drews, and R. Schmidt, *J. Photochem.*, **12**, 293 (1980).
(2) C. Dufraisse and M.-T. Mellier, *C. R. Acad. Sci.*, **215**, 541 (1942).
(3) H. Wagener and H.-D. Brauer, *Mol. Photochem.*, **7**, 441 (1976).
(4) W. Drews, R. Schmidt, and H.-D. Brauer, *J. Photochem.*, **6**, 391 (1977).
(5) W. Drews, R. Schmidt, and H.-D. Brauer, to be published.
(6) R. Scholl, H. K. Meyer, and W. Winkler, *Justus Liebigs Ann. Chem.*, **494**, 201 (1932).
(7) H.-C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebigs Ann. Chem.*, 1984 (1973).
(8) R. Schmidt, H. Kelm, and H.-D. Brauer, *J. Photochem.*, **11**, 145 (1979).
(9) Y. Takezaki, T. Miyazaki, and N. Nakahara, *J. Chem. Phys.*, **25**, 536 (1956).
(10) T. Kobayashi and S. Nagakura, *Chem. Phys. Lett.*, **43**, 429 (1976).
(11) D. E. Damschen, C. D. Merrit, D. L. Perry, G. W. Scott, and L. D. Talley, *J. Phys. Chem.*, **82**, 2268 (1978).
(12) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972).
(13) W. Adam, C.-C. Cheng, O. Cueto, K. Sabanishi, and K. Zinner, *J. Am. Chem. Soc.*, **101**, 1324 (1979).
(14) R. Schmidt, H.-D. Brauer, and H. Kelm, *J. Photochem.*, **8**, 217 (1978).
(15) R. Schmidt, H. Kelm, and H.-D. Brauer, *Z. Phys. Chem. (Frankfurt am Main), Teil I*, **113**, 37 (1978).
(16) R. Schmidt, H.-C. Steinmetzer, H.-D. Brauer, and H. Kelm, *J. Am. Chem. Soc.*, **98**, 8181 (1976).
(17) D. R. Kearns, *J. Am. Chem. Soc.*, **91**, 6554 (1969).
(18) D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, **10**, 193 (1969).
(19) A. U. Khan, *J. Phys. Chem.*, **80**, 2219 (1976).
(20) W. Adam, *Angew. Chem.*, **86**, 683 (1974).
(21) J. Rigaudy, C. Brelière, and P. Scribe, *Tetrahedron Lett.*, 687 (1978).
(22) P. B. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 120 (1971).
(23) H. H. Wassermann, J. R. Scheffer, and L. Cooper, *J. Am. Chem. Soc.*, **94**, 4991 (1972).
(24) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).
(25) B. Stevens, J. A. Ors, and M. L. Pinsky, *Chem. Phys. Lett.*, **27**, 157 (1974).
(26) J. R. Huber and M. Mahaney, *Chem. Phys. Lett.*, **30**, 410 (1975).
(27) M. Mahaney and J. R. Huber, *Chem. Phys.*, **9**, 371 (1975).
(28) N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, **78**, 125 (1978).
(29) R. W. Anderson Jr. and R. M. Hochstrasser, *Chem. Phys. Lett.*, **43**, 224 (1976).
(30) N. J. Turro, M.-F. Chow, and J. Rigaudy, *J. Am. Chem. Soc.*, **101**, 1300 (1979).
(31) N. J. Turro and M.-F. Chow, *J. Am. Chem. Soc.*, **101**, 3701 (1979).
(32) A. P. Schaap in "Singlet Molecular Oxygen", Benchmark Papers in Organic Chemistry, Vol. 5, Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1976, p 230.
(33) J. Rigaudy, A. Defoin, and J. Baranne-Lafont, *Angew. Chem.*, **91**, 443 (1979).

Thermal Isomerization of Allyl-Substituted Cyclopropenes. An Example of a Nonsynchronous Cope Rearrangement

Albert Padwa* and Thomas J. Blacklock

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322. *Received August 13, 1979*

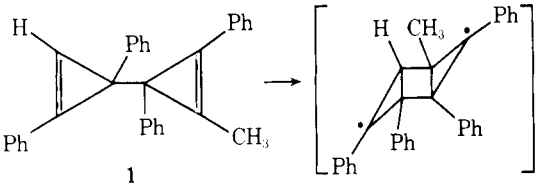
Abstract: The thermal Cope rearrangement of a number of allyl-substituted cyclopropenes has been studied in mechanistic detail. Thermolysis of 1,2-diphenyl-3-allyl-3-methylcyclopropene produced an equilibrium mixture of recovered starting material (35%), 1,3-diphenyl-2-methyl-3-allylcyclopropene (13%), and 1,2-diphenyl-6-methyltricyclo[2.2.0.$0^{2,6}$]hexane (52%). The rates and corresponding Arrhenius parameters were determined and compared to model systems. The thermal chemistry of the closely related 3-(1-methylallyl)-substituted diphenylcyclopropene system was also studied in order to determine the preferred transition-state geometry for the rearrangement. The data obtained indicates that these systems proceed through a four-center, chair-like conformation. The thermal [2 + 2]-cycloaddition reactions to produce the tricyclohexane skeleton proceed with total inversion of stereochemistry about the olefinic π system. The reaction was shown to proceed via initial formation of a biradical intermediate in a conformation which is analogous to the conformation of cyclohexane. Ring inversion of the initially formed chair intermediate generates a boat diradical which undergoes subsequent coupling. The ring flip of the initially formed chair intermediate to the boat diradical is the major factor responsible for the overall inversion of stereochemistry. The results obtained indicate that the Cope rearrangement of the allyl-substituted cyclopropene system is not a true pericyclic process but rather involves the formation of an intermediate analogous to the 1,4-cyclohexylene biradical.

The Cope rearrangement of hexa-1,5-dienes[1] has been commonly regarded as a typical example of an orbital symmetry controlled sigmatropic reaction.[2,3] As a result of the elegant stereochemical labeling studies of Doering and Roth[4] and Hill,[5] the lowest energy Cope process has been accepted as that involving a chair transition state. It is, however, possible for the reaction to take place via the alternative boat conformation,[4,6] especially if the rearrangement is facilitated by relief of ring strain.[7-10] Despite intensive work,[11] the mechanism of the [3,3]-sigmatropic shift of 1,5-hexadienes remains unclear. Mechanistic considerations of the Cope rearrangement include (1) cleavage of the diene into two allyl radicals followed by

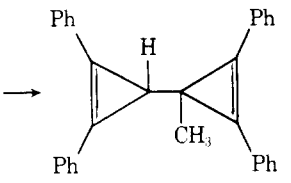
0002-7863/80/1502-2797$01.00/0

subsequent recombination and (2) passage through a single transition state with partial bonding between C_1–C_6 and C_3–C_4 of the diene skeleton. More recently, Doering[12] and Dewar[13,14] have drawn attention to the possibility of a third mechanism, in which formation of the new C–C bond precedes rupture of the old one, so that the reaction involves a biradical intermediate. This possibility[12,15] is supported both theoretically by MINDO calculations[14,16] and McIver's rules[17] and experimentally by a constant multiplicative rate increase upon 2-phenyl and 2,5-diphenyl substitution.[13] At the current time the mainstream view is that the Cope reaction of hexa-1,5-diene proceeds via a single transition state.[18,19] Substituents at the various positions of the diene, however, can alter the geometry of the transition state. Thus, the presence of radical stabilizing groups on C_3 and C_4 as well as on C_2 and C_5 of the diene system accelerates the rate of the 3,3 shift.[13,20] In the former case the rate response suggests that the transition state resembles more two allyl radicals, while in the latter case it resembles more cyclohexane-1,4-diyl. Indeed, these two extremes represent, to a first approximation, the range of transition-state structures available to the 3,3-sigmatropic shift.[20]

During the course of our studies dealing with the chemistry of cyclopropene derivatives,[21] we found that the thermolysis of allyl-substituted cyclopropenes results in a novel Cope rearrangement.[22] Since there are very few reports of Cope rearrangements involving cyclopropene moieties, we decided to investigate this reaction in greater detail. The first example of a 3,3-sigmatropic shift involving a cyclopropene ring was described in 1975 by Weiss and Kölbl.[23] These authors postulated that the Cope rearrangement of bicyclopropenyl **1** to **3** was a two-step process proceeding through an *anti*-1,4-tri-

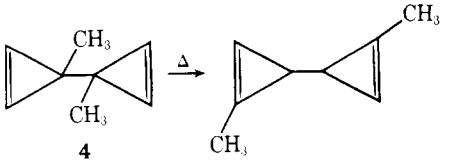


1 **2**



3

cyclohexylene diradical (**2**). This pathway was claimed to be favorable on the basis of an estimate by the authors that **2** has 25 kcal mol^{-1} less strain energy than the pericyclic transition state. The Cope rearrangement of 3,3′-dimethyl-3,3′-bicyclopropenyl (**4**) was also investigated by two other research groups.[24,25]

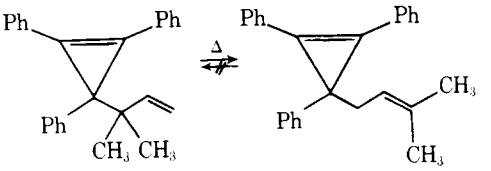


4 **5**

We have found the results of our work dealing with the 3,3-sigmatropic rearrangement of allyl-substituted cyclopropenes to be quite pertinent to the general question of the mechanism of the Cope rearrangement. The data obtained indicates that the Cope rearrangement of this system does not proceed via a pericyclic process but rather involves the formation of an intermediate analogous to the 1,4-cyclohexylene biradical. In this paper we present some arguments in favor of this pathway.

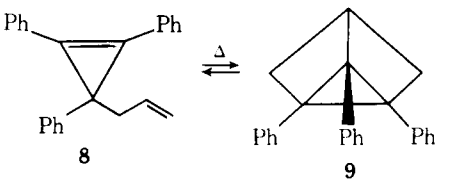
Results

We initially examined the thermal chemistry of 3-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**6**).[26,27] Thermolysis of **6** in benzene–pyridine at 175 °C for 8 h afforded 2-methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**7**) in 93% isolated yield. In this case the reaction was irreversible, since extended heating of **7** did not produce any detectable quantities of **6**.



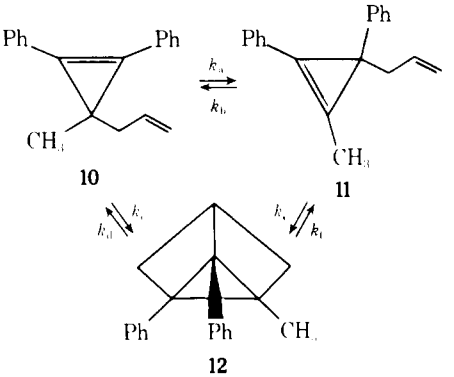
6 **7**

The thermal chemistry of cyclopropene **8** was also investigated since the 3,3-sigmatropic shift of this system leads to recovered starting material. When heated at 175 °C for 18h, **8** was partially converted into 1,2,6-triphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**9**). The same equilibrium distribution (i.e., **8**:**9** = 9/1) was obtained by heating tricyclohexane **9** at 175 °C.



8 **9**

Rate Studies. In order to help elucidate the mechanism involved in the thermal reorganization of the allyl-substituted cyclopropene system, a study of the rate of the reaction was undertaken. Thermolysis of 1,2-diphenyl-3-allyl-3-methylcyclopropene (**10**) at 150 °C for 48 h produced an equilibrium mixture of recovered starting material (35%), 1,3-diphenyl-2-methyl-3-allylcyclopropene (**11**, 13%), and 1,2-diphenyl-6-methyltricyclo[2.2.0.$0^{2,6}$]hexane (**12**, 52%). The same distribution of products was obtained by heating either **11** or **12** at 150 °C for 48 h. As a result of the reversibility of the reactions, the pyrolyses do not follow first-order kinetics, but the kinetic scheme can be solved numerically. Early points in the kinetic runs provide approximate values of the rate constants. Numerical integration of the differential kinetic equations (six rate constants) using these trial values then generates a set of reactant and product concentrations as functions of time. This is effected using a computer program SCKIN to select rate constants for the best least-squares fit of the experimental data for simultaneous and consecutive first-order reactions involving up to six species. The approximate rate constants are adjusted until a satisfactory fit to the experimental data is obtained. The rates and the corresponding Arrhenius parameters, which were



10 **11**

12

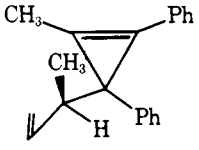
Table I. Rearrangement of Diphenylmethylallylcyclopropenes **10** and **11**

process	first-order rate constant, $s^{-1} \times 10^5$, at (°C) 140	150	160	Arrhenius parameters[a-c] E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol[d]	$\Delta G^{\ddagger}$, kcal/mol[e]	$\Delta S^{\ddagger}$, eu
k_a	0.59	1.64	3.7	32.8 ± 1.7	32.0 ± 1.7	34.5 ± 1.7	−5.86 ± 4.1
k_c	0.32	0.84	1.68	29.8 ± 2.3	29.0 ± 2.3	35.0 ± 2.3	−14.10 ± 5.5
k_b	1.85	5.25	11.2	31.9 ± 2.5	31.2 ± 2.5	33.5 ± 2.5	−5.40 ± 5.9
k_e	0.69	2.29	5.13	35.8 ± 3.5	35.0 ± 3.5	33.9 ± 3.5	+2.60 ± 8.3
k_d	0.17	0.56	1.27	35.5 ± 3.0	34.7 ± 3.0	35.2 ± 3.0	−1.28 ± 7.2
k_f	0.12	0.48	1.28	42.4 ± 3.5	41.6 ± 3.5	35.5 ± 3.5	+14.3 ± 8.2

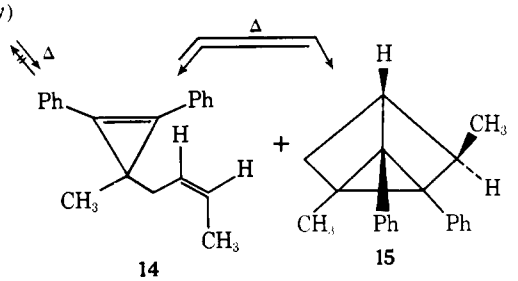
[a] Arrhenius parameters were determined by plotting log k vs. $1/T$; the slope of the line = $-E_a/2.303R$. [b] $\Delta S^{\ddagger} = 4.576(\log A - 13.23)$ at 25 °C. [c] All values calculated at 25 °C. [d] $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. [e] $\Delta H^{\ddagger} = E_a - RT$.

determined over a 20 °C temperature range (see Table I), are comparable to those determined for the Cope rearrangement of 2-phenyl-3,3-dideuterio-1,5-hexadiene[13] ($k_{150°C} = 4.02 \times 10^{-5}\ s^{-1}$; $E_a = 30.2 \pm 1.6$ kcal/mol). It is interesting to note that the rate of rearrangement of **11** → **10** (k_b) is approximately three times faster than the reverse process **10** → **11** (k_a). This is probably due to the restoration of conjugation between the phenyl substituents. This added conjugation could also account for the fact that **11** cyclizes to tricyclohexane **12** at a faster rate than does **10** (i.e., $k_e \sim 2.5k_c$). Also noteworthy is the fact that the rate of the Cope reaction (i.e., **10** ⇆ **11**) is significantly faster than cycloreversion of tricyclohexane **12** to cyclopropenes **10** or **11**. The fact that the highly rigid tricyclohexane structure is the major component in the thermal equilibrium deserves some comment. It would seem as though the strain energy present in the tricyclohexane skeleton is less than that present in the cyclopropene ring.[28]

Stereochemical Aspects. The thermal chemistry of the 3-(1-methylallyl)-substituted diphenylcyclopropene system **13** was also studied in order to determine the preferred transition-state geometry for the rearrangement. The synthetic route used to prepare cyclopropene **13** resulted in an inseparable 1:1 mixture of diastereomers. One of the diastereomers (**13a**) was found to undergo the Cope rearrangement at a slightly faster rate (i.e., twofold) than the other. By carrying out the reaction of the 1:1 mixture of diastereomers to ca. 80% conversion, it was possible to obtain a pure sample of the slower reacting diastereomer (**13b**) after column chromatography. Thermolysis of this diastereomer (**13b**) at 130 °C for 36 h afforded a mixture of (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**14**, 50%) and *exo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**15**, 50%).[29] Heating a pure sample



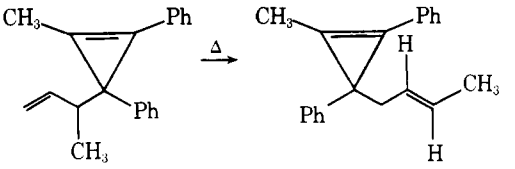
13b (slow)



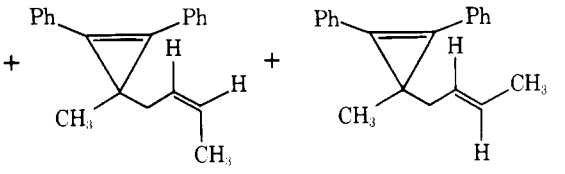
14 **15**

of cyclopropene **14** at 190 °C for 48 h resulted in an equilibrium mixture of recovered starting material (55%) and *exo*-3,6-dimethyl-1,2-diphenyltricyclohexane **15** (45%). The same distribution of products was obtained by heating tricyclohexane **15** at 190 °C for 48 h. Prolonged heating of the equilibrium mixture did not regenerate cyclopropene **13**.

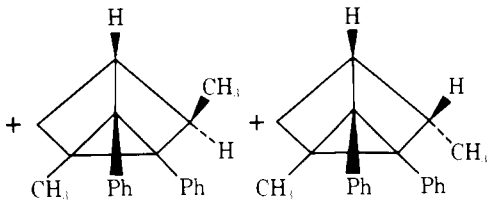
When the thermolysis of the 1:1 diastereomeric mixture of **13** was carried out to low conversions (ca. 25%), a mixture of **16** (2%), **14** (5%), **15** (4%), **17** (10%), and **18** (1%) was obtained. The distribution of the 1,2-diphenyl substituted *E* (**17**) and *Z* (**14**) isomers formed in this experiment (ratio **17**/**14** = 2/1) corresponds exactly to the ratio of reacted starting material (i.e., **13a**/**13b** = 2/1), thereby establishing the complete stereospecificity of the reaction. The structures of **14** and **17**



13 **16**

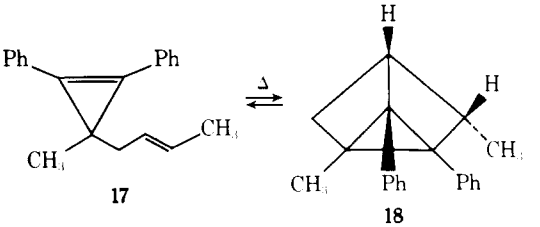


14 **17**



15 **18**

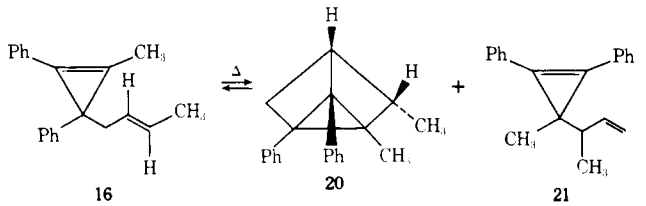
were verified by comparison with independently synthesized samples. Cyclopropene **17** did not undergo a reverse Cope rearrangement on heating. Instead, the thermolysis of this compound resulted in an equilibrium mixture of recovered starting material and *endo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**18**, 20%). Appropriate control experiments established that no cis-trans isomerization of either the starting materials (i.e., **14** ≠ **17**) or the products (i.e., **15** ≠ **18**) was operative under the reaction conditions.



17 **18**

The striking feature of these results is that the intramolecular [2 + 2] cycloaddition reaction of these allyl-substituted cyclopropenes proceeds with total inversion of stereochemistry about the olefinic π bond. In order to provide additional documentation for the stereochemical course of the cycloaddition reaction, the thermal chemistry of the closely related (*E*)-(**16**)

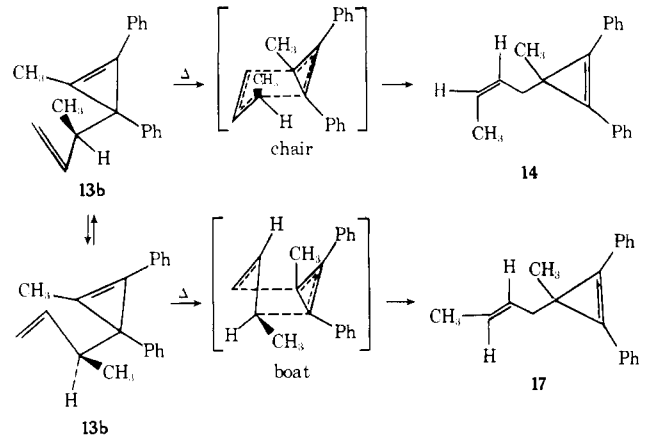
and (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butenes (**19**) was studied. Thermolysis of cyclopropene **16** at 175 °C for 12 h afforded a mixture of *endo*-tricyclohexane **20** and cyclopropene **21** (ratio **20**/**21** = 2:1). Subjection of **19** to

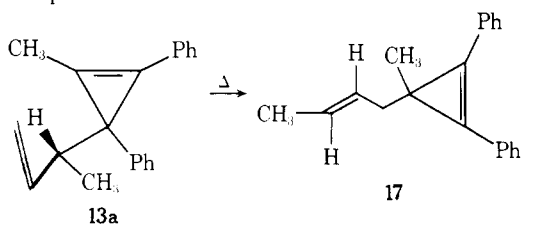


similar thermolysis conditions produced a mixture of *exo*-tricyclohexane **22** and cyclopropene **21** (ratio **22**/**21** = 1.5:1). The thermolysis of these two cyclopropenes was only carried out to ca. 30% conversion since further heating resulted in the subsequent reorganization of cyclopropene **21.** A control experiment showed that cyclopropenes **14** and **17** and tricyclohexanes **20** and **22** were not interconverted under the thermal conditions employed. Finally, when *endo*-tricyclohexane **20** was heated at 175 °C for 20 h, a mixture of cyclopropenes **21** (8%) and **16** (25%) was formed. Subjection of *exo*-tricyclohexane **22** to similar reaction conditions gave cyclopropene **21** (5%) and **19** (6%) in addition to unreacted starting material.

Discussion

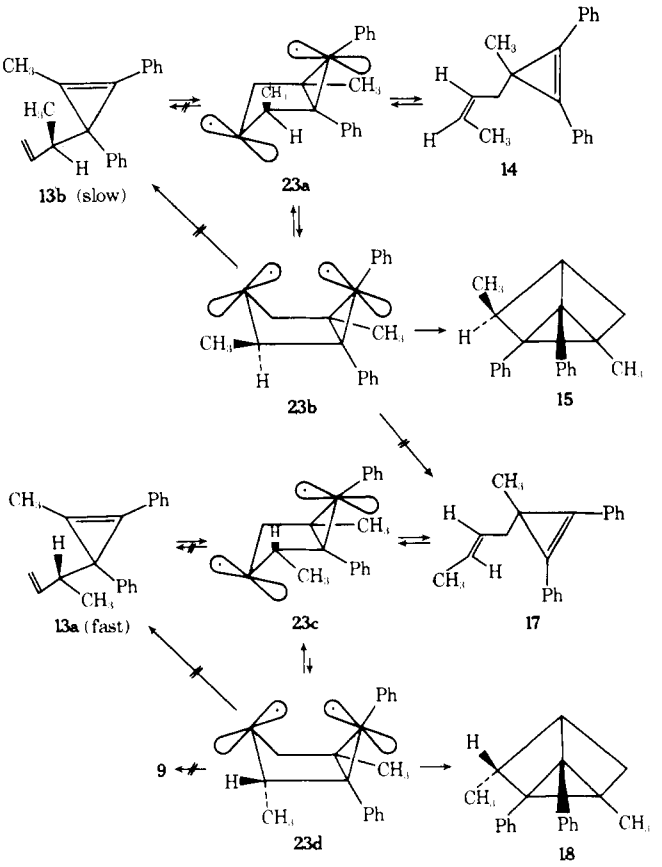
The single-stage concerted path for the Cope rearrangement should proceed suprafacially (or antarafacially) on both allylic moieties according to the orbital symmetry conversion principle.[30] Although the rate of the chair-like, four-center Cope rearrangement of acyclic biallyls is faster than that of the boat-like, six-center one by a factor of more than 300, there are several cases in the literature in which the order of preference is qualitatively reversed.[6-10] The two different transition states which are available for the Cope rearrangement of allyl-substituted cyclopropene **22b** are shown below. Goldstein[31] and Gajewski[32] have suggested that the Cope rearrangement in acyclic systems might be proceeding through other transition states (e.g., twist or plane). With the allyl-substituted cyclopropenes, however, the rigidity of the system prevents rearrangement through many of the conformations which might be available in more flexible acyclic systems. The virtually exclusive formation of **14** from **13b** confirms the preference for the chair conformation and places an upper limit of 1-2% on the contribution of the boat conformation. Rearrangement of diastereomer **13a** to the *E*-substituted isomer **17** also requires a four-center transition state.





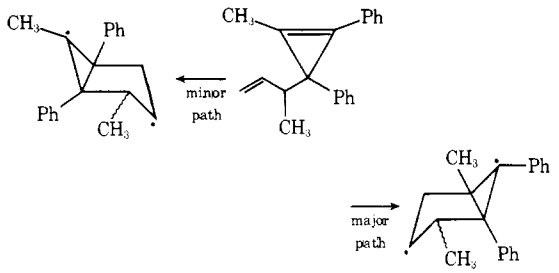
The most significant finding here is that the Cope rearrangement of **13a** and **13b** proceeds through the four-center, chair-like conformation under conditions where a substantial amount of tricyclohexane is *being formed simultaneously*. The formation of tricyclohexane **15** from cyclopropene **14** occurs at a much slower rate than the formation of **15** from **13b,** thereby eliminating the sequential process **13b** → **14** → **15.** Similarly, the conversion of **17** to **18** proceeds at a much slower rate than the formation of **18** from **13a.** *These observations indicate that the tricyclic products are not formed by a separate path but rather are produced in competition with the Cope products.* A mechanism which accounts for the stereochemical results and which is consonant with all of the available data is outlined in Scheme I. This process involves the initial formation of a biradical intermediate in a conformation (e.g., **23a** or **23c**) which is analogous to the chair conformation of cyclohexane. Subsequent fragmentation of this species affords the Cope rearrangement product. Ring inversion of the initially formed chair intermediate generates the boat biradical (e.g., **23b** and **23d**), which cyclizes to the tricyclo[2.2.0.$0^{2,6}$]-hexane ring system at a faster rate than bond fragmentation. This contention is substantiated by the fact that cyclopropenes **14** and **17** are not isomerized under conditions where substantial quantities of tricyclohexanes **15** and **18** are formed.

Scheme I



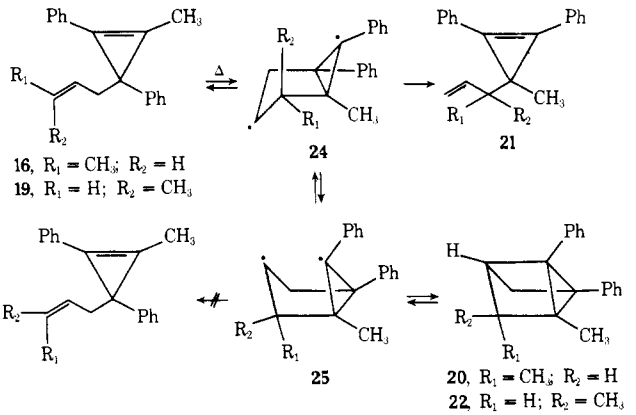
It should be noted that bond fragmentation from the boat diradical (i.e., **23b** or **23d**) does not occur here. Such a fragmentation would have resulted in the formation of a mixture of isomeric cyclopropenes from the thermolysis of tricyclohexanes **15** or **18**, a process which clearly does not occur. This result indicates that the boat cyclohexa-1,4-diyl recyclizes or ring flips more rapidly than it undergoes the ring-opening reaction.

It is important to note that the thermolysis of diastereomer **13b** results in a significantly larger quantity of the tricyclohexane ring system (i.e., **15**, 50%) than is obtained from the thermolysis of **13a** (i.e., **18**, 8%). This can be attributed to the fact that the initially formed biradical intermediate **23a** (axial methyl) undergoes ring inversion to **23b** (equatorial methyl) at a rate which is competitive with bond fragmentation. Thus, **13b** reacts about equally from each of the conformers **23a** and **23b**. However, **13a** gives mainly cyclopropene **17**, a result indicating preferential reaction from conformer **23c** (equatorial methyl). The difference in product distribution is undoubtedly related to the lack of a significant driving force for the ring-flipping process. The diradical initially formed from **13a** (i.e., **23c**) already has the methyl group located in the equatorial position. It should also be pointed out that in the case of cyclopropene **13** there is a distinct preference for that product arising from bonding between the terminal olefinic carbon and the cyclopropene carbon bearing the methyl group. This is undoubtedly related to the fact that π–π bridging will give the most stable biradical and thus lead to the preferential formation of cyclopropenes **14** and **17** rather than to cyclopropene **16**.



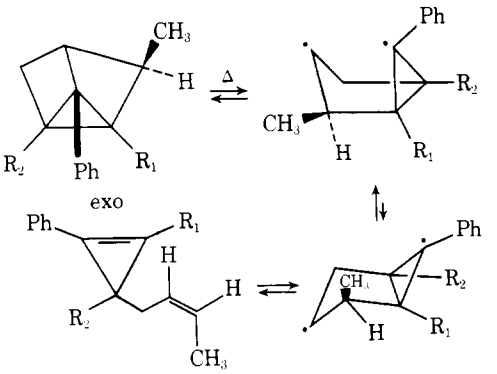
Another striking feature of these results is that the intramolecular thermal cycloadditon reaction of cyclopropenes **16, 19, 14,** and **17** proceeds with total inversion of stereochemistry about the olefinic π bond. The cycloaddition of two olefins and its reverse, cycloreversion or the cleavage of cyclobutane, have been the object of extensive theoretical[33-36] and experimental studies in recent years.[37-42] Thermal [2 + 2]-cycloaddition reactions of olefins can be symmetry allowed and therefore concerted if the $[_{\pi}2_s + {}_{\pi}2_a]$ combination mode is followed. No authenticated examples of this phenomenon have been reported to date with simple π systems.[43-49] Presumably this is because steric hindrance and angle strain factors generally develop to rather prohibitive levels as the two π bonds attempt to attain the requisite orthogonality. Related studies dealing with the pyrolysis of stereochemically labeled alkylcyclobutanes have disclosed that antarafacial motion by at least one of the developing olefinic moieties is not readily achieved.[50-52] As a result, little stereoselectivity has been observed. Thus our finding that the intramolecular [2 + 2] cycloaddition of the allyl-substituted cyclopropene system proceeds with total inversion of stereochemistry is of considerable interest. The mechanism outlined in Scheme I nicely rationalizes the stereochemical results. The ring flip of the initially formed chair intermediate **24** to the boat diradical **25** is the major factor responsible for the overall inversion of stereochemistry in the thermal cycloaddition.

It is also of interest to note that the thermolyses of **16** and **19** produce both the tricyclohexane ring and the Cope-rearranged product **21**. Cyclopropenes **14** and **17**, on the other hand, give only [2 + 2] cycloadducts. This difference in behavior is probably a consequence of the restoration of conjugation between the phenyl substituents which can take place with **16** and **19** but not with **14** and **17**. The distribution of the cyclopropenes produced in the thermal equilibration studies depends on two factors, namely, the location of the double bond in the cyclopropene ring and the degree of substitution about the olefinic π bond. For example, thermolysis of tricyclohexane **20** produces a 1:3 mixture of cyclopropenes **21** and **16**. Additionally, the major products formed in the thermolysis of **21** consist of cyclopropenes **16** and **19**. The energetic advantage of having the double bond in the cyclopropene ring between the two phenyl substituents is apparently not as important as the degree of substitution about the olefinic π bond. This explanation nicely accounts for the direction of the equilibrium with cyclopropene **6**. In all of the cases studied, the isomer with the di- or trisubstituted double bond is always the major or exclusive product formed. When the substituent side chain consists of a simple allyl group, the 1,2-diphenyl substituted isomer is the major cyclopropene produced. This can be attributed to the greater thermodynamic stability of the 1,2-diphenyl conjugated isomer.



The transition state for the Cope rearrangement is a variable entity, with a six-membered ring nearly dissociated into two allyl radicals at one extreme and almost fully converted to a 1,4-cyclohexadiyl diradical at the other. The 3,3-sigmatropic shift of 2-phenyl-1,5-hexadiene has been reported to have an activation energy (E_a) of 30.2 ± 1.6 kcal/mol[13] and has been proposed by Dewar to proceed via a 1,4-cyclohexylene diradical.[13] Marvell and Li,[18] on the other hand, have suggested that the Cope rearrangement of this system proceeds by a concerted single transition state which possesses significant diradical character. Rearrangement of the allylmethyldiphenyl-substituted cyclopropene system (i.e., **10** or **11**) was found to require a E_a of 32 ± 2 kcal/mol, which is essentially identical with that found with 2-phenyl-1,5-hexadiene.[13] The transition states for both of these reactions are probably very similar in structure.

An additional point worth mentioning relates to the rate of



the cycloreversion reaction of the *exo*- and *endo*-methyl substituted tricyclohexanes. The results obtained indicate that the endo-substituted isomers (i.e., **20** and **18**) react much faster than the corresponding exo isomers (**22** and **15**). Formation of the cyclopropene ring involves initial central bond rupture to a boat diradical which ring flips into the chair form. The subsequent cleavage proceeds only through the chair diradical, as even the MINDO calculations suggest.[16] The slower rate of reaction of the exo isomer is presumably related to an unfavorable "envelope flip" which places the methyl group in a higher energy axial position in the chair diradical. Thus, the initially generated diradical obtained from the thermolysis of the *exo*-tricyclohexane system prefers to re-form the transannular bond rather than undergo interconversion to the chair form.

Finally, the facility with which these systems undergo internal cycloaddition relative to other 1,5-dienes merits some comment. The thermal [2 + 2] cycloaddition of untwisted ethylenes to form cyclobutanes is a rare phenomenon.[53-58] The formation of the tricyclo[2.2.0.0^{2,6}]hexane ring system from the thermolysis of allyl-substituted cyclopropenes is unique in that the other reported examples of thermal olefin cycloadditions either occur in compounds in which the double bond is subjected to severe torsional strain[59-64] or else involve reactants that bear substituents capable of stabilizing diradical or dipolar intermediates.[65-67] In cyclopropene, the torsional angle is close to zero and p-p overlap should not be significantly different from that of a normal olefin.[68] Thus the propensity of the cyclopropene ring to undergo internal cycloaddition is primarily due to relief of angle bending rather than torsional strain. Undoubtedly, the high degree of strain present in the cyclopropene ring (54 kcal/mol)[68] makes the tricyclo[2.2.0.0^{2,6}]-hexane skeleton thermodynamically more stable. The strain relieved in bond making results in a lower energy pathway for cycloaddition than bond breaking to an allyl and cyclopropenyl radical.

In conclusion, the results obtained with the above systems may be most simply interpreted on the basis of an unusually easy bond formation between the double bond and the cyclopropene ring to produce a diradical intermediate which collapses to the observed cycloadduct. The driving force for these reactions is undoubtedly associated with the considerable relief of bond-angle strain of the cyclopropene ring. The facility with which the internal cycloaddition occurs makes this type of approach particularly attractive for the synthesis of some unusual tricyclic compounds. Further studies on the scope of the internal [2 + 2]-cycloaddition reaction are in progress and will be reported in due course.

Experimental Section[69]

Preparation and Thermolysis of 3-Methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (6). To a stirred suspension containing 1 g of 1,2,3-triphenylcyclopropenylium perchlorate[26] in 50 mL of anhydrous tetrahydrofuran was added 50 mL of a 0.3 N solution of prenylmagnesium chloride in ether. The reaction mixture was stirred for 30 min and a saturated ammonium chloride solution was added. The reaction mixture was stirred until both phases became clear. The organic layer was then taken up in ether, washed twice with equal volumes of water and with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure produced 0.845 g (92%) of a white, crystalline solid which was identified as 3-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**6**) on the basis of its spectral properties: IR (KBr) 3.30, 3.40, 3.47, 5.55, 6.24, 6.72, 6.93, 7.10, 7.28, 9.03, 9.31, 9.73, 9.90, 10.40, 10.81, 10.96, 12.40, 12.80, 13.27, 13.86, 14.30, and 14.58 μ; NMR ($CDCl_3$, 100 MHz) δ 1.8 (s, 3 H), 4.96 (d, 1 H, J = 16.0 Hz), 4.99 (d, 1 H, J = 6.0 Hz), 6.24 (dd, 1 H, J = 6.0 and 16.0 Hz), and 7.0–7.9 (m, 15 H); UV (ethanol) 323 and 226 nm (ϵ 23 280 and 23 060); *m/e* 336 (M^+), 321, 268, and 267 (base).

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.68; H, 7.22.

A solution containing 0.5 g of 3-methyl-3-(1,2,3-triphenyl-2-cyclopropen-1-yl)-1-butene (**6**) in 5 mL of a 20% pyridine in benzene mixture was degassed and sealed in a glass ampule. The ampule was heated in a thermostated oil bath at 175 °C for 8 h. Removal of the solvent at reduced pressure produced a yellow oil which was taken up in hexane and passed through a 2 × 3 cm column of silica gel eluting with 200 mL of hexane. Removal of the solvent produced 0.42 g (93%) of a crystalline solid, mp 84–85 °C, whose structure was assigned as 2-methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-butene (**7**) on the basis of its spectral properties: IR (KBr) 3.25, 3.27, 3.33, 3.40, 5.47, 6.24, 6.68, 6.90, 7.22, 9.30, 9.69, 10.90, 13.17, and 14.55 μ; NMR ($CDCl_3$, 100 MHz) δ 1.48 (s, 3 H), 1.56 (s, 3 H), 3.01 (d, 2 H, J = 8.0 Hz), 5.24 (t, 1 H, J = 8.0 Hz), and 7.0–7.65 (m, 15 H); UV (absolute ethanol) 333, 318, and 228 nm (ϵ 21 780, 25 770, and 28 860); *m/e* 336 (M^+) and 267 (base).

Anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.72; H, 7.23.

Preparation and Thermolysis of 3-Allyl-1,2,3-triphenylcyclopropene (8). To a stirred suspension containing 5.0 g of triphenylcyclopropenylium perchlorate in 100 mL of anhydrous ether at 0 °C was added 37 mL of a 0.67 N solution of allylmagnesium bromide in ether. The reaction mixture was stirred for 1 h at 0 °C and then allowed to warm to room temperature. After the mixture was stirred for an additional 1 h, a saturated ammonium chloride solution was added and the reaction mixture was stirred until both phases became clear. The organic layer was then taken up in ether, washed twice with equal volumes of water and with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow semisolid which was chromatographed on a 1.5 × 60 cm column of silica gel using a 15% acetone–hexane mixture as the eluent. The only component isolated contained 3.9 g (93%) of a solid which was identified as 3-allyl-1,2,3-triphenylcyclopropene (**8**), mp 64–65 °C (methanol), on the basis of its spectral properties: IR (KBr) 3.49, 3.64, 5.67, 6.26, 6.43, 6.89, 7.02, 9.52, 10.10, 11.09, 13.34, and 14.64 μ; NMR ($CDCl_3$, 60 MHz) δ 3.10 (d, 2 H, J = 7.5 Hz), 4.96 (d, 1 H, J = 17 Hz), 5.05 (d, 1 H, J = 7.5 Hz), 5.50–6.20 (m, 1 H), and 7.0–7.8 (m, 15 H); UV (95% ethanol) 333, 316, and 228 nm (ϵ 21 980, 26 630, and 28 690); *m/e* 308 (M^+), 306, and 267 (base).

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.16; H, 6.66.

A mixture containing 650 mg of **8** in 5 mL of a 20% pyridine–benzene solution was heated at 175 °C for 18 h. The NMR spectrum of the crude reaction mixture indicated the presence of starting material (90%) and a new compound (10%). Further heating did not alter the composition of the mixture. Chromatography of the mixture on a 2 × 30 cm column of neutral alumina with a 20% benzene–hexane mixture gave recovered starting material (585 mg) and 65 mg (10%) of a crystalline solid, mp 103–104 °C, whose structure was assigned as 1,2,6-triphenyltricyclo[2.2.0.0^{2,6}]hexane (**9**) on the basis of its spectral properties: IR (KBr) 3.3, 3.4, 3.46, 3.52, 6.24, 6.70, 6.94, 7.23, 8.02, 9.65, 9.71, 12.71, 13.02, 13.51, and 14.35 μ; NMR ($CDCl_3$, 100 MHz) δ 2.49 (d, 2 H, J = 7.6 Hz), 2.80 (t, 1 H, J = 4.4 Hz), 3.02 (dd, 2 H, J = 7.64 and 4.4 Hz), and 6.5–7.30 (m, 10 H); UV (ethanol) end absorption 300 nm; *m/e* 308 (M^+), 307, 306, 267, 217 (base), 215, and 105.

Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.38; H, 6.60.

Thermolysis of a sample of tricyclohexane **9** at 175 °C for 14 h produced an equilibrium mixture consisting of 90% cyclopropene **8** and 10% tricyclohexane **9**.

Preparation and Thermolysis of 1,2-Diphenyl-3-methyl- (10) and 1,3-Diphenyl-2-methyl-3-allycyclopropene (11). To a stirred suspension containing 0.5 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 50 mL of anhydrous ether at −78 °C was added 10 mL of a 0.67 N allylmagnesium bromide solution in ether. The mixture was stirred for 4 h and allowed to warm to room temperature. A saturated ammonium chloride solution was then added and the mixture was stirred until both phases became clear. The organic layer was taken up in ether, washed twice with water and with a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting yellow oil was chromatographed on a 1.5 × 100 cm column of silica gel using hexane as the eluent. The first component isolated contained 0.23 g (55%) of a clear oil which was identified as 3-allyl-3-methyl-1,2-diphenylcyclopropene (**10**): IR (neat) 3.38, 3.47, 5.52, 6.08, 6.26, 6.70, 6.94, 7.31, 8.64, 9.33, 9.73, 10.95, 13.25, and 14.55 μ; NMR ($CDCl_3$, 100 MHz) δ 1.46 (s,

3 H), 2.56 (d, 2 H, J = 7.5 Hz), 4.95 (d, 1 H, J = 9.5 Hz), 4.99 (d, 1 H, J = 19 Hz), 5.68–6.16 (m, 1 H), and 7.08–7.76 (m, 10 H); UV (95% ethanol) 338, 320, and 229 nm (ϵ 21 380, 28 630, and 18 170); *m/e* 246 (M^+), 231, 206, 205 (base), and 77.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.59; H, 7.35.

The second fraction obtained from the column contained 0.13 g (31%) of a clear oil which was identified as 3-allyl-2-methyl-1,3-diphenylcyclopropene (**11**) on the basis of its spectral properties: IR (neat 3.27, 3.44, 5.39, 6.25, 6.69, 6.93, 9.33, 10.02, 10.94, 13.14, and 14.4 μ; NMR ($CDCl_3$, 100 MHz) δ 2.26 (s, 3 H), 2.90 (d, 2 H, J = 8.0 Hz), 4.90 (d, 1 H, J = 8.0 Hz), 5.01 (d, 1 H, J = 14 Hz), 5.56–6.04 (m, 1 H), and 6.84–7.52 (m, 10 H); UV (95% ethanol) 262 nm (ϵ 16 390); *m/e* 246 (M^+), 231, 205 (base), and 77.

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.55; H, 7.37

A solution containing 310 mg of **10** in 5 mL of a 20% pyridine-benzene mixture was heated at 150 °C for 15 h. Analysis of the crude reaction mixture by NMR spectroscopy indicated the existence of an equilibrium mixture of **10** (35%), **11** (13%), and 6-methyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**12,** 52%). The same equilibrium mixture was obtained from the thermolysis of cyclopropene **11** or tricyclohexane **12.** A pure sample of tricyclohexane **12** was obtained by thick layer chromatography using hexane as the eluent: IR (neat) 3.29, 3.42, 3.51, 6.24, 6.67, 6.92, 7.22, 10.10, and 14.30 μ; UV (95% ethanol) 240 nm (ϵ 10 800); *m/e* 246 (M^+), 231, 155, 154 (base), 115, 91, and 77; NMR ($CDCl_3$, 270 MHz) δ 1.33 (s, 3 H), 2.11 (d, 1 H, J = 8.0 Hz), 2.29 (d, 1 H, J = 8.0 Hz), 2.62 (dd, 1 H, J = 8.0 and 4.0 Hz), 2.77–2.85 (m, 2 H), 6.80–7.40 (m, 10 H). External irradiation of the doublet at δ 2.11 resulted in the collapse of the doublet of doublets at δ 2.62 into a doublet (J = 4.0 Hz). Irradiation of the doublet at δ 2.29 collapsed the multiplet at δ 2.77–2.85 into a doublet (J = 4.0 Hz) and a triplet (J = 4.0 Hz). Irradiation of the doublet of doublets at δ 2.62 collapsed the doublet at δ 2.11 into a singlet and the multiplet at δ 2.77–2.85 into a six-peak signal. Irradiation of the multiplet at δ 2.77–2.85 resulted in the collapse of the doublet at δ 2.29 into a singlet and the collapse of the doublet of doublets at δ 2.62 into a doublet (J = 8.0 Hz).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.60; H, 7.36.

Preparation and Thermolysis of 3-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butene (13). To a stirred suspension containing 2 g of 1-methyl-2,3-diphenylcyclopropenylium perchlorate in 50 mL of anhydrous tetrahydrofuran at −78 °C was added 30 mL of a 0.67 N crotylmagnesium bromide solution in ether. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. At the end of this time a saturated ammonium chloride solution was added and the mixture was stirred until both phases became clear. The organic layer was taken up in ether, washed twice with water and with a saturated salt solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a clear yellow oil which was chromatographed on a 1.5 × 100 cm column of silica gel using hexane as the eluent. The first fraction eluted contained 0.75 g (37%) of a colorless oil whose structure was assigned as 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**21**) on the basis of its spectral properties: IR (neat) 3.22, 3.36, 3.48, 5.54, 6.25, 6.69, 7.25, 9.30, 9.70, 10.00, 11.00, 13.10, and 14.40 μ; NMR ($CDCl_3$, 60 MHz) δ 0.90 (d, 3 H, J = 7.0 Hz), 1.40 (s, 3 H), 2.65 (p, 1 H, J = 7.0 Hz), 4.95 (dd, 1 H, J = 9.0 and 2.0 Hz), 5.00 (dd, 1 H, J = 16.0 and 2.0 Hz), 5.95 (ddd, 1 H, J = 16.0, 9.0, and 7.0 Hz), and 7.20–7.80 (m, 10 H); UV (95% ethanol) 338, 322, and 228 nm (ϵ 19 690, 27 040, and 17 930); *m/e* 260 (M^+), 245, 206, 206 (base), and 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.90.

The second fraction from the column contained a colorless oil (34%) which was shown by NMR spectroscopy to consist of a 1:1 mixture of diastereomeric 3-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-1-butenes (**13a** and **13b**): IR (neat) 3.46, 3.56, 5.56, 6.43, 6.88, 7.10, 9.46, 7.12, 13.13, 14.48, and 14146 μ; NMR ($CDCl_3$, 60 MHz) δ 0.94 (d, 3 H, J = 7.0 Hz), 0.97 (d, 3 H, J = 7.0 Hz), 2.30 (s, 6 H), 3.05–3.60 (m, 2 H), 4.70–5.20 (m, 4 H), 5.45–6.15 (m, 2 H), and 7.0–7.63 (m, 20 H); UV (95% ethanol) 267 nm (ϵ 15 650); *m/e* 260 (M^+), 246, 206, and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.30; H, 8.05.

A solution containing 600 mg of the 1:1 diastereomeric mixture of cyclopropenes **13a** and **13b** in 10 mL of a 20% pyridine-benzene solution was heated at 175 °C for 12 h. Analysis of the reaction mixture by NMR spectroscopy revealed the presence of four new compounds whose structures were eventually assigned as (*E*)- (**17,** 39%) and (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**14,** 26%) and *exo*- (**15,** 22%) and *endo*-3,6-dimethyl-1,2-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**18,** 8%). Removal of the solvent followed by chromatography of the mixture on a 10% silver nitrate–silica gel column with hexane as the eluent afforded pure samples of each component. The first fraction isolated from the column was a colorless oil whose structure was assigned as *exo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**15**) on the basis of its spectral data: IR (neat) 3.31, 3.34, 3.42, 3.46, 3.52, 6.24, 6.73, 6.95, 7.33, 13.50, 13.89, and 14.66 μ; UV (95% ethanol) 245 nm (ϵ 14 100); *m/e* 260 (M^+, base), 245, 115, 91, and 77; NMR ($CDCl_3$, 270 MHz) δ 1.25 (d, 3 H, J = 6.6 Hz), 1.26 (s, 3 H), 2.14 (d, 1 H, J = 8.1 Hz), 2.46 (d, 1 H, J = 4.4 Hz), 2.57 (dd, 1 H, J = 8.1 and 4.4 Hz), 2.62 (q, 1 H, J = 6.6 Hz), and 6.78–7.16 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.80.

The second component isolated from the column contained a colorless oil whose structure was assigned as *endo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexane (**18**) on the basis of its spectral properties: IR (neat) 3.31, 3.34, 3.42, 3.46, 3.52, 6.24, 6.73, 6.95, 7.33, 13.50, 13.89, and 14.66 μ; UV (95% ethanol) 246 nm (ϵ 14 200); *m/e* 260 (M^+, base), 245, 169, and 91; NMR ($CDCl_3$, 270 MHz) δ 0.91 (d, 3 H, J = 6.2 Hz), 1.28 (s, 3 H), 2.24 (d, 1 H, J = 7.4 Hz), 2.43 (dd, 1 H, J = 7.4 and 4.4 Hz), 2.80 (dd, 1 H, J = 6.2 and 4.4 Hz), 2.99 (dq, 1 H, J = 6.2 and 4.4 Hz), 6.69–7.20 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.82.

The third component isolated from the column was a clear oil whose structure was assigned as (*E*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**17**): IR (neat) 3.23, 3.27, 3.34, 3.40, 5.51, 6.24, 6.70, 6.91, 7.30, 9.30, 9.70, 10.30, 10.91, 13.29, and 14.5 μ; NMR ($CDCl_3$, 100 MHz) δ 1.40 (s, 3 H), 1.56 (d, 3 H, J = 4.0 Hz), 2.41 (d, 2 H, J = 5.5 Hz), 5.20–5.70 (m, 10 H); UV (95% ethanol) 338, 322, 237, and 229 nm (ϵ 19 800, 26 570, 13 410, and 17 420); *m/e* 260 (M^+), 245, 205 (base), 105, and 77.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H. 7.74. Found: C, 92.20; H, 7.77.

The fourth component isolated from the column consisted of a colorless oil whose structure was assigned as (*Z*)-1-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**14**): IR (neat) 3.23, 3.27, 3.34, 3.40, 5.51, 6.24, 6.70, 6.91, 7.30, 9.30, 9.70, 10.91, 12.23, and 14.50 μ; NMR ($CDCl_3$, 100 MHz) δ 1.44 (s, 3 H), 1.50 (d, 3 H, J = 4.5 Hz), 2.52 (d, 2 H, J = 5.5 Hz), 5.24–5.64 (m, 2 H), and 7.00–7.74 (m, 10 H); UV (95% ethanol) 338, 327, and 228 nm (ϵ 20 300, 27 170, and 17 600); *m/e* 260 (M^+), 245, 205 (base), 105, and 107.

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.03; H, 7.72.

Diastereomer **13a** was found to undergo the Cope rearrangement at a slightly faster rate (i.e., twofold) than diastereomer **13b.** By carrying out the reaction of the 1:1 mixture of diastereomers to 80% conversion, it was possible to obtain a pure sample of the slower reacting diastereomer **13b** after column chromatography. Thermolysis of this diastereomer (**13b**) at 130 °C for 36 h afforded cyclopropene **14** (50%) and tricyclohexane **15** (50%) as the only two products of reaction. When the thermolysis of the 1:1 diastereomeric mixture of **13** was carried out to 25%, a mixture of **16** (2%), **14** (5%), **15** (4%), **17** (10%), and **18** (4%) was isolated by column chromatography. The ratio was verified by analysis of the crude NMR spectrum.

Independent Synthesis of (*Z*)- (14) and (*E*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (17). The structures of the two Cope-rearranged products **14** and **17** obtained from the thermolysis of cyclopropenes **13a** and **13b** were verified by comparison with independently synthesized samples. To a solution containing 4.0 g of *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate in 200 mL of dry hexane at −78 °C was added 7.6 mL of 25% by weight solution of diisobutylaluminum hydride in toluene over a 30-min period. The reaction mixture was stirred for 1 h at −78 °C and quenched by the addition of 4-mL of methanol and 4 mL of water. The reaction mixture was allowed to warm to room temperature and filtered through diatomaceous earth to remove any aluminum salts. The reaction mixture was washed three times with equal volumes of water and with a saturated salt solution and dried over magnesium sulfate.

Removal of the solvent under reduced pressure left a thick, yellow oil which was chromatographed on a 1.5 × 100 cm column of silica gel using 5% acetone–hexane as the eluent. The first component isolated from the column contained 1.0 g (25%) of a clear oil which was identified as unreacted starting material. The second component obtained contained 1.8 g (55%) of 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetaldehyde as a clear oil whose structure was assigned on the basis of its spectral properties and subsequent chemical behavior: IR (neat) 3.30, 3.42, 3.50, 3.69, 5.51, 5.81, 6.24, 6.70, 6.94, 7.30, 9.30, 9.71, 10.9, 13.2, and 14.5 μ; NMR ($CDCl_3$, 100 MHz) δ 1.55 (s, 3 H), 2.84 (d, 2 H, J = 2 Hz), 7.1–7.6 (m, 10 H), and 9.85 (t, 1 H, J = 2 Hz). The aldehyde was used without further purification in the next step.

To a stirred suspension containing 7.5 g of ethyltriphenylphosphonium bromide in 50 mL of anhydrous tetrahydrofuran and 300 mL of anhydrous ether at 0 °C was added 18.3 mL of a 1.1 N phenyllithium solution in ether over a 10-min period. After the addition, the reaction mixture was stirred for 45 min and then cooled at −78 °C. To the above solution was added 4.0 g of 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetaldehyde in 10 mL of anhydrous ether. The reaction mixture was stirred for 3 h at −78 °C, allowed to warm to room temperature, and stirred overnight. Excess ylide was destroyed by the addition of a saturated ammonium chloride solution. The organic phase was separated, dried over magnesium sulfate, and concentrated under reduced pressure to a dark yellow oil. The oil was taken up in hexane and chromatographed through a 2.5 × 5.0 cm column of silica gel eluting with 200 mL of hexane. Removal of the solvent under reduced pressure afforded 3.35 g (80%) of a colorless oil which was shown by NMR spectroscopy to contain a mixture of E and Z olefins. A 1.0-g sample of the above oil was chromatographed on a 1.5 × 60 cm column of silica gel impregnated with silver nitrate (10% w/w) eluting with 10% ether in hexane. The first component eluted from the column contained 400 mg (40%) of a colorless oil which was identical in every respect with a sample of cyclopropene **17** isolated from the thermolysis of **13a.** The second component contained 580 mg (58%) of a colorless oil which was identified as cyclopropene **14** by comparison with a sample obtained from the thermolysis of **13b.**

Thermolysis of (*Z*)- (14) and (*E*)-1-(1-Methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-butene (17). A solution containing 100 mg of Z cyclopropene **14** in 0.5 mL of a 20% deuterated pyridine–benzene mixture was heated at 190 °C for 48 h. Analysis of the reaction mixture by NMR spectroscopy indicated the presence of recovered starting material (55%) and *exo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**15,** 45%). Chromatography of the reaction mixture on a thick layer plate afforded a pure sample of tricyclohexane **15.** The same equilibrium mixture was obtained by heating a sample of *exo*-tricyclohexane **15** at 190 °C for 48 h.

A solution containing 100 mg of the isomeric E cyclopropene **17** in 0.5 mL of a 20% deuterated pyridine–benzene mixture was heated at 190 °C for 48 h. Analysis of the reaction mixture by NMR spectroscopy indicated the presence of unreacted starting material (80%) and *endo*-3,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**18,** 20%). Chromatography of the reaction mixture on a thick layer plate afforded a pure sample of tricyclohexane **18.** The same equilibrium mixture was obtained by heating a sample of *endo*-tricyclohexane **18** at 190 °C for 48 h.

Preparation of (*E*)- (16) and (*Z*)-1-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (19). A solution containing 5 g of lithium *tert*-butyl acetate in 100 mL of anhydrous hexane was prepared according to the procedure of Rathke and Sullivan.[71] A 250-mL round-bottom flask charged with 90 mL of dry hexane and 17 mL of a 2.4 M solution of *n*-butyllithium in hexane was cooled to 0 °C in an ice-water bath. To this solution was added 4.2 g of diisopropylamine over a 15-min period. The reaction mixture was stirred for an additional 15 min and then cooled to −78 °C in a dry ice–acetone bath. A 4.8-g sample of *tert*-butyl acetate was added dropwise over a 15-min period. The reaction mixture was stirred at −78 °C for 30 min and was then allowed to warm to room temperature. The above solution of lithium *tert*-butyl acetate was added to a suspension of 10 g of 1,2-diphenyl-3-methylcyclopropenylium perchlorate in 200 mL of anhydrous ether at −78 °C over a 30-min period. The reaction mixture was allowed to stir for 16 h gradually warming to room temperature over the first 4 h. Water was added to quench any excess lithium *tert*-butyl acetate and the reaction mixture was washed three times with equal volumes of water and with a saturated salt solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a thick, yellow oil which was chromatographed on a 2.5 × 100 cm column of silica gel using 3% ether in hexane as the eluent. The first component isolated contained 6.8 g (68%) of a clear oil which was identified as *tert*-butyl 1-methyl-2,3-diphenyl-2-cyclopropene-1-acetate on the basis of its spectral properties: IR (neat) 3.26, 3.37, 3.44, 5.51, 5.77, 6.24, 6.69, 6.93, 7.18, 7.33, 7.47, 8.69, 13.2, and 14.6 μ; NMR ($CDCl_3$, 100 MHz) δ 1.30 (s, 9 H), 1.51 (s, 3 H), 2.69 (s, 2 H), and 7.15–7.74 (m, 10 H); UV (95% ethanol) 333, 316, 236, and 227 nm (ϵ 20 950, 27 040, 12 690, and 16 990); *m/e* 264, 263, 236, 220, 105, 77, and 56 (base).

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.20; H, 7.28.

The second component isolated from the column contained 1.57 g (15%) of a clear oil which was identified as *tert*-butyl 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetate on the basis of its spectral properties: IR (neat) 3.26, 3.37, 3.42, 5.37, 5.78, 6.23, 6.69, 6.93, 7.18, 7.33, 7.50, 8.75, 13.10, and 14.4 μ; NMR ($CDCl_3$, 100 MHz) δ 1.25 (s, 9 H), 2.18 (s, 3 H), 2.92 (dd, 2 H, J = 21 and 12 Hz), and 6.84–7.36 (m, 10 H); UV (95% ethanol) 262 and 203 nm (ϵ 14 180 and 24 100); *m/e* 320 (M^+), 263, 220, 219, 205 (base), 204, 115, 105, and 77.

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.46; H, 7.55. Found: C, 82.36; H, 7.43.

To a well-stirred solution containing 500 mg of *tert*-butyl 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetate in 100 mL of hexane at −78 °C was added 1.3 mL of a 25% by weight solution of diisobutylaluminum hydride in hexane. The reaction mixture was allowed to stir for 1 h at −78 °C and then quenched by the addition of 5 mL of methanol and 5 mL of water. The reaction mixture was allowed to warm to room temperature and stirred for an additional 1 h. The organic phase was filtered through diatomaceous earth, washed three times with equal volumes of water and with a saturated salt solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a colorless oil which was chromatographed on a 1.5 × 100 cm column of silica gel using a 5% acetone in hexane mixture as the eleuent. The first fraction eluted contained 125 mg (25%) of unreacted starting material. The second fraction contained 275 mg (55%) of a colorless oil which was identified as 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetaldehyde on the basis of its spectral properties: IR (neat) 3.34, 3.47, 3.58, 3.60, 5.40, 5.83, 6.24, 6.73, 6.96, 9.31, 12.15, 13.22, and 14.34 μ; NMR ($CDCl_3$, 100 MHz) δ 2.24 (s, 3 H), 3.03 (d, 2 H, J = 2 Hz), 7.00–7.45 (m, 10 H), and 9.78 (t, 1 H, J = 2 Hz); *m/e* 248 (M^+, base), 246, 233, 220, 219, 205, 115, 105, 91, and 77. The aldehyde was used in subsequent synthetic steps without further characterization.

To a well-stirred solution containing 270 mg of ethyltriphenylphosphonium bromide in 5 mL of anhydrous tetrahydrofuran and 3 mL of anhydrous ether at 0 °C was added 0.61 mL of a 1.2 N solution of phenyllithium in ether. The solution was stirred for 1 h at 0 °C. At the end of this time the reaction mixture was cooled to −78 °C and a solution containing 180 mg of 2-methyl-1,3-diphenyl-2-cyclopropene-1-acetaldehyde in 5 mL of anhydrous ether was added. The reaction mixture was allowed to stir overnight. A saturated ammonium chloride solution was added and the reaction mixture was stirred until both phases became clear. The organic layer was washed three times with equal volumes of water and with a saturated salt solution and dried over magnesium sulfate. Removal of the solvent left behind a colorless oil which was chromatographed on a 1.5 × 60 cm column of silica gel impregnated with 10% silver nitrate (w/w) using a 10% ether in hexane mixture as the eluent. The first fraction eluted contained 67 mg (36%) of a colorless oil which was identified as (*E*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**16**) on the basis of its spectral properties: IR (neat) 3.30, 3.34, 3.41, 3.47, 3.55, 5.49, 6.24, 6.74, 6.96, 9.39, 10.42, and 14.61 μ; NMR ($CDCl_3$, 100 MHz) δ 1.56 (d, 3 H, J = 4.0 Hz), 2.25 (s, 3 H), 2.84 (m, 2 H), 5.15–5.64 (m, 2 H), and 7.0–7.6 (m, 10 H); UV (95% ethanol) 264 nm (ϵ 15 700); *m/e* 260 (M^+) and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.72.

The second component isolated from the column contained 89 mg (47%) of a colorless oil whose structure was assigned as (*Z*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**19**): IR (neat) 3.30, 3.34, 3.41, 3.47, 3.55, 5.39, 6.24, 6.74, 7.95, 9.39, 13.39, and 14.61 μ; NMR ($CDCl_3$, 100 MHz) δ 1.58 (d, 3 H, J = 5.0 Hz), 2.28 (s, 3 H), 2.90 (d, 2 H, J = 6.0 Hz), 5.32–5.58 (m, 2 H), and 7.10–7.55

(m, 10 H); UV (95% ethanol) 264 nm (ϵ 15 640); *m/e* 260 (M^+) and 205 (base).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.21; H, 7.73.

Thermolysis of (*E*)- (16) and (*Z*)-1-(2-Methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (19). A solution containing 100 mg of cyclopropene **16** in 0.5 mL of a 20% deuterated pyridine-benzene-d_6 mixture was heated at 175 °C for 12 h. Analysis of the reaction mixture by NMR spectroscopy revealed the presence of unreacted starting material (46%), *endo*-5,6-dimethyl-1,2-diphenyltricyclo-[2.2.0.$0^{2,6}$]hexane (**20,** 36%), and 3-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-1-butene (**21,** 18%). Chromatography of the mixture on a thick layer plate resulted in the isolation of pure samples of tricyclohexane **20** and cyclopropene **21.** The major component (21%) was fractionally crystallized from the mixture with methanol and was identified as *endo*-5,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**20**): mp 66-67 °C; IR (KBr) 3.32, 3.43, 3.52, 6.24, 6.71, 6.95, 8.13, 8.30, 9.31, 9.46, 9.69, 9.93, 11.00, 14.15, and 14.30 μ; UV (95% ethanol) 244 nm (ϵ 16 690); *m/e* 260 (M^+, base), 245, 186, 160, and 91; NMR ($CDCl_3$, 270 MHz) δ 1.00 (d, 3 H, J = 6.5 Hz), 1.31 (s, 3 H), 2.40 (d, 1 H, J = 9.0 Hz), 2.77 (dd, 1 H, J = 9.0 and 4.5 Hz), 2.78 (t, 1 H, J = 4.5 Hz), 2.84 (dq, 1 H, J = 6.5 and 4.5 Hz), 6.93-7.40 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.20; H, 7.77.

Thermolysis of a pure sample of tricyclohexane **20** at 175 °C for 20 h resulted in the formation of (*E*)-1-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-butene (**16,** 25%) and cyclopropene **21** (8%) in addition to unreacted starting material (67%).

A solution containing 100 mg of the isomeric *Z* cyclopropene **19** in 0.5 mL of a benzene-pyridine mixture was heated at 175 °C for 12 h. Analysis of the reaction mixture by NMR spectroscopy revealed the presence of unreacted starting material (73%), *exo*-5,6-dimethyl-1,2-diphenyltricyclo[2.2.0.$0^{2,6}$]hexane (**22,** 16%), and cyclopropene **21** (11%). Chromatography of the reaction mixture on a thick layer plate resulted in the isolation of pure samples of tricyclohexane **22** and cyclopropene **21.** Tricyclohexane **22** was assigned on the basis of its characteristic spectra: IR (neat) 3.32, 3.50, 6.24, 6.70, 6.93, 7.39, 7.42, 8.08, 9,30, 9.70, 10.11, 11.00, 12.70, 13.20, and 14.38 μ; UV (95% ethanol) 246 nm (ϵ 12 600); *m/e* 260 (M^+, base), 245, 169, 141, 115, 91, and 77; NMR ($CDCl_3$, 270 MHz) δ 1.23 (s, 3 H), 1.31 (d, 3 H, J = 6.0 Hz), 2.27 (d, 1 H, J = 7.4 Hz), 2.39 (d, 1 H, J = 4.4 Hz), 2.39 (q, 1 H, J = 6.0 Hz), 2.78 (dd, 1 H, J = 7.4 and 4.4 Hz), 6.88-7.28 (m, 10 H).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.79.

Thermolysis of a pure sample of tricyclohexane **22** at 175 °C for 20 h gave back mostly unreacted starting material (89%) with small amounts of cyclopropenes **21** (5%) and **19** (6%).

Rate Studies. Stock solutions containing 2.0 g of the appropriate cyclopropene or tricyclo[2.2.0.$0^{2,6}$]hexane, 35 mL of triethylamine, and 100 mL of chlorobenzene were prepared. From each stock solution, 9-mL aliquots were withdrawn and sealed in glass ampules under an argon atmosphere. The ampules were immersed in a thermostated (±0.1 °C) oil bath at the designated temperatures and were periodically withdrawn for analysis. The solvent was removed under reduced pressure and the residue was taken up in deuterated chloroform. Equilibrium concentrations were determined by NMR spectroscopy of high-pressure column chromatography on an Altex 3.2 × 250 mm LiChroSorb 5-μm C-18 reverse phase silica gel column. The analyses were continued until no further changes were observed in the relative equilibrium concentrations.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE-7900919) for financial support.

References and Notes

(1) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940,** *62,* 441.
(2) Rhoads, S. J. "Molecular Rearrangements", Vol. I; de Mayo, P., Ed.; Interscience: New York, 1963.
(3) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969,** *8,* 781.
(4) Doering, W. von E.; Roth, W. R. *Tetrahedron* **1962,** *18,* 67.
(5) Hill, R. K.; Gilman, N. W. *Chem. Commun.* **1967,** 619.
(6) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972,** *94,* 5119, 7147.
(7) Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964,** *86,* 899.
(8) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966,** *88,* 183.
(9) Berson, J. A.; Dervan, P. B. *J. Am. Chem. Soc.* **1972,** *94,* 7597. Berson, J. A.; Dervan, P. B.; Jenkins, J. A. *Ibid.* **1972,** *94,* 7598.
(10) Doering, W. von E.; Franck-Neumann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972,** *94,* 3833.
(11) For a review see: Rhoads, S. J.; Rawlins, R. N. *Org. React.* **1975,** *22,* 1.
(12) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971,** *27,* 5299.
(13) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1973,** *95,* 290; **1977,** *99,* 4417.
(14) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977,** *99,* 5069.
(15) Grob, C. A.; Link, H.; Schiess, P. *Helv. Chim. Acta* **1963,** *46,* 483.
(16) Komornicki, A.; McIver, J. W. *J. Am. Chem. Soc.* **1976,** *98,* 4553.
(17) McIver, J. W. *Acc. Chem. Res.* **1974,** *7,* 72.
(18) Marvell, E. N.; Li, T. H. C. *J. Am. Chem. Soc.* **1978,** *100,* 883.
(19) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1978,** *100,* 6268, 6269.
(20) Wehrli, R.; Schmid, H.; Bellus, D. E.; Hansen, H. J. *Helv. Chim. Acta* **1977,** *60,* 1325. *Chimia* **1976,** *30,* 416.
(21) Padwa, A. *Acc. Chem. Res.,* **1979,** *12,* 310.
(22) Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1978,** *100,* 1321; **1979,** *101,* 3390.
(23) Weiss, R.; Kolbl, H. *J. Am. Chem. Soc.* **1975,** *97,* 3222, 3224.
(24) de Wolf, W. H.; Landheer, I. J.; Bickelhaupt, F. *Tetrahedron Lett.* **1975,** 179, 349; **1974,** 2813.
(25) Davis, J. H.; Shea, K. J.; Bergman, R. G. *Angew. Chem.* **1976,** *88,* 254. *J. Am. Chem. Soc.* **1977,** *99,* 1499.
(26) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962,** *84,* 3168.
(27) Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976,** 4685.
(28) Schleyer, P. von R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970,** *92,* 2377.
(29) For some related proton couplings in the tricyclo[2.2.0.0] system, see: Ho, C. Y.; Bond, F. T. *J. Am. Chem. Soc.* **1974,** *96,* 7355.
(30) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965,** *87,* 4389.
(31) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972,** *94,* 7149.
(32) Gajewski, J. J. *Mech. Mol. Migr.* **1972,** *4,* 1.
(33) Hoffmann, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970,** *92,* 7091.
(34) Wright, J. S.; Salem, L. *J. Am. Chem. Soc.* **1972,** *94,* 322.
(35) Segal, G. A. *J. Am. Chem. Soc.* **1974,** *96,* 7892.
(36) Fujimoto, H.; Sugiyama, T. *J. Am. Chem. Soc.* **1977,** *99,* 15.
(37) Baldwin, J. E. In "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, p 273.
(38) Scacchi, G.; Richard, C.; Back, M. H. *Int. J. Chem. Kinet.* **1977,** *9,* 513.
(39) Scacchi, G.; Back, M. H. *Int. J. Chem. Kinet.* **1977,** *9,* 525.
(40) Bartlett, P. D.; Mallet, J. B. *J. Am. Chem. Soc.* **1976,** *98,* 143.
(41) Bartlett, P. D.; Hummel, K.; Elliott, S. P.; Minns, R. A. *J. Am. Chem. Soc.* **1972,** *94,* 2898.
(42) Bartlett, P. D.; Cohen, G. M.; Elliott, S. P.; Hummel, K.; Minns, R. A.; Sharts, C. M.; Fukunaga, J. Y. *J. Am. Chem. Soc.* **1972,** *94,* 2899.
(43) The case of Kraft and Koltzenburg dealing with the stereoselective dimerization of bicyclo[4.2.2]deca-*trans*-3-*cis*-7,9-triene can be attributed to a multistep process:[44] Kraft, K.; Koltzenburg, G. *Tetrahedron Lett.* **1967,** 4357.
(44) Padwa, A.; Koehn, W.; Masaracchia, J.; Osborn, C. L.; Trecker, D. J. *J. Am. Chem. Soc.* **1971,** *93,* 3633.
(45) Cycloadditions of olefins to allenes,[46,47] ketenes,[48] and reactive isocyanates[49] are known to proceed with very high degrees of stereospecificity, thereby suggesting that cumulative π-bond systems can function more readily as $_{\pi}2_s$ donors than isolated double bonds.
(46) Keifer, E. F.; Okamura, M. Y. *J. Am. Chem. Soc.* **1968,** *90,* 4187.
(47) Baldwin, J. E.; Roy, U. V. *Chem. Commun.* **1969,** 1225.
(48) Brady, W. T.; Hoff, E. F.; Roe, R.; Parry, F. H. *J. Am. Chem. Soc.* **1969,** *91,* 5679.
(49) Mariconi, E. J.; Kelly, J. F. *Tetrahedron Lett.* **1968,** 1435.
(50) Frey, H. M. *Adv. Phys. Org. Chem.* **1966,** *4,* 170.
(51) Cocks, A. T.; Frey, H. M.; Stevens, I. D. R. *Chem. Commun.* **1969,** 458.
(52) Baldwin, J. E.; Ford, P. W. *J. Am. Chem. Soc.* **1969,** *91,* 7192.
(53) Meinwald, J.; Kapecki, J. A. *J. Am. Chem. Soc.* **1972,** *94,* 6236.
(54) Nelson, S. F.; Gillespie, J. P. *J. Am. Chem. Soc.* **1972,** *94,* 6237, 6238.
(55) Wittig, G.; Koenig, G.; Claus, K. *Justus Liebigs Ann. Chem.* **1955,** *593,* 127.
(56) Mitchell, R. H.; Sondheimer, F. *Tetrahedron Lett.* **1968,** 2872.
(57) Doering has recently shown that 2,5-diphenyl-1,5-heptadiene undergoes internal [2 + 2] thermal cycloaddition; see footnote 43 in ref 13.
(58) Roberts, J. D.; Sharts, C. M. *Org. React.* **1962,** *12,* 1.
(59) Keese, R.; Krebs, E. D. *Angew. Chem., Int. Ed. Engl.* **1971,** *10,* 262.
(60) Burns, W.; McKervey, M. A. *J. Chem. Soc., Chem. Commun.* **1974,** 858.
(61) Lenoir, D. *Tetrahedron Lett.* **1972,** 4049.
(62) Gano, J. E.; Eizenberg, L. *J. Am. Chem. Soc.* **1973,** *95,* 972.
(63) Adams, B. L.; Kovacic, P. *J. Am. Chem. Soc.* **1973,** *95,* 8206.
(64) Farcasiu, M.; Farcasiu, D.; Conlin, R. T.; Jones, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973,** *95,* 8207.
(65) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978,** 2283.
(66) Bartlett, P. D. *Science* **1968,** *159,* 833.
(67) Huisgen, R. *Acc. Chem. Res.* **1977,** *10,* 117.
(68) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976,** *76,* 311.

(69) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc lamp.
(70) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974,** *96,* 1775.
(71) Rathke, M. W.; Sullivan, D. F. *J. Am. Chem. Soc.* **1973,** *95,* 3050.

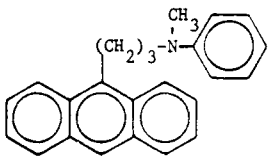
Chemistry of Exciplexes. 9. Viscosity Effect on Intramolecular Exciplex Formation in Saturated Hydrocarbons

Nein-chu C. Yang,* Soon Bin Neoh, Takeaki Naito, Lay-Keow Ng, Donald A. Chernoff, and Daniel B. McDonald

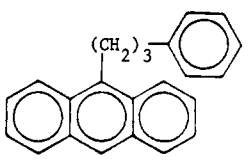
Department of Chemistry, University of Chicago, Chicago, Illinois 60637.
Received October 9, 1979

Abstract: The relative intensities of the anthracene-like fluorescence and the intramolecular exciplex fluorescence of *N*-phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane in saturated hydrocarbons are dependent on the solvent viscosity. Both the rates of exciplex formation and dissociation are retarded in more viscous solvents, but the solvent viscosity has only little effect on the equilibrium of intramolecular exciplex formation.

Photoexcited anthracenes form exciplexes with tertiary amines.[1] Since exciplexes are more polar than the uncomplexed excited aromatic hydrocarbons, it is well known that the polarity of solvent exerts a marked effect on the properties of exciplexes.[2] Bichromophoric molecules containing both an aromatic group and a tertiary amino substituent may form intramolecular exciplexes.[3-9] Recently these phenomena have been applied to study the macroscopic environment in polymers.[10] Anthracene–dimethylaniline exciplex will undergo interesting chemical reactions with another molecule of the amine.[11] In connection with our interest in the chemistry of exciplexes, we synthesized *N*-phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane (**1**)[7] and are investigating the chemical interaction between its intramolecular exciplex with a variety of amines.[12] When the fluorescence of **1** was examined carefully in a variety of solvents including several saturated hydrocarbons, we found that the emission varies from one hydrocarbon to another. The results were analyzed by kinetic spectroscopy and it was found that both the rates of exciplex formation and dissociation are retarded in a more viscous solvent, but the solvent viscosity has little effect on the equilibrium of exciplex formation.[13]



1



2

Experimental Methods

All solvents used were the spectroscopic grade solvents purchased from the Aldrich Co. *N*-Phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane (**1**) was prepared according to a known procedure.[7] 3-(9-Anthryl)-1-phenylpropane (**2**) was prepared from 9-anthranilydene acetophenone in two steps.

3-(9-Anthryl)-1-phenyl-1-propanone. A solution of 9-anthranilydene acetophenone[14] (4.0 g) in tetrahydrofuran (250 mL) was hydrogenated in the presence of 800 mg of Pd/C (10%) catalyst at room temperature (21 °C) and atmospheric pressure. The pale green residue solidified upon trituration with ether. An analytical sample was prepared from this solid by recrystallization from ether: mp 116–117 °C; NMR ($CDCl_3$), δ 3.44 (t, 2 H), 4.08 (t, 2 H), 7.48 (m, 7 H), 7.94 (d, 2 H), 8.12 (d, 2 H), 8.26 (d, 2 H), 8.34 ppm (s, 1 H). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.60; H, 6.00.

3-(9-Anthryl)-1-phenylpropane (2). A mixture of 3-(9-anthryl)-1-phenylpropanone (1 g), anhydrous hydrazine (1 mL), NaOH (0.9 g), and diethylene glycol (10 mL) was heated gradually to 200 °C and was maintained at 200–205 °C for 3.5 h. After cooling, the mixture was poured into water and extracted with benzene. The benzene extract was washed, dried, and evaporated under reduced pressure. The yellow semicrystalline residue was chromatographed over silica gel packed in benzene. The product **2** was isolated from the benzene eluant by evaporation and recrystallization from petroleum ether: mp 79–80 °C; NMR ($CDCl_3$) δ 2.19 (quintet, 2 H), 2.92 (t, 2 H), 3.62 (t, 2 H), 7.17 (m, 5 H), 7.52 (m, 4 H), 7.98 (d, 2 H), 8.12 (d, 2 H), 8.30 ppm (s, 1 H). The overall yield from 9-anthranylidene acetophenone was 40–45%. Anal. Calcd for $C_{23}H_{30}$: C, 93.20; H, 6.80. Found: C, 89.95; H, 6.98.

All fluorescence spectra were measured at 22.0 ± 0.5 °C on a Perkin-Elmer MPF-4 spectrofluorimeter with an integrated electronic corrected spectra unit and a thermostatic sample compartment. Samples were prepared at 1.5×10^{-5} M concentration in **1** or **2** and were degassed by multiple freeze–thaw cycles at a pressure <0.01 Torr.

The instrument used for the kinetic spectroscopy had been described previously.[15,16] The excitation source was an acousto-optically mode-locked argon ion laser with a synchronously pumped doubled dye laser system. The excitation wavelength was arbitrarily set at 2941.5 Å. The fluorescence signals from the PMT were processed via a timing filter amplifier to a constant fraction discriminator, a biased time to pulse height converter, and a multichannel pulse height analyzer successively. The data were collected at the teletype and analyzed by an IBM 370-168 or PDP 11/03 computer according to a known procedure.[16] The resolution in lifetime measurements was estimated to be >0.2 ns.

Results

The fluorescence spectra of **1** in four hydrocarbons, *n*-pentane, *n*-heptane, methylcyclohexane, and *n*-hexadecane, are given in Figure 1. The spectra consist of two discernable but overlapping groups of emissions, a structured anthracene-like emission (emission A*) at 391 and 412 nm, and broad structureless emission (emission E*) with a maximum at 487

0002-7863/80/1502-2806$01.00/0