Spiro[cyclopropane-1,2′-adamantane-1′-ol] (6a). The synthesis of this compound follows essentially the procedure for the preparation of **13**. Purification of the crude reaction product by chromatography on alumina and recrystallization from petroleum ether yields 70–80% of **6a**: mp 192–194° (lit.[2] mp 192–194°); ir (CCl_4) 3550, 3400, 3050, 1110, 1085, 1010, 975, 935 cm^{-1}; nmr (CCl_4) δ 0.1 and 0.85 (2 g, 2.3 and 2, C_3H_4 ring), 1.15 (broad s, 1), 1.75 (m, 6), 2.1 (m, 7); mass spectrum *m/e* 178. *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.86; H, 10.17. Found: C, 80.81; H, 10.28.

2,2-Dimethyladamantan-1-ol (7a). (a) From 6a. Hydrogenolysis of **6a**, under the conditions described above for the preparation of **14**, yielded 80% of **7a**, which after recrystallization from petroleum ether had a melting point of 220–222° (lit.[2] mp 220–22°); ir (CCl_4) 3650, 3500, 1450, 1110, 1075, 955, 925 cm^{-1}; nmr (CCl_4) δ 1.0 (s, 6, *gem*-dimethyl); mass spectrum *m/e* 180. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.86; H, 11.23.

(b) From 7c. Hydrolysis of **7c** in water–THF with $AgNO_3$–K_2CO_3 yielded 70–80% of one product, which was identical with **7a** obtained from **6a**, with respect to all analytical and spectral properties.

2-Methyleneadamantane 1-Tosylate (5b). In a 25-ml round-bottomed flask connected to a source of dry N_2, 82 mg (0.5 mmol) of **5a** was dissolved in 10 ml of dry ether and 0.31 ml of 1.6 *M* *n*-butyllithium (0.5 mmol) in hexane was added. After 10 min 95.3 mg (0.5 mmol) of *p*-toluenesulfonyl chloride in 2 ml of ether was added to the stirred reaction mixture. After 24 hr the mixture was washed with 1 *N* HCl, $NaHCO_3$ solution, and water, and dried over $MgSO_4$. Removal of solvent gave an oily residue which was chromatographed over alumina and eluted with ether. Recrystallization from pentane at −60° gave 102 mg (0.32 mmol, 64%) of **5b**: mp 63–64° (lit.[2] mp 58–61°); nmr ($CDCl_3$) δ 7.8 and 7.3 (2 d, 4, J = 8 Hz), 4.86 and 4.68 (2 d, 2, $=CH_2$, J = 1.5 Hz), 2.9–1.3 (m, 17.8 *p*-CH_3 at 2.4).

Spiro[cyclopropane-1,2′-adamantyl 1′-chloride] (6b), Spiro[cyclopropan-1,4′-adamantyl 1′-chloride] (8b), and 4,4-Dimethyladamantyl 1-Chloride (9b). For conversion of the alcohols into the corresponding chlorides, 2 mmol of the alcohol was treated with 2.1 mmol of freshly distilled thionyl chloride at room temperature for 3 hr and then at 80° for 5 more hr. The reaction mixture was evaporated to dryness under vacuum; the residue was dissolved in pentane several times and the solvent was removed. After recrystallization from pentane in a Dry Ice–acetone bath the chlorides were obtained in varying (30–60%) yields and were identified by mass and nmr–ir spectral analysis: **6b**, mp 97–99°; ir (CCl_4) 3000, 1450, 1055, 1015, 875 cm^{-1}; nmr (CCl_4) δ 0.1 and 0.82 (2 q, 4, C_3H_4 ring), 1.1 (broad s, 1), 1.73 (s, 6), 2.1 (s, 6); mass spectrum *m/e* 196/198; **8b**, mp 38–39°; ir (CCl_4) 3000, 1460, 1055, 1015, 885 cm^{-1}; nmr (CCl_4) δ 0.28 (s, 4, C_3H_4) ring), 1.15 (broad s, 2), 1.75 (broad s, 5), 2.15 (broad s, 6); mass spectrum *m/e* 196/198; **9b**, mp 61–62°; ir (CCl_4) 1450, 1395, 1370, 1345, 1295, 1025, 800 cm^{-1}; mass spectrum *m/e* 198/200.

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The Thermal Reorganizations of C_6H_8 Hydrocarbons

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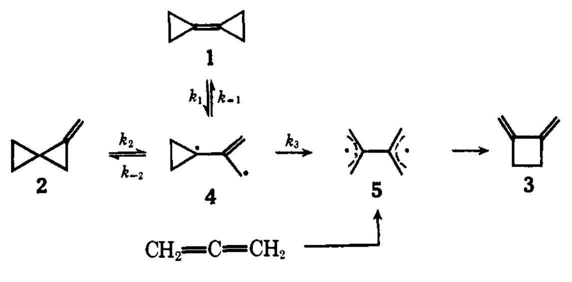
Abstract: Thermal isomerizations of *cis*- and *trans*-2,2,2′,2′-tetramethylbiscyclopropylidene and the further equilibration of their methylenespiropentane products have been quantitatively investigated. The results are discussed in view of the thermal isomerizations of homologous cyclopropylidenecycloalkanes, and *nonplanar* trimethylenemethane diradicals are hypothesized as the key intermediates. An improved synthesis of methylenespiropentane is presented along with its high-activation-energy isomerization to 1,2- and 1,3-dimethylenecyclobutane, and the relationship of this rearrangement to other thermal isomerizations thought to proceed *via* diallyl diradicals is described.

A number of molecules having the empirical formula C_6H_8 (*i.e.*, biscyclopropylidene, methylenespiropentane, and 1,2-dimethylenecyclobutane), and which are related through thermal reorganizations, have been of considerable interest since the degenerate reorganization of 1,2-dimethylenecyclobutane was first investigated by Gajewski and Shih[2a] and by Doering and Dolbier[2b] in 1967. These molecules are ostensibly interconverted *via* the pair of diradicals **4** and **5** (Scheme I), which are themselves of no small interest. The thermodynamic driving force is apparently strongly from **1** → **2**[3] and from **2** → **3**,[3a] with there being a signif-

Scheme I



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(1) (a) Alfred P. Sloan Fellow, 1970–1972; (b) NSF-RPCT Participant, Summer 1969; (c) NSF-URP Participant, Summer 1969.

(2) (a) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967).

(3) (a) W. R. Dolbier, Jr., *Tetrahedron Lett.*, 393 (1968); (b) J. K. Crandall, D. R. Paulson, and C. A. Bunnel, *ibid.*, 4217 (1969), and personal communication; (c) W. R Dolbier, Jr., K. Akiba, M. Bertrand, A. Bezaguet, and M. Santelli, *Chem. Commun.*, 717 (1970); (d)

icant energy barrier between **4** and **5** (*vide infra*). For completeness, the dimerization reactions of allenes which also possibly proceed *via* the diallyl diradical **5** are included in the above scheme.[4] In this paper we would like to present an improved synthesis of methylenespiropentane along with details of our investigations into the thermal reorganizations of both this interesting molecule and other molecules whose rearrangements should contribute knowledge as to the energy surface relating C_6H_8 isomers.

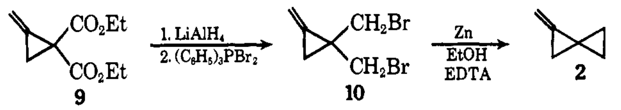
Results

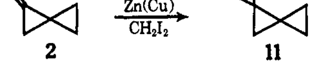
Molecules with the biscyclopropylidene structure have been known since 1965 when Skattebøl synthesized the 3,3,3′,3′-tetrahalo-2,2,2′,2′-tetramethylbiscyclopropylidenes.[5] They were investigated as precursors of cumulenes.

The first totally hydrocarbon biscyclopropylidenes, that is, *cis*- and *trans*-2,2,2′,2′-tetramethylbiscyclopropylidenes (**6** and **7**), were synthesized in 1967.[6] In this paper we shall present details of the thermal reorganizations of these two molecules.

In addition Crandall has synthesized a hexamethylbiscyclopropylidene **8**[3b] and Conia the parent molecule[3e] and they have investigated aspects of these molecules' thermal reorganizations (*vide infra*).

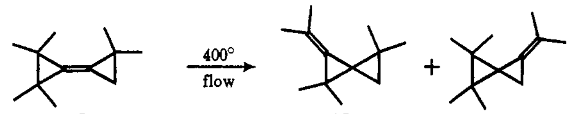
Synthesis of Methylenespiropentane and Dispiro[2.1.2.0]heptane. The second molecule of interest on the energy surface of the C_6H_8 series is methylenespiropentane. In this case, the parent hydrocarbon was the first one to be synthesized, in 1968.[3a] The synthesis was accomplished by a series of straightforward reactions starting from diethyl methylenecyclopropane-2,2-dicarboxylate (**9**)[7] and *via* the dibromide **10**. The final step was carried out in a manner completely analogous to Applequist's spiropentane synthesis.[8,9] Part of the structure proof of the methylenespiropentane included its conversion to the interesting dispiro[2.1.2.0]heptane (**11**). The chemistry of this molecule is presently under investigation.





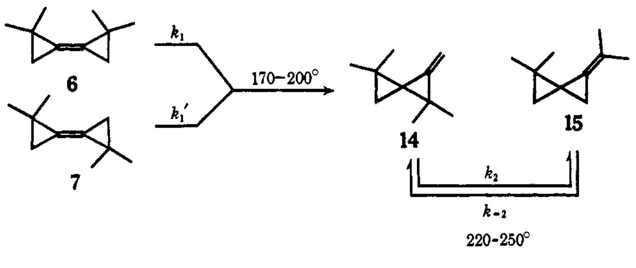
The nmr spectra of **2** and **11** are worth mentioning. **2** shows three cyclopropyl absorptions, two broad peaks with ill-defined splitting (J = 1 cps) at 1.02 and 1.12, and a broad triplet (J = 2 cps) at 1.33 ppm. The vinyl absorptions are at 5.08 and 5.21 ppm with the former appearing as a triplet (J = 2 cps) and probably representing the transoid proton which generally has larger allylic coupling constants.[10] The latter peak is of ill-defined multiplicity (J < 1 cps). The spectrum of **11** shows two broad multiplet absorptions at 0.57 and 0.78 ppm. These peaks are symmetrical about each other and are characteristic of a 1,1′-disubstituted dicyclopropyl system.[11] The methylene group of the central cyclopropyl ring appears as a singlet at 1.14 ppm.

Thermal Reorganizations of Biscyclopropylidenes. Crandall has reported that **8** rearranges in a flow system at 400° to methylenespiropentane molecules **12** and **13**



in the relative yields of 87 and 9%, respectively.[3b]

We have examined quantitatively the thermal reorganizations of the isomeric tetramethylbiscyclopropylidenes, **6** and **7**.



The activation parameters for these unimolecular rearrangements are very similar, as might be expected. For the cis molecule **6**, E_a = 39.2 ± 1.0 kcal/mol with log A = 14.94, $\Delta H^{\ddagger}$ = 38.3 ± 1.0 kcal/mol, and $\Delta S^{\ddagger}$ = 7.0 ± 2 eu at 190°, while for the trans species **7**, E_a = 38.8 ± 1.0 kcal/mol with log A = 14.77, $\Delta H^{\ddagger}$ = 37.9 ± 1.0 kcal/mol, and $\Delta S^{\ddagger}$ = 6.2 ± 2.6 eu at 190°.

The reactions followed simple first-order kinetics and Arrhenius plots gave the activation parameters. There is no equilibration of **6** and **7** under these conditions. Indeed the destruction of **6** and **7** gives every indication of being irreversible under these reaction conditions. *No* **6** or **7** could be detected (<1%) by glpc when either **14** or **15** was heated under the reaction conditions. Dioxane was used as an internal standard in certain control reactions which showed that the *yields* for these rearrangements were >90%.

The only significant difference is the *ratio* of the products **14** and **15** obtained from the two systems. The cis molecule **6** produces the *less stable* isomer **14** in excess of the thermodynamically more stable isomer **15** in a ratio of ~3.50:1. Moreover, this ratio is relatively constant at all temperatures studied up to 90% reaction. Trans species **7** favors product **14** even more dramatically with a ratio of ~14:1 being produced.

The relative constancy of these ratios is indicative of a rather slow interconversion of the two products. Indeed, the activation parameters for this isomerization

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W. R. Dolbier, Jr., K. Akiba, J. M. Riemann, M. Bertrand, and A. Bezaquet, *Chem. Commun.*, 718 (1970); (e) P LePerchec and J. M. Conia, *Tetrahedron Lett.*, 1587 (1970).

(4) (a) W. R. Dolbier, Jr., and S. H. Dai, *J. Amer. Chem. Soc.*, **92**, 1774 (1970); (b) J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969); (c) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970).

(5) L. Skattebøl, *ibid.*, 2175 (1965).

(6) B. duLaurens, A. Bezaguet, G. Davidovics, M. Bertrand, and J. Chouteau, *Bull. Soc. Chim. Fr.*, 799 (1967).

(7) E. F. Ullman, *J. Amer. Chem. Soc.*, **81**, 5386 (1959).

(8) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Org. Chem.*, 23, 1715 (1958).

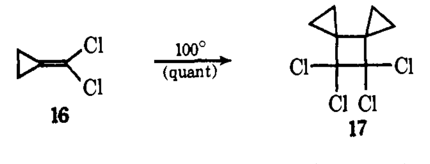
(9) The final two steps as reported here are a definite improvement in the synthesis as reported in the earlier communication.[3a]

(10) L. M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 322.

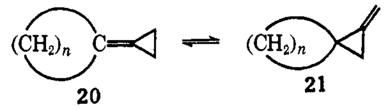
(11) W. R. Dolbier, Jr., D. Lomas, and P. Tarrant, *J. Amer. Chem. Soc.*, **90**, 3594 (1968).

process were also determined: log $(k_2 + k_{-2}) = 15.72 - (46{,}100 \pm 1.300/2.303RT)$ with $\Delta H^{\ddagger} = 45.1 \pm 1.3$ kcal/mol and $\Delta S^{\ddagger} = 10.3 \pm 2.5$ eu at 240°. Thus, it is seen that, indeed, isomer **15** *is* the thermodynamically favored product. Even in the equilibration at 250°, the recovered yields of **14** and **15** were excellent.

Recently, Conia has found that, as expected, the *parent* biscyclopropylidene is converted thermally to methylenespiropentane.[3e] An unexpected surprise was observation of a competitive dimerization process. We had not experienced any such competitive dimerization in our *gas phase* pyrolyses. However, this reaction is very interesting and may turn out to be characteristic of methylenecyclopropane systems. We first observed such a reaction in our study of the dimerization of dichloromethylenecyclopropane **16**.[11,12]



Thermal Equilibrations of Cyclopropylidenecycloalkanes. The above data on the two biscyclopropylidene systems can be fruitfully compared with similar data for the homologous cyclopropylidenecycloalkanes.



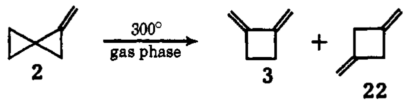
One can see the obvious trend in the activation energies, but the most outstanding observation is the incongruency of the equilibrium constant for $n = 2$, that is, for the biscyclopropylidene system.

Table I. Composite of Activation and Equilibrium Parameters for Cyclopropylidenecycloalkane Equilibrations

n	E_a	Log A	$\Delta H^{\ddagger}$ (220°)	$\Delta S^{\ddagger}$ (220°)	K_{eq} (220°)
5	45.6 ± 2	15.86	44.6 ± 2	11.0 ± 4	1.15
4	41.4 ± 2	14.92	40.5 ± 2	6.8 ± 4	0.312
3	39.7 ± 2	14.25	38.7 ± 2	3.7 ± 4	0.823
2[a]	38.9 ± 2	14.81[b]	38.0 ± 2[b]	6.4 ± 4[b]	>100

[a] For tetramethyl species **6**. [b] At 190°.

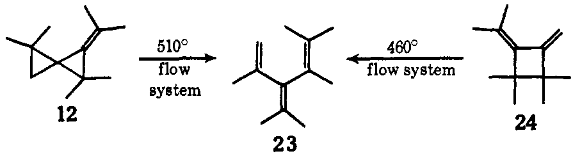
Thermal Reorganization of Methylenespiropentane. Of interest, of course, was the possible conversion of methylenespiropentane systems to diallyl diradicals and thus hopefully to the 1,2-dimethylenecyclobutane system. Such a conversion was obviously not occurring at the temperatures required for biscyclopropylidenemethylenespiropentane conversion. Apparently cleavage of the cyclopropyl radical to an allyl radical has a significant energy barrier. Thus temperatures in excess of 300° have been found necessary for the thermal reorganization of methylenespiropentane. After 10 hr at 300 ± 2°, approximately 8% **2** had been converted to two products, 1,2- and 1,3-dimethylenecyclobutane, which were in a ratio of 7:1, respectively.



Heating to 320 ± 2° for 20 hr led to a mixture containing 60.6% **2**, 15.8% **3**, and 19.8% **22**, plus 3.8% of a very volatile product which had the same glpc retention time as allene. Recovery yield in the latter, higher temperature system was not good (~40%), due undoubtedly to dimerization and polymerization reactions of the 1,2-dimethylenecyclobutane product, which apparently took place under the conditions of the pyrolysis (*i.e.*, 18.7 mm gas pressure at 27°). The products were characterized by their infrared, nmr, and mass spectra, the first two being available from the literature.[13]

The remarkable observations in these experiments were the apparent stability to cleavage of the cyclopropyl radical, under these conditions, and the formation of **22** at a rate competitive with the formation of **3**.

Alkylated methylenespiropentanes apparently also show this same reluctance to rearrangement as evidenced by the severe conditions required by Crandall to isomerize **12**.[3b] As seen, however, the comparable rearrangement to 1,2-dimethylenecyclobutane **24** is not observed. Apparently the process is derived *via* a 1,5-hydrogen shift mechanism either at the diradical stage or from **24** itself to form the triene **23**.[14] We observed similar trienic products being formed in static pyrolysis conditions at temperatures >300° for **14** and **15**, but did not characterize these reactions in greater detail in view of Crandall's results.



Discussion

It is apparent that there is a very definite energy barrier which separates the reactions of the biscyclopropylidenes from the more drastic rearrangements of the methylenespiropentanes. This energy barrier appears to be essentially that of cleavage of the cyclopropyl radical to the allyl radical. The activation energy for this electrocyclic ring opening has not been accurately ascertained, but a maximum value of 18 kcal/mol has been placed on the process by Gordon.[16] Others have noted this unexpected energy barrier in various reactions thought to involve the cyclopropyl radical.[17]

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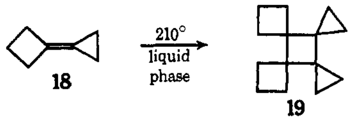
(12) We have also only recently observed the dimerization of cyclopropylidenecyclobutane in the liquid phase. Further amplification of the scope of these dimerization processes is forthcoming.



(13) F. F. Caserio, S. H. Parker, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5507 (1958).

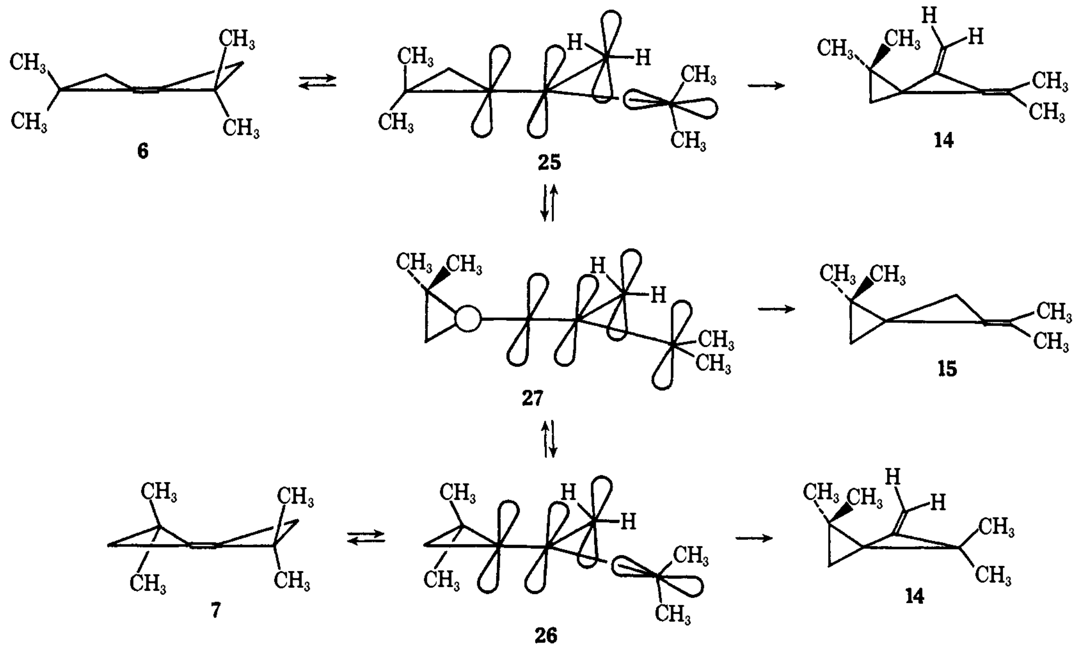
(14) Kiefer has reported a detailed study of such 1,5-hydrogen shifts of 1-alkylidene-2-methylenecyclobutanes and finds that they occur at temperatures as low as 200°.[15]

(15) E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969).

(16) A. S. Gordon, *Pure Appl. Chem.*, **5**, 441 (1962).

(17) D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).

Scheme II



Reactions Involving Trimethylenemethane Intermediates. The lower temperature conversions of biscyclopropylidenes to methylenespiropentanes and the equilibration of methylenespiropentanes seem to bear very close analogy to simple methylenecyclopropane rearrangements which have been of considerable interest ever since Chesick did his initial pyrolytic study on ethylidenecyclopropane.[18]

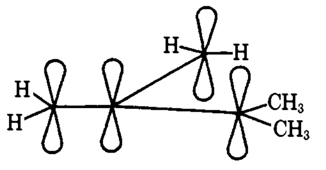
There has been considerable literature in recent years on the possible intermediacy of trimethylenemethane diradicals in such rearrangements[19] and most recently there has been much discussion as to the importance of *nonplanar* trimethylenemethane species in methylenecyclopropane rearrangements.[3c,20] It seems that indeed our results on the thermal conversions of 6 and 7 can only be rationalized satisfactorily by the invocation of *nonplanar* diradicals **25**, **26**, and **27**.[21]

Thus **6** and **7**, upon initial cleavage, form diradicals **25** and **26**, respectively (Scheme II). Doering has demonstrated that in such cleavages the atom which bears the substituents more highly stabilizing a free radical assumes the role of the perpendicular or pivot group.[20c] Other than simple reverse of the cleavage step, both **25** and **26** should show a kinetic preference for cyclization to **14**, the formation of which requires merely a rotation of the cyclopropyl moiety so as to interact with the reactive orthogonal tertiary radical. The most acceptable alternative to formation of **14** is the conversion of **25** or **26** to another orthogonal diradical, **27**. Thermodynamically **27**, should be similar in energy to **25** and **26**, since the dimethylcyclopropyl group should be similar in steric demand to the dimethyl tertiary group. **27**, contrary to **25** and **26**, should be able to close readily to **15**. Thus **6** and **7** *via* initially formed **25** and **26** produce a product mixture of **14** and **15** because of a leakage of **25** and **26** to **27**.

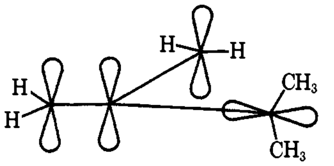
If this mechanistic model is correct it should also be able to predict the *larger* ratio of **14**:**15** found in the pyrolysis of **7**. While not being unambiguous, one can be reasonably safe in suggesting that the cis diradical **25** should be *less stable* than the trans diradical **26** because of the interactions of the four methyl groups in **25**, and that **25** then might be more prone to rotation to diradical **27** which would provide release of such steric strain.

It should be noticed that the *planar* diradicals have *not* been invoked as being key intermediates in these reactions, and *with good reason*. First such diradicals would be expected to cyclize predominantly to **15** in that it has been demonstrated that the primary radical center should be more reactive than the tertiary center. Holroyd and Klein have shown, for instance, that the primary site of the 1-methylallyl radical is *twice* as reactive as the secondary site in trapping methyl radicals.[22]

Second, extended Hückel calculations have been used to establish the preferred geometry of the 1,1-dimethyltrimethylenemethane diradical **28**. These calculations indicate that the *nonplanar* species **28b** is substantially more stable than in the planar **28a**, perhaps by as much



28a



28b

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[18] J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963).

[19] P. Dowd, G. Senqupta, and K. Sackdev, *ibid.*, **92**, 5726 (1970), and references therein.

[20] (a) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970); (b) J. J. Gajewski, *ibid.*, **90**, 7178 (1968); (c) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

[21] Stereochemical studies by Doering and Gajewski have conclusively ruled out symmetrical intermediates. The possibility of concerted mechanisms has been discussed by them also and ruled out as a probable dominant pathway.[20b,c]

[22] R. A. Holroyd and G. W. Klein, *J. Phys. Chem.*, **69**, 194 (1965).

as 14 kcal/mol.[23] Other nonplanar species (*i.e.*, a methylene out of plane) are even less stable than **28a**. It thus seems appropriate to propose a mechanism which does *not* necessitate the intermediacy of planar diradicals.

While **14** and **15** are not interconverted appreciably under the conditions of the pyrolyses of **6** and **7**, by heating to higher temperatures one can effect this interconversion, thus determining that **15** indeed *is* thermodynamically favored by about 3:1 over **14**. This interconversion, based on the arguments just made, probably takes place largely *via* the nonplanar diradical **27** (Scheme III). While **25** and **26** should be formed equally as readily as **27** from **14**, except for some leakage to **27**, they should be relatively unimportant in the interconversion of **14** and **15**.

Scheme III

$$\begin{tikzcd} \mathbf{14} \arrow[r, rightleftharpoons] \arrow[d, shift left] & \mathbf{27} \arrow[r, rightleftharpoons] & \mathbf{15} \\ \textbf{25 and 26} \arrow[u, shift left] \end{tikzcd}$$

Thus while it is still possible that the planar trimethylenemethane diradical could be more stable in the case of the parent molecule, it appears that the mere substitution of *a single* methyl group in the system swings the thermodynamic conformational preference to a nonplanar species.[20b] While this kind of substituent sensitive variability of ground-state geometry preference for diradicals has only been verified for the trimethylenemethane diradical, one can be quite certain that the same principle will also apply to other diradicals. Indeed, the rather general usage of methyl groups and even larger substituents as stereochemical *labels* in cycloaddition processes and in thermal reorganizations should be always subjected to the closest scrutiny. It should be apparent that *stereospecificity* in such reactions can be rationalized not only in terms of concerted processes, but also by invoking *steric control* of the reaction pathways.

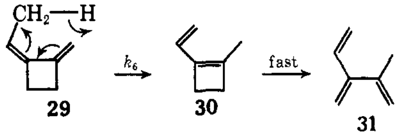
Comment should also be made about the absence of biscyclopropylidene (**1**) in equilibrium with **2**, and the lack of **6** or **7** in equilibrium with **14** and **15**. This is particularly unexpected in view of the equilibrations of the cyclopropylidenecycloalkanes as shown in Table I.

The change in activation parameters as one goes from $n = 5$ to $n = 2$ indicates an increase in inherent[24] strain in *both* **20** and **21**, with the values for k_{eq} showing that at least from $n = 5$ to $n = 3$ the strain factors are similar for **20** and **21**. Since the strain values for methylenespiropentane and for biscyclopropylidene have not been determined experimentally, one must speculate as to the source of the large equilibrium constant where $n = 2$. It is possible, however, to obtain a measure of the *difference* in heats of formation of biscyclopropylidenes **6** and **7** and methylenespiropentanes **14** and **15** from our kinetic data. Since conversion of **6** and **7** to **14** and **15** and interconversion of **14** and **15** pass through a common intermediate **27**, the difference in the activation energies for these two processes should provide a *minimum* value for the difference in energy between **6** or **7** and **14** and **15**. The difference in heats of formation of the transition states for the two processes would have to be known to get a more accurate measure by this method. In any event, this calculated minimum value turns out to be *7 kcal/mol*, a rather substantial difference.

An estimate can be made of the differences of heats of formation of biscyclopropylidene (**1**) and methylenespiropentane (**2**) using Franklin's group equivalents[25] and the known strains of model compounds. Strain-free $\Delta H_f°$'s are +3.0 and +5.0 kcal/mol for **1** and **2**, respectively. To the $\Delta H_f°$ of **1** one must add twice the strain due to an exocyclic double bond on a cyclopropane, a value which has been ascertained to be between +11 and +13.5 kcal/mol.[26] To the $\Delta H_f°$ of **2** one must add +8.7 kcal/mol (strain of spiropentane system) and a single increment of strain due to the exocyclic double bond on cyclopropane. Thus the $\Delta\Delta H_f°$ between **1** and **2** would be predicted to be from −4.3 to −6.8 kcal/mol. This, of course, indicates that the strong thermodynamic preference for **2** is roughly predictable. A knowledge of heats of combustion of the various homologs of **20** and **21** would be of great value in interpreting our data on the systems definitively.

Thus by providing energies of between 39 and 46 kcal/mol, one can observe the methylenecyclopropane interconversions of **1** and **2** *via* some type of trimethylenemethane diradical **4**. At elevated temperatures (*i.e.*, >300°) one begins to see k_3 become significant, and it appears that diallyl diradicals, **5**, are formed. From these observations it appears that $k_1 > k_2$ and that $k_{-2} >> k_3$. It also seems probable that the diallyl diradicals **5**, when formed, should cyclize rapidly to the appropriate 1,2-dimethylenecyclobutane species **3**.

This, however, has in fact only been observed in the case of the *parent* molecule. It has now been reasonably established that *methylated* 1,2-dimethylenecyclobutanes easily undergo 1,5-hydrogen shifts *via* transition states such as **29** under conditions *even milder* than those required for k_3 to be significant. The activation energy for similar 1,5-hydrogen shifts has been found to be around 35 kcal/mol.[27] It seems probable that the trienes are formed *via* such intermediate, short-lived 1,2-dimethylenecyclobutane species, although a 1,5-hydrogen shift (k_5) of diradical **5** itself competing with cyclization to **3** cannot be ruled out at this time. The energy surface for the C_6H_8 system as we now understand it is summarized in Figure 1.



29 **30** **31**

One last interesting point should be raised regarding the results of the methylenespiropentane rearrangement. This has to do with the significant amount of 1,3-dimethylenecyclobutane (**22**) formed in competition with the formation of 1,2-dimethylenecyclobutane (**3**). With **22** constituting about one-seventh of the kinetic

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(23) M. T. Vala and J. Wrobel, unpublished results; personal communication.

(24) By inherent strain, one means that strain which cannot be accounted for by simple summing of the component strains; *i.e.*, spiropentane with a strain energy of 63.1 kcal/mol has 8.7 kcal/mol *inherent* strain since each cyclopropane unit should contribute only 27.2 kcal/mol.

(25) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(26) (a) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (b) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

(27) W. R. Roth and J. Konig, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966).

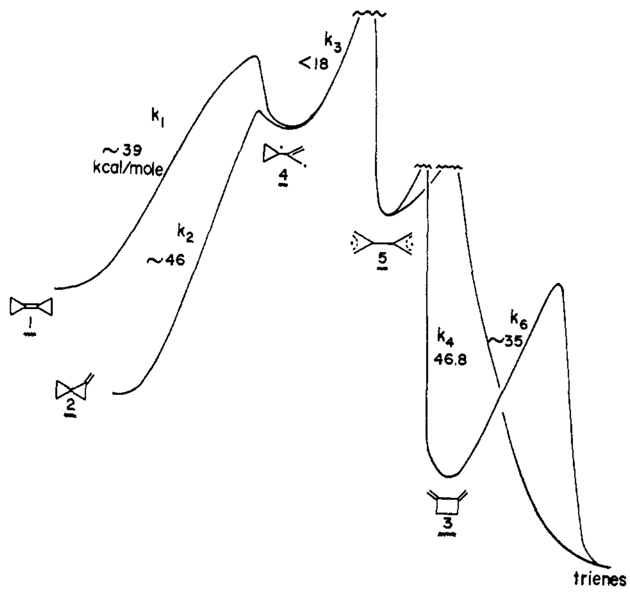
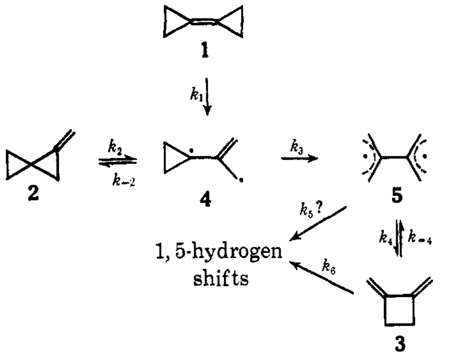


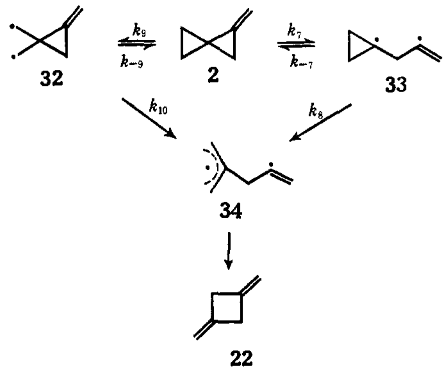
Figure 1. Energy surface for C_6H_8 molecules.

product, this means that the transition state leading to diradical **34**, formed *via* either **32** or **33**, cannot be much different in energy from that leading to the diallyl diradical (Scheme IV). If this effective competition arises from steps 2 and 3 (of Scheme IV) competing with steps 7 and 8 (of Scheme V), then one has no alternative but to say that cleavage to a vinyl radical (step 7) competes kinetically with cleavage to an allyl radical (step 2) in the initial cleavage process since steps 3 and 8 should be energetically alike.

Scheme IV. Reorganizations Involving the Diallyl Diradical



Scheme V



On the other hand, if the route to **22** were *via* steps 9 and 10, then one has a rational explanation for its formation. The activation energy for formation of diradical **32** should be quite high, significantly higher than that for formation of **4**. The two possible second steps, that is, cleavage either to diallyl species **5** or to allylvinyl species **34**, should be of relatively *low* activation energy.[28] If this second step is, as postulated, of relatively low activation energy, then the *selectivity* of cleavage should become less pronounced. Moreover, in such a process where the products are so much more stable than the precursor, the transition states for cleavage should resemble closely the structure of the *precursor* diradical **32** and should have attained very little of the final stabilization (or lack of it) of **5** (or **34**).

Thus, while the methylenecyclopropane-type rearrangements discussed in the earlier section undoubtedly proceed *via* cleavage to the trimethylenemethane species **4**, it may well be that because of the high activation energy necessary for cleavage of the cyclopropyl radical, a significant amount of high activation energy product may come *via* the alternative pathway of initial C_4–C_5 cleavage followed by either C_2–C_3 or C_3–C_1 cleavage.

Experimental Section

Analyses were determined by Atlantic Microlab, Inc., Atlanta, Ga. 30308. The glpc analyses were carried out on a Varian Aerograph Model A-90-P3 gas chromatograph combined with a Leeds and Northup Model H recorder equipped with a Disc integrator. Ir spectra were recorded with a Perkin-Elmer Model 137 spectrophotometer, KBr prism; nmr spectra on a Varian Model A-60-A spectrometer, utilizing TMS as an internal standard; mass spectra on a Hitachi Perkin-Elmer RMU-6E mass spectrometer; uv spectra on a Cary 15 spectrometer.

2,2-Dihydroxymethylmethylenecyclopropane. The reaction procedure was that of Buchta.[30] Diethyl methylenecyclopropane-2,2-dicarboxylate (32.0 g, 0.162 mol) in 425 cc of ether was used with 9.4 g (0.249 mol) of $LiAlH_4$ in 275 cc of ether. The yield of diol was 12.0 g and the nmr indicated that it was somewhat contaminated by H_2O and EtOH. Soxhlet extraction yielded an additional 3.3 g of diol of similar purity. The total crude yield was thus 83%. Drying under vacuum improved the purity somewhat and the resulting still impure diol was used directly in the subsequent reaction. The nmr of the diol as a relatively viscous liquid gave only broad singlets at δ 1.15, 3.60, 4.87, 5.34, and 5.51 ppm, with the relative areas of 2:4:2:1:1. These peaks undoubtedly represent the cyclopropyl, the hydroxymethy, the hydroxy, and the two vinyl protons, respectively.

2,2-Dibromomethylmethylenecyclopropane (10). To 28 g of triphenylphosphine in 50 cc of DMF at 0° under nitrogen was added 14.4 g of Br_2. The temperature was kept below 20° during the addition. After stirring the white slurry for 0.5 hr, a solution of 5 g of diol in 6.9 g of pyridine and 15 cc of DMF was added and the mixture was stirred for 6–7 hr below 40°. The pale yellow solution was distilled under vacuum into a trap cooled by a Dry Ice bath. The distillate was poured into water and the organic layer was separated and dried. The nmr indicated the product to be quite pure dibromide: a triplet (J = 2.2 cps) at δ 1.43 ppm (2 H), a singlet at δ 3.50 (4 H); a pair of triplets at 5.26 (J = 2.0 cps) (1 H) and 5.51 ppm (J = 2.8 cps) (1 H). These peaks represent the cyclopropyl, the bromomethyl, the cisoid, and the transoid vinyl protons, respectively. The dibromide was used without further purification for the next step.

Methylenespiropentane (2). The procedure was essentially that of Applequist.[8] To a mixture of 9.05 g of NaOH, 11.4 g of EDTA, 0.25 g of NaI, and 3.25 g of zinc dust in 14.9 cc of water and 24 cc of ethanol was added 6.0 g of dibromide in 10 cc of ethanol. The

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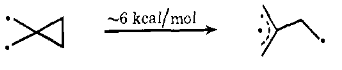
[28] Gilbert has shown that geometrical isomerization of 1,2-dideuteriospiropentane has an activation energy reasonably close (51.5 kcal/mol) to that for rearrangement to methylenecyclobutane (57.6 kcal/mol).[29] This *difference* may be due to a process very similar to the one we are interested in.



[29] J. C. Gilbert, *Tetrahedron*, **25**, 1459 (1969).

[30] E. Buchta and M. Fischer, *Ber.*, **99**, 1509 (1966).

mixture was refluxed gently for 12 hr with a slow stream of nitrogen blowing volatile product into a trap cooled by a Dry Ice–acetone slurry. The product was taken up in a small amount of ether, washed with water, and dried over anhydrous K_2CO_3. Glpc on 0.25 in. × 9 ft 10% SE-30 on Chromosorb P column at 40° showed two equal size components, methylenespiropentane and 2,3-dimethylbutadiene, which were easily collected and purified. The nmr showed three cyclopropyl absorptions, two broad peaks with ill-defined splitting ($J < 1$ cps) at δ 1.02 (2 H) and 1.2 ppm (2 H), and a broad triplet ($J = 2$ cps) at δ 1.33 ppm. The vinyl absorptions appeared as a broad triplet ($J > 2$ cps) at δ 5.08 ppm (1 H) and as a broad peak of ill-defined multiplicity ($J < 1$ cps) at δ 5.21 ppm (1 H). Bands in the ir spectrum (gas, 39 mm) appear at 3081 (s), 3010 (s), 1797, 1743 (w), 1360 (w), 1165, 1084, 1005, and 881 cm^{-1} (s). The mass spectrum showed a parent peak at *m/e* 80.

Anal. Calcd for C_6H_8: C, 89.94; H, 10.06. Found: C, 90.01; H, 10.02.

Dispiro[2.1.2.0]heptane (11). Zn/Cu couple was prepared using granular zinc.[31] To 3 g of Zn/Cu couple in 10 cc of ether were added 1 g of the methylenespiropentane–2,3-dimethylbutadiene mixture and 14 g of methylene iodide. The mixture was stirred for 48 hr under N_2 using a balloon so as to retain the solvent and starting materials. All of the volatile components of the mixture were transferred from the nonvolatile residue on a vacuum line and the volatile components were purified by glpc on the 0.25 in. × 9 ft SE-30 column at 40°. The last two peaks, the major product peaks, were collected and shown to be dispiro[2.1.2.0]heptane and 1,1′-dimethyldicyclopropyl, respectively. The dispiro[2.1.2.0]heptane revealed an nmr with two multiplets, symmetrical about each other at δ 0.57 and 0.78, and a singlet at δ 1.14 ppm, with relative intensities of 2:2:1. The mass spectrum showed a parent peak at *m/e* 94.

Anal. Calcd for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.08; H, 10.69.

Pyrolysis of *cis*- and *trans*-2,2,2′,2′-Tetramethylbiscyclopropylidenes (6 and 7). The reorganizations were carried out smoothly and without appreciable variation in the rate constant using 11–200 mm pressure of either cis or trans starting material, sealed under vacuum in a 6.3–27.3 cc Pyrex tube. Wall effects were noticeable but could be eliminated by conditioning the tube by at least three runs. The tubes were heated in a well-insulated, well-stirred bath containing GE-SF-1093 (100) silicone fluid. This oil did not decompose even at the highest temperatures used in our studies. Evaporation of the fluid was slow. The bath was heated by one 500-W bar heater to a temperature 10° below that desired. A smaller 100-W coiled-wire heater enclosed in glass tubing was used in conjunction with a Hallikainen platinum resistance thermometer (Model 1146) and a Hallikainen Resistotrol, on-off type, temperature regulator to bring the temperature to the desired value and to maintain it there. The temperature variation at the highest temperature used was no more than ±0.15°. The bath temperature was homogeneous to better than ±0.02° in the region of the sample tubes. Temperatures were monitored using a calibrated iron–constantan thermocouple in conjunction with a Honeywell Model 2702 potentiometer. Each tube was withdrawn from the bath at an appropriate time, cooled, opened, the contents diluted with methylene chloride and analyzed by glpc using a 0.25 in. × 10 ft DEGS, 10% on Chromosorb P column. Each tube's glpc results constituted a single point in determining a rate constant (Tables II and III).

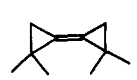
Table II. Kinetic Data for Thermal Reorganization of **6**

Temp, °C	$k_1 \times 10^5$ sec^{-1}	**14:15**
170	4.04 ± 0.20	3.50
180	10.61 ± 0.40	3.45
190	27.67 ± 1.1	3.39
200	66.53 ± 3.5	3.40

Table III. Kinetic Data for Thermal Reorganizations of **7**

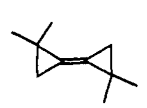
Temp, °C	$k_1 \times 10^5$ sec^{-1}	**14:15**
180	12.21 ± 0.15	14.7
190	30.90 ± 0.7	13.8
200	75.12 ± 1.5	13.2

The nmr spectra (δ, parts per million) of the starting materials **6** and **7** and the products **14** and **15** are below.



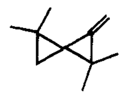
6

δ 0.96 singlet (4 H)
1.13 singlet (12 H)



7

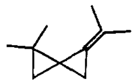
δ 0.93 singlet (4 H)
1.15 singlet (12 H)



14

δ 0.67 doublet (1 H)
0.91 doublet (1 H)

1.17 triplet (12 H)
4.90 singlet (1 H)
5.11 singlet (1 H)



15

δ 0.88 singlet (2 H)
1.03 broad multiplet (2 H)
1.16 doublet (6 H)
1.72 singlet (3 H)
1.86 singlet (3 H)

Thermal Equilibration of 2,2,4,4-Tetramethylmethylenespiropentane (14) and 4,4-Dimethylisopropylidenespiropentane (15). Pyrolyses were carried out exactly as in the previous set of experiments. The recovery yields were >90% as based on experiments utilizing dioxane as an internal standard (Table IV).

Table IV. Kinetic Data for the Thermal Interconversion of **14** and **15**

Temp, °C	$(k_2 + k_{-2}) \times 10^6$ sec^{-1}	K_{eq}/**14:15**
220	2.12 ± 0.15	0.337
230	5.43 ± 0.15	0.340
240	12.7 ± 0.8	0.318
250	21.2 ± 1.0	0.323

Thermal Reorganizations of Cyclopropylidenecycloalkanes.[32] These experiments were carried out explicitly as in the previous two sets of experiments, except that pressures <100 mm were necessary to eliminate bimolecular processes which were later determined to be dimerizations[12] (Tables V–VII).

Table V. Thermal Equilibration of Cyclopropylidenecycloalkanes, $n = 3$

Temp, °C	$(k_1 + k_{-1}) \times 10^5$ sec^{-1}	K_{eq}
190	2.99 ± 0.03	0.744
200	7.52 ± 0.7	0.777
205	12.2 ± 0.5	0.792
211	18.5 ± 0.3	0.791
220	42.2 ± 2.0	0.823

Table VI. Thermal Equilibration of Cyclopropylidenecycloalkanes, $n = 4$

Temp, °C	$(k_1 + k_{-1}) \times 10^5$ sec^{-1}	K_{eq}
190	2.40 ± 0.10	
200.3	6.24 ± 0.35	0.314
311	15.7 ± 1.0	
220.8	38.8 ± 3.0	0.312

Thermal Reorganization of Methylenespiropentane (2). These pyrolyses were carried out using 10–23 mm pressure of hydrocarbon in a 566 cm^3 Pyrex tube sealed under vacuum and heated in a stainless steel tube furnace. **2** could be recovered unchanged after 20 hr at 209 ± 2°. When heated for 10 hr at 300°, however, reaction

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(31) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(32) The cyclopropylidenecycloalkanes were prepared as described in J. Vincent, A. Bezaguet, and M. Bertrand, *Bull. Chim. Soc. Fr.*, 3550 (1967).

Table VII. Thermal Equilibration of Cyclopropylidenecycloalkanes, $n = 5$

Temp, °C	$(k_1 + k_{-1}) \times 10^5$ sec^{-1}	K_{eq}
211	1.95 ± 0.07	1.23
220	4.76 ± 0.20	1.15
225	7.13 ± 0.73	1.20
229.9	12.2 ± 0.65	1.14
239.9	27.6 ± 1.4	1.06

did occur. Glpc analyses on a 0.25 in. × 15 ft 10% dimethylsulfolane on 60–80 Chromosorb P column indicated that 92% **2** remained with two products being formed in a ratio of 7:1. A good recovery yield was obtained in this case. When heated to 320 ± 2° for 20 hr, only a 40% recovery of volatile materials was possible. The volatile mixture was shown to consist of 60.6% **2**, 15.8% 1,2-dimethylenecyclobutane, and 18.8% 1,3-dimethylenecyclobutane. The nmr and ir spectra of the former product were identical with those of an authentic sample, while those of the latter product were consistent with those in the literature.[13]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grants 753G and 35210A1, 4), and to the Research Council of the University of Florida for partial support of this research.

Cleavage of Cyclopropanes by Diborane[1]

Bruce Rickborn* and Stanley E. Wood

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. Received October 14, 1970

Abstract: Cyclopropanes are cleaved by diborane at about 100°. The reaction is quite regioselective, the products being derived from the addition of hydrogen to the most substituted and boron to the least-substituted carbon. In contrast to the hydroboration of olefins, the cyclopropane cleavage reaction is inhibited by ethereal solvents. The reaction with 1-methylnorcarane was studied in detail; the predominant products after oxidation are (initially) *cis*- (60%) and *trans*-2-methylcyclohexylmethanol (40%). Nonstereospecificity is inherent in the cleavage reaction, and a planar intermediate is proposed. Tetraborane (B_4H_{10}) is comparable to, or somewhat more reactive than diborane. Pentaborane (B_5H_9) under similar conditions does not cause cleavage. The rearrangement of 1,2-dimethylcyclohexylborane (from hydroboration of 1,2-dimethylcyclohexene) was found to occur with initial high selectivity, giving up to 97% *cis*-2-methylcyclohexylmethylborane. An intramolecular borane–olefin complex mechanism is proposed to account for this observation.

Cyclopropane cleavage reactions are of special interest as potential models for the stereochemical study of electrophilic substitution at saturated carbon.[2] Numerous Lewis acid reagents will open the three-membered ring, but in general these give complex mixtures of products.[3] The analogy between olefins and cyclopropanes has often been drawn, and the reactions of one group frequently are paralleled by those of the other. In view of the synthetic importance of hydroboration,[4] it was of interest to explore the reaction of diborane with cyclopropanes. Graham and Stone[5] some time ago reported that unsubstituted cyclopropane reacts in the vapor phase with diborane to give moderate amounts of tri-*n*-propylborane.[6] Apparently no other studies of this reaction have been made.

Regioselectivity of the Cleavage Reaction. Norcarane (**1**) reacts smoothly with diborane at 100° (sealed tube), in a highly regioselective cleavage process.[10] Representative results, obtained by analysis of the alcohols obtained after alkaline peroxide oxidation of the boranes, are shown in Table I. The borane leading to cyclohexylmethanol (**2**) comprises ≥95% of the initially formed cleavage product; scission of the interior C_1–C_6 bond (giving cycloheptanol **4**) occurs to the extent of at most a few per cent. The methylcyclohexanols **3** result largely or exclusively from rearrangement of the initially formed cyclohexylmethylborane (see Table I, footnote *a*, and later discussion).

The runs shown in Table I were carried out to explore the effects of changes in variables on product distribution. Increasing temperature and time, while causing greater reaction, do not appreciably affect the regioselectivity of the reaction. The addition of pentane (run 9) has little effect; the hydrocarbon apparently functions only as a diluent. The oxygen-containing solvents ether, THF, and diglyme, on the other hand, all

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[1] This work was supported in part by the Petroleum Research Fund (1442-A4), administered by the American Chemical Society, and by the National Science Foundation (GP 6043).

[2] F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

[3] See, for example, (a) R. T. LaLonde, J. Ding, and M. A. Tobias, *J. Amer. Chem. Soc.*, **89**, 6651 (1967), and earlier references; (b) R. J. Ouellette, R. D. Robins, and A. South, Jr., *ibid.*, **90**, 1619 (1968); (c) S. Moon, *J. Org. Chem.*, **29**, 3456 (1964); (d) R. Ya Levina, V. N. Kostin, P. A. Gembitskii, and A. D. Vinogradov, *Vestn. Mosk. Univ., Khim.*, **16** (II), 67 (1961) (*Chem. Abstr.*, **56**, 14091*b* (1962)); (e) D. J. Abraham and W. E. Truce, *J. Org. Chem.*, **28**, 2901 (1963).

[4] H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

[5] W. A. G. Graham and F. G. A. Stone, *Chem. Ind.* (*London*), 1096 (1957).

[6] The cleavage of unsubstituted cyclopropane by lithium aluminum hydride in ether has also been reported.[7] However, later work[8] and our own attempts[9] indicate that this reaction is not general.

[7] C. F. H. Tipper and D. A. Walker, *Chem. Ind.* (*London*), 730 (1957).

[8] H. Goldwhite, M. S. Gibson, and C. Harris, *Tetrahedron*, **20**, 1613 (1964).

[9] Unpublished work of J. H. Chan.

[10] A preliminary report of this result has been published: B. Rickborn and S. E. Wood, *Chem. Ind.* (*London*), 162 (1966).