Table I. Kinetic and Thermodynamic Data for the Thermal Isomerization of Metacyclophane-1,9-dienes (17 and 18) to Dihydropyrenes (16 and 15)[a]

Compound	$k(4°)$	$k(17°)$	$k(30°)$	$k(50°)$	$E_a(30°)$	$\Delta G^{\ddagger}(30°)$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
17[b]			0.00020	0.0016	20.1	25.3	19.5	−19.2
18[c]	0.91	4.8	>6		20.4	18.3	19.8	+4.8

[a] Rates are in min^{-1}, E_a, $\Delta G^{\ddagger}$, and $\Delta H^{\ddagger}$ in kcal/mole, $\Delta S^{\ddagger}$ in $caldeg^{-1}\ mol^{-1}$. [b] Solvent, cyclohexane. [c] Solvent, methanol.

Photoisomerization Studies of *trans*-1,3,15,16-Tetramethyl-2-azadihydropyrene (16). A. Nmr Spectrum of the Photoisomer 17. A solution of **16** in deuteriochloroform contained in an nmr tube was irradiated using a 100-W Mazda lamp until most of the dark green color had disappeared. The loss in intensity of the normal nmr signals for **16** indicated about a 65% conversion to the photoisomer **17**. The new signals introduced by irradiation and assigned to **17** included a multiplet at τ 2.5–3.5 (7 H, Ar*H* and -C*H*=C*H*-), singlet at 7.53 (6 H, $ArCH_3$), and singlets at 8.50 and 8.58 (3 H each, $ArCH_3$). When this sample was allowed to stand in the dark for 3 days, the signals corresponding to **16** increased and those for **17** decreased, indicating a ratio of **16** to **17** of 9:1 after this period of time in the dark.

When a solution of **15** in methanol was irradiated, it quickly became colorless. However, on removal of the solution from the light, the color returned within seconds and it was not possible under these conditions to obtain an nmr spectrum of **18**.

B. Kinetic Studies of the Thermal Reversion (17 → 16, and 18 → 15). The kinetics of the thermal reversion were studied by irradiating solutions of **15** or **16** with a 100-W Mazda lamp until essentially all of the color had disappeared and then the solutions were placed in a Cary 15 spectrometer equipped with a temperature-controlled holder and the increase in concentration of **15** or **16** was followed using the change in optical density at 538 mμ for **15** and that 478 mμ for **16**. These data were utilized in a computer program to obtain the activation parameters.[8] The results are summarized in Table I.

(8) C. E. Klopfenstein and C. Wilkins, "Chemistry 40 Rate Constant Calculator" University of Oregon, 1964.

Alkyl Shifts in Thermolyses. II.[1] Rearrangement of Isopropenylspiropentane and Its Axially Dissymmetric 4-Methyl Derivatives[2]

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Contribution No. 1801 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received October 15, 1969*

Abstract: Upon thermolysis, isopropenylspiropentane is found to undergo unimolecular rearrangement to 5-methylspiro[2.4]hept-4-ene and 1-isopropenyl-2-methylenecyclobutane. Both products are most easily derived by initial 1,2 (peripheral) bond fission, and the latter material is formed by a vicinal alkyl shift pathway that may be related to the cyclopropylcarbinyl radical rearrangement. Evidence for reversible peripheral bond fission was obtained from partial pyrolysis of the four axially dissymmetric 1-isopropenyl-4-methylspiropentanes in which epimerization only at C-1 occurred at the same rate as rearrangement. Discussion focuses on the relative ease of the vicinal alkyl shift in spiropentane thermolysis and on the relative rates of various steps on the energy surface characteristic of the compounds described.

Migrations of groups to adjacent atoms deficient in electrons[3a,b] are well known in organic chemistry, while vicinal shifts to radical[3c,d] and anionic[3e] sites are rare, particularly when the migrating group is a hydrogen or a saturated carbon. Well-known theoretical considerations have justified these observations.[4] On the other hand, vicinal hydrogen atom rearrangements are commonplace in cyclopropane thermolyses,[5] suggesting that there might be favorable electron interaction in the transition state for this process. Unfortunately, there is a dearth of bonafide examples of pyrolytic vicinal alkyl shifts in the cyclopropane series or, for that matter, in any organic system.[6]

A rearrangement which could proceed by a vicinal alkyl shift pathway is the spiropentane (**1**) to methylenecyclobutane (**5**) thermal rearrangement studied by Burkhardt[7] and by Frey[8] who also determined that log k (unimol) at medium to high pressures is $15.86–57{,}570/2.3RT$. There is, however, another likely pathway for this isomerization. The two pathways involve sequential cleavages of the two different kinds of carbon–carbon bonds in the starting material and differ only in

(1) For part I, a preliminary communication of some of these results, see J. J. Gajewski, *Chem. Commun.*, 920 (1967).

(2) Presented in part at the 155th American Chemical Society National Meeting, San Francisco, Calif., 1968, P-28, and at the IUPAC Symposium on "Valence Isomerism," Karlsruhe, Germany, Sept 1968.

(3) (a) "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963; (b) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967; (c) C. Walling in ref 3a, Chapter 7; (d) R. Kh. Freidlinn in "Advances in Free-Radical Chemistry," Vol. I, G. H. Williams, Ed., Academic Press, New York, N. Y., 1965; (e) H. E. Zimmerman in ref 3a, Chapter 6.

(4) See, for example, H. E. Zimmerman in ref 3a, pp 394–379.

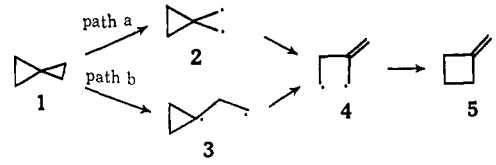
(5) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 148 (1966).

(6) For examples of alkyl shifts in rearrangements, see (a) E. T. McBee, J. A. Bosome, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966); (b) J. W. Perlaan and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 1594 (1965); (c) M. Jones, Jr., *J. Org. Chem.*, **33**, 2538 (1968); (d) C. McKnight and F. S. Rowland, *J. Amer. Chem. Soc.*, **88**, 3179 (1966); (e) D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Can. J. Chem.*, **43**, 1389 (1965); (f) W. Adam and Y. M. Cheng, *J. Amer. Chem. Soc.*, **91**, 2109 (1969); W. Adam, *et al.*, *ibid.*, **91**, 2111 (1969).

(7) P. J. Burkhardt, *Dissertation Abstr.*, **23**, 1524 (1962).

(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961).

the order of cleavage. Thus, homolysis of a peripheral bond (path a, the vicinal shift pathway) to form the diradical **2** followed by rupture of what was initially a radial bond in the other cyclopropane ring gives the diradical **4** which may close to form product. In the alternative process (path b), a radial bond may be broken to give **3**, and subsequent peripheral bond cleavage[9] would give the diradical precursor to methylenecyclobutane. The diradical intermediates envisioned could be replaced by a partly or wholely concerted sequence of bond fissions and formations.



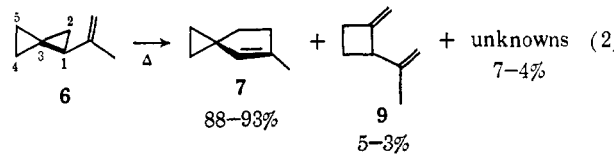
(1)

These possibilities were suggested previously but could not be distinguished experimentally, although initial peripheral bond fission was favored.[10] Other arguments might be mustered to support this conclusion, but a direct test is desirable. We wish to report the results of experiments designed to determine the relative energetics of the two pathways utilizing substituted spiropentanes and to survey the terrain of the energy surface by the use of axially dissymmetric spiropentane systems.

Results

Pyrolysis of Isopropenylspiropentane. At the outset it was clear that no simple or even complex labeling scheme would distinguish between pathways a and b because each one was eightfold degenerate, and the eight different distributions of carbon atoms in the product derived *via* path a (eq 1) were equivalent to those gotten by path b. The approach chosen, then, was one of destroying the reaction path degeneracy by forcing initial bond fission to only one of the four external carbon atoms in spiropentane. It is well known that attachment of a vinyl side chain to cyclopropane systems lowers the activation energy for bond fission by about 15 kcal due to development of allyl radical resonance energy at the transition state.[5] At the same time, in the spiropentane system different products would be expected to result depending on which of the two bonds to the carbon bearing the unsaturated side chain was cleaved initially. Moreover, the presence of the side chain might be expected not to influence dramatically the relative energetics of the two different pathways.

Thus, isopropenylspiropentane (**6**) was prepared and subjected to vapor phase pyrolyses in the range of 235–275° in carefully neutralized sealed tubes at calculated internal pressures of $^1/_3$ to 1 atm. There were two major products formed: 5-methylspiro[2.4]hept-4-ene (**7**) and 1-isopropenyl-2-methylenecyclobutane (**9**) in yields of 88 and 5%, respectively. Approximately ten unknowns constituted the remainder of the product, and none of these latter materials represented more than 1% of the total product. While precise kinetics were not determined, it was found that the activation free energy for loss of starting material was in the neighborhood of 41 kcal/mol.



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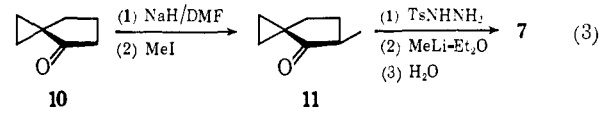
Subsequent experiments using a well-conditioned static reactor with better temperature control revealed that loss of **6** was a clean first-order reaction, and the product distributions were similar to those of the sealed tube pyrolyses except that it proved possible to make more accurate analyses. Thus, the ratio of **7** to **9** at 256° was 16.7 ± 3.6:1, while at 237.8° this ratio was 26:1. Therefore, it can reasonably be assumed that the pyrolyses conducted in the sealed tubes were also homogeneous, unimolecular reactions.

The major product from these pyrolyses was isolated by preparative vpc and identified as **7** by its spectroscopic properties and later by synthesis. As expected for a vinyl cyclopropane in which the π orbital of the double bond is fixed in a position of maximum overlap with the cyclopropyl ring bonds, **7** had a significant uv absorption.[11a–c] In addition, the relatively high field magnetic resonance position of the vinyl hydrogen (δ 4.74) indicated that it was in the shielding region of the cyclopropane ring which again was consistent with structure **7**. While the nmr of **7** might also have been characteristic of an isomer, namely, 5-methylspiro[2.4]-hept-5-ene (**8**), also a possible product from **6**, a Nuclear Overhauser Effect (NOE) experiment confirmed structure **7**.[11d–f] Thus, irradiation of the cyclopropyl hydrogen broad singlet resulted in a 10–20% increase in the intensity of the vinyl hydrogen and one of the methylene groups relative to the methyl hydrogens. Finally, methylation of spiro[2.4]heptan-4-one followed by methyl lithium treatment of the *p*-toluenesulfonylhydrazone gave **7**[12] (eq 3).



(3)

The second most abundant product from pyrolysis of **6** was isolated by preparative vpc and identified as **9**, also by its spectroscopic properties and synthesis. Thus, very strong terminal methylene absorptions in the ir and characteristic *exo* methylene as well as ring proton magnetic resonances served to establish the structure which was confirmed by synthesis from 2-methylenecyclobutane-1-methanol (**12**).[13]

The formation of **7** and **9** could only result from peripheral bond fission if initial cleavage in **6** occurred to C-1. Thus, **7** could be formed *via* an allylic rearrangement of the vinylcyclopropane type, in which the C-1,

(9) For examples of cyclopropyl radical isomerizations to allyl radicals, see G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, **63**, 1369 (1967); **62**, 3338 (1966).

(10) W. von E. Doering and J. C. Gilbert, *Tetrahedron Suppl.*, **5**, 397 (1966).

(11) (a) C. H. Heathcock and J. R. Poulter, *J. Amer. Chem. Soc.*, **90**, 3766 (1968); (b) M. J. Jorgenson and T. Leung, *ibid.*, **90**, 3769 (1968); (c) for examples of cyclopropyl ketones in rigid systems, see W. G. Dauben and C. H. Berezin, *ibid.*, **89**, 3449 (1967); (d) we thank Professor M. R. Willcott for this spectrum; (e) a Nuclear Overhauser experiment (NOE)[11f] suggested and performed by Professor Willcott also points to the structure **7**; (f) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

(12) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 3734 (1967).

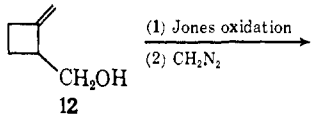
(13) P. S. Bailey, *et al.*, *ibid.*, **77**, 2787 (1955).

Table I. Distribution of Products from Pyrolysis[a-e] of 18, 19, 20, and 21

Starting material	Unknown A	18	21	20	19	22	Unknown B	Unknown C	23	Unknown D
18 (*medial, anti*)[e]	0.4	89	?[d]	0.2	3.6	4.4	0.6	0.7	0.4	0.7
19 (*proximal*)	0.5	11.1	<0.1	0.2	20.2	33.5	12.1	6.5	6.8	7.4
20 (*distal*)	2.1	<0.5	14.5	38	<0.2	5.4	1.8	0.3	3.7	
21 (*medial, syn*)	1.5	<0.05	77	9.6	<0.02	0.6	2.2	0.2	9.2	

[a] At about 245° for approximately 1.25 hr. [b] Products listed in order of increasing retention times on capillary vpc; didecyl phthalate and UCON 50HB2000 were substrates. [c] Up to 5% of as many as six additional materials were also formed in each pyrolysis. [d] Overlapped with tailing edge of **18** on both columns. [e] The stereochemical designations introduced in ref 15 are in parentheses.

C-2 bond of **6** was cleaved (eq 2), and **9** could be formed in a manner analogous to path a (eq 1). However, it



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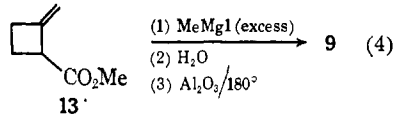
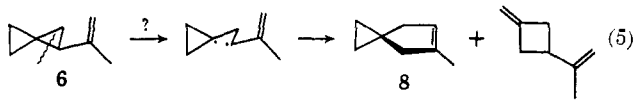


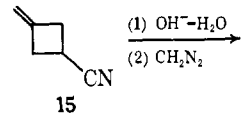
13 9 (4)

was of interest to see if products derived from initial radical bond fission to C-1 were formed. These could be 5-methylspiro[2.4]hept-5-ene (**8**) and particularly 1-isopropenyl-3-methylenecyclobutane (**14**). The latter



6 8 14 (5)

compound was synthesized from 1-cyano-3-methylenecyclobutane (**15**)[14] by hydrolysis, esterification, methyl Grignard addition, and dehydration.



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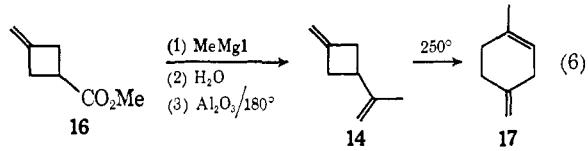
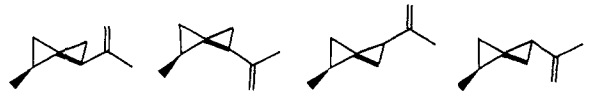


16 14 17 (6)

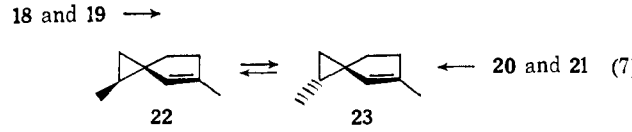
Under conditions necessary to effect rearrangement of **6**, **14** was quantitatively converted to 1-methyl-4-methylene-1-cyclohexene (**17**). A small peak (corresponding to about 1%) in the vapor chromatogram of the pyrolysis reaction mixture from **6** had the same retention time as **17**. Thus, a small amount of radial bond fission in **6** was indicated but not established beyond doubt.

Pyrolysis of the Four 1-Isopropenyl-4-methylspiropentanes. Having established that the predominant mode of reaction in the thermolysis of **6** involved initial peripheral bond fission, it was of interest to determine if intermediates were formed reversibly under the reaction conditions. Recognizing that the ultimate products from thermolysis of **6** need not have represented the relative energetics of only cleavage of the two possible bonds but that of the overall pathways, it was necessary to devise an experiment that might distinguish between reversible peripheral and radial bond fission. Since radial cleavage could disturb the configuration about the axis of dissymmetry in 1,4-disubstituted spiropentanes while peripheral cleavage would not, all four 1-isopropenyl-4-methylspiropentanes, **18–21**, were prepared from the corresponding esters[15] and were subjected to vapor phase pyrolysis at 245°.



18 19 20 21

In every case complex mixtures resulted (Table I); however, the epimerized spiropentane materials were identified by their vpc retention times on two different capillary vpc columns. Among the major products besides the spiropentane epimers were the two 2,5-dimethylspiro[2.4]hept-4-enes, **22** and **23**, which were isolated from pyrolysis of **21** by preparative vpc albeit in only 90–95% purity and identified by the similarity of their nmr spectra to that of **7**. It is clear from Table I that equilibration of the pairs of compounds epimeric at C-1, **18** and **19**, and **20** and **21**, was competitive with the vinylcyclopropane rearrangement analogous to the **6** to **7** conversion. Further, interconversion of the pairs, (**18**, **19**) and (**20**, **21**), took place slowly, if at all, relative to the epimerization at C-1. Finally, it was found in subsequent experiments that the two rearrangement products, **22** and **23**, were interconverted under the reaction conditions at roughly the same rate at which they were formed.



22 23

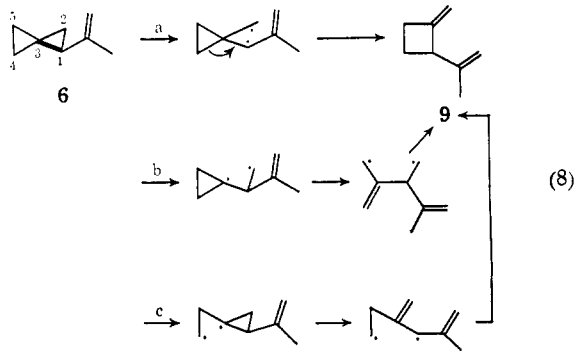
Discussion

Alkyl Shifts in the Thermolysis of Isopropenylspiropentane (6). The formation of 5-methylspiro[2.4]hept-4-ene (**7**) in the pyrolysis of **6** can most economically be derived by a vinylcyclopropane rearrangement involving initial cleavage of the 1,2 (peripheral) bond. Indeed, there appears to be no other precedented sequence of bond shifts that will allow for production of **7** from **6**. However, 1-isopropenyl-2-methylenecyclobutane (**9**) can conceivably arise by three different routes: (a) 1,2 bond cleavage followed by a vicinal alkyl shift to C-1; (b) 2,3 bond fission with subsequent cyclopropyl radical rearrangement to an allyl radical[9] followed by ring closure; (c) 3,4 bond fission with subsequent 1,2 bond

(14) We thank Dr. O. W. Webster of E. I. du Pont de Nemours and Co., Inc., for a generous sample of this material.

(15) J. J. Gajewski and L. T. Burka, *J. Org. Chem.*, in press.

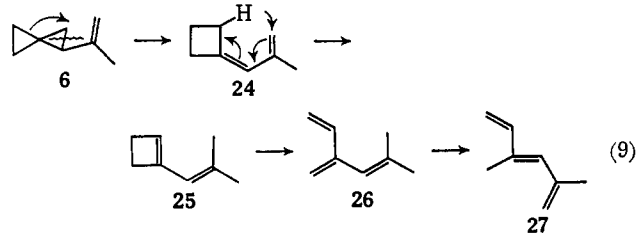
homolysis[9] resulting in a pentadienyl radical which closes to **9**.



(8)

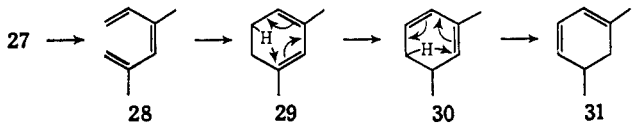
Pathways b and c require initial cleavage of bonds not adjacent to a double bond, and these processes should be at least 10 kcal higher in energy[16] than cleavage of the 1,2 allylic bond (path a). Further evidence against paths b and c arises from the fact that they are mechanistically similar to that depicted in eq 5 wherein 1,3 (allylic, radial) bond fission could give rise to 1-isopropenyl-3-methylenecyclobutane (**14**) and this latter pathway is not traversed despite its relatively favorable energetics. Thus, the vicinal alkyl shift pathway (8a) appears to be the low-energy route to **9** starting with **6**.

However, if **9** were derived by an alkyl shift, it might have been anticipated that a second alkyl-shifted product, namely **24**, should also have been formed (eq 9).



(9)

This material is a good candidate for a 1,5-hydrogen shift[17] leading to **25**, a cyclobutene that could open under the reaction conditions[18] to the triene, **26**. After simple bond rotation, **26** could, in turn, undergo a 1,5-hydrogen shift to the fully conjugated *trans* triene, **27** (eq 9). The latter material then can undergo *trans* to *cis* isomerization[19] resulting in **28** which can cyclize[19] to the cyclohexadiene, **29**. Then **29** can undergo successive 1,5-hydrogen shifts resulting in **30** and **31** (eq 10). All of this is speculative, of course, and isolation and careful analysis of the reaction rates of these materials could verify these predictions—all of which have ample precedence at the temperatures necessary to effect the rearrangement of **6**. Nevertheless, **24**, if formed, would be expected to give a myriad of isomeric materials, some, if not all, of which may constitute the fraction of the product from **6** which is made up of small quantities of unidentified materials.



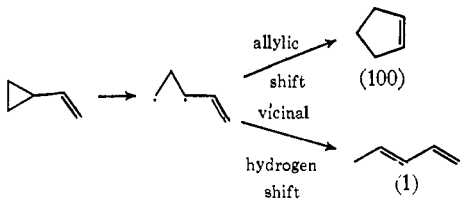
(10)

Comparison of the Alkyl Shift in 6 to Hydrogen and Other Alkyl Shifts in Analogous Rearrangements. The literature does not abound with reports of vicinal alkyl and hydrogen shifts in radical or thermolytic reactions save for the cyclopropane isomerizations. It is interesting that in all substituted cyclopropane isomerizations studied, few, if any, of the derived products can be associated with an alkyl shift pathway. For the most part, this is due to the fact that bond fission invariably occurs to the more highly substituted carbons which usually results in trimethylene-type diradicals with only hydrogen on the β carbon. The thermolyses of the 1,2,3-trimethylcyclopropanes, however, are instances where a hydrogen and a methyl group are necessarily pitted against one another, and the olefinic product is derived exclusively from a vicinal hydrogen shift.[20]

A related comparison of vicinal alkyl and hydrogen shifts is available in the methyl-substituted cyclopentadiene system, although here the rearrangement is, in fact, a 1,5 shift in a 1,3 diene. Nevertheless, the hydrogen shift occurs with remarkable facility below 100°,[21] but a methyl shift requires temperatures above 200°.[6b] Such comparisons are, however, not unique in light of the vast body of information available from simple radical reactions. Radical displacements at hydrogen in hydrocarbons (hydrogen abstraction) and at β hydrogens in radicals (disproportionation) are commonplace, but radical displacements at carbon resulting in alkyl group abstraction are exceedingly rare. Further tributes to the sluggishness of the vicinal alkyl group migration in monoradicals derive from the work of Berson with the 2-bornyl radical[22] and of Kaplan with the cyclobutylcarbinyl radical.[23] The latter example is particularly noteworthy in that a possible alkyl-shifted radical, the cyclopentyl radical, is estimated to be 20 kcal/mol more stable than the starting radical or the actual product-forming species in the reaction, the 1-pent-4-enyl radical.

In light of the lack of proclivity of vicinal alkyl group migrations, it is important to have some estimate of the ease of the rearrangement of **6** to **9**. Conveniently, the thermolysis of **6** includes a reaction component which can serve in this capacity, namely, the vinylcyclopropane rearrangement. Vinylcyclopropane, when heated, gives cyclopentene as well as small quantities of hydrogen-shifted materials.[24] The most abundant of these, *trans*-1,3-pentadiene, is most easily derived by cleavage of the cyclopropyl allylic bond followed by hydrogen transfer (eq 11). The relative ratio of the two products is about 100:1 at 600°K. In the rearrangement of **6**, the vinylcyclopropane rearrangement is only 18–27 times faster than the alkyl shift to give **9** near 500°K. Thus, the alkyl shift in **6** is substantially faster

(16) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2137 (1969), and references contained therein.
(17) (a) J. Wolinsky, B. Chollar, and M. D. Baird, *ibid.*, **84**, 2775 (1962); (b) the activation parameters for the rearrangement in 1,3-pentadiene itself are $\Delta S^{\ddagger} = -7.1$ eu, $\Delta H^{\ddagger} = 35.4$ kcal/mol: W. R. Roth and J. Konig, *Ann.*, **699**, 24 (1966).
(18) K. W. Egger, *Helv. Chim. Acta*, **51**, 422 (1968).
(19) M. R. Willcott and R. Cargill, "Thermal Unimolecular Rearrangements—A Compilation," University of South Carolina Printing Department, Columbia, S. C., 1968, p 3.
(20) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 5717 (1963).
(21) W. Roth, *Tetrahedron Lett.*, 1009 (1964).
(22) J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Amer. Chem. Soc.*, **84**, 3337 (1962).
(23) L. Kaplan, *J. Org. Chem.*, **33**, 2531 (1968).
(24) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962).

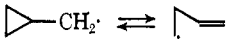


(11)

in a relative sense than a hydrogen shift in a similarly constituted material—vinylcyclopropane.

It is, perhaps, significant that there seems to be no dramatic overall rate enhancement for the alkyl shift in spiropentane thermolyses.[7,8] If it can be argued that the behavior of **6** reflects that of spiropentane itself, *i.e.*, the methylenecyclobutane product results from the vicinal alkyl shift, then the energetics of the spiropentane thermolysis do not suggest[10] any substantial energy benefit from the alkyl shift. Of course, activation parameters for isomerizations do not reflect the energetics for individual steps but for the overall process. Thus, Gilbert has found that the activation energy for geometric isomerization of 1,2-dideuteriospiropentane is about 5 kcal/mol more than what would be anticipated on comparison with the activation energy for the 1,2-dideuteriocyclopropane geometric isomerization including the effect of the extra strain in the spiropentane system.[25] Gilbert's data also indicate that the ratio of geometric to structural isomerization for spiropentane (about 10) is similar to the same ratio in cyclopropane. This suggests that the alkyl shift in spiropentane is about as facile as the hydrogen shift in cyclopropane relative to geometric isomerization. Again this is in accord with the notion previously developed that the spiropentane vicinal alkyl shift is singular among previously reported vicinal shifts in radical and pyrolytic reactions.

The facility of the alkyl shift in spiropentanes may be related to the ring opening of cyclopropylcarbinyl radicals.[26-29] Generation of these radicals invariably leads to products derived from the homoallyl radical (eq 12).



(12)

The rearrangement, therefore, must be faster than chain transfer. Stereochemical studies[26b,27] indicate that the ring-opened radical is reversibly converted to the cyclopropylcarbinyl radical but that the former either reacts faster or is more stable than the latter. Recent esr studies by Kochi[29] reveal that the homoallyl radical is more stable than the ring-closed radical.

In the spiropentane thermolysis an intermediate 1,3 diradical can result from complete fission of the peripheral bond, and this species is, in fact, a cyclopropyl-1,1-biscarbinyl radical. Ring opening *a la* cyclopropylcarbinyl can give a homoallyl-type radical with a carbon bearing a half-filled p orbital fused to C-3, and this additional free spin can trap the homoallylic radical intramolecularly (eq 13). It should be noted that products derived from cyclobutyl radicals are not formed from cyclopropylcarbinyl radicals,[26-29] so the spiropentane alkyl shift is a unique variation on the usual cyclopropylcarbinyl radical rearrangement.

(13)

Mechanistic Scheme for the Thermolysis of 6 and Its Methyl-Substituted Derivatives. A question that invariably arises when discussing thermal rearrangements is whether or not discernible diradical intermediates are formed. To obtain an answer, appropriate stereochemically labeled materials that can undergo inversion of configuration in the intermediate faster than rearrangements or radical–radical recombination are necessary. Thus, a negative result may be meaningless since stereochemical inversion may be slower than other processes or because rearrangements occur faster than reformation of starting material. A positive result, however, may also be interpreted in terms of a distinct pathway for stereochemical inversion which is unrelated to the subsequent rearrangement. With isopropenylspiropentane the labeled materials chosen were the four 4-methyl derivatives **18**, **19**, **20**, and **21**. This selection was made with the hope that not only could reversible formation of intermediates be detected but also the relative ease of peripheral and radial cleavage could be ascertained.

Keeping in mind the aforementioned limitations, the data of Table I make it clear that reversible formation of intermediate species is occurring in the isopropenylspiropentane thermolysis. Further, the fact that epimerization occurs only at C-1 suggests that it is the peripheral bond that is being cleaved reversibly, although this point will be taken up in detail below. A secondary observation in this connection is that the activation free energy for the rearrangement of **6** is about 41 kcal/mol which is just about what would be expected for a vinylcyclopropane rearrangement in a spiropentane system with about 8 kcal/mol extra strain[30] (50 − 8 = 42), and the vinylcyclopropane rearrangement does appear to be a nonconcerted reaction proceeding *via* diradicals.[31]

On the basis of these data, Scheme I[32] is presented as the most parsimonious array of pathways involved in the thermolyses of the 4-methyl-1-isopropenylspiropentanes. It follows for interconversion of **18** and **19** *via* **38c** and t (where **c** and **t** refer to cisoid and transoid substituted allyl radicals,[33] and rotation about bonds is assumed to be competitive with ring closure or rearrangement) and for interconversion of **20** and **21** *via* **40c** and **t**. It allows for conversion of **18** and **19** to **22** (*via* the cisoid diradical, **38c**[34]) for conversion of **20** and **21** to **23** (*via* the cisoid diradical, **40c**) and for interconversion

(25) (a) J. C. Gilbert, *Tetrahedron*, **25**, 1459 (1969); (b) the entropy of activation (7.3 eu) appears to be lower than what might have been expected on comparison to the entropies of activation for spiropentane rearrangement and the cyclopropane isomerizations.

(26) (a) W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964); (b) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 3051 (1967).

(27) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 6556 (1967), and references contained therein.

(28) L. H. Slaugh, *ibid.*, **87**, 1522 (1965).

(29) J. K. Kochi, P. J. Krusic, and D. K. Eaton, *ibid.*, **91**, 1877 (1969).

(30) F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.*, **54**, 143 (1955).

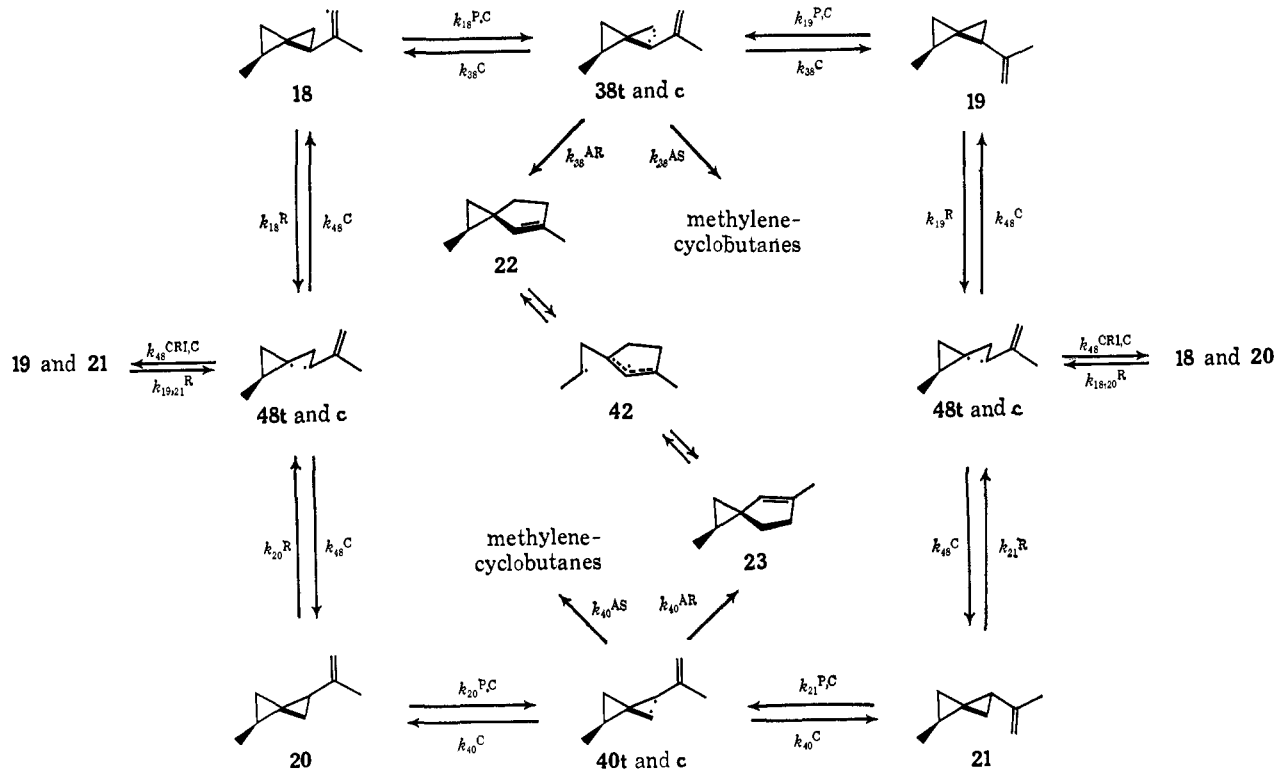
(31) (a) M. R. Willcott, III, and V. H. Cargle, *J. Amer. Chem. Soc.*, **91**, 4310 (1969); (b) *ibid.*, **89**, 723 (1967).

(32) All rate constants have a subscript denoting the species undergoing reaction and a superscript indicating the type of reaction or the species being formed. Thus, AR is allylic rearrangement; C is ring closure; P,T is peripheral bond fission to a transoid diradical; CRI is cyclopropyl radical inversion; CRI,C is cyclopropyl radical inversion followed by closure; AS is alkyl shift.

(33) (a) Rotation about allyl radicals has a relatively high activation free energy[33b,c] ($\geq$10 kcal) because of allyl radical resonance energy;[16] (b) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961); (c) D. B. Denney, R. M. Hoyte, and P. T. MacGregor, *Chem. Commun.*, 1241 (1967).

(34) Transoid diradicals cannot undergo the allylic rearrangement without giving a cyclopentene with a *trans* double bond.

Scheme I. Mechanistic Pathways for Thermolyses of the 4-Methyl-1-isopropenylspiropentanes



of **22** and **23** *via* **42**.[35] In addition, pathways for conversion of all the peripheral bond cleaved diradicals to the methyl-substituted cyclobutyl products which while not isolated in these pyrolyses must be involved considering the conversion of **6** to **9**. It also allows for interconversion of **18** and **19** and **20** and **21** *via* radical bond cleavage involving **48c** and **t**.

Rates of Peripheral and Radial Bond Fission. The major, isolated thermal products from **6** and its methyl derivatives require peripheral (1,2) bond fission as the initial act. However, this need not mean that peripheral bond homolysis occurs faster than radial bond cleavage or that peripheral spiropentane bonds are weaker than radial ones since the energetics of steps subsequent to ring cleavage can determine the product distribution. The partial pyrolytic studies with **18–21** were an attempt to ascertain the relative rates of 1,2 *vs.* 1,3 bond homolysis since 1,2 cleavage would only result in interconversion of **18** and **19** or of **20** and **21** but not all four. Radial bond fission, however, could conceivably allow interconversion of all four axially dissymmetric species.

The fact that epimerization only at C-1 of **18–21** occurred at about the same rate as rearrangement to **22** and **23** suggests that reversible peripheral fission occurs and bond rotation in the cisoid and transoid diradicals, *e.g.*, **38c** and **t**, is competitive with other processes. However, it is also possible for only C-1 epimerization of **18–21** to occur *via* **48c** and **t**, the diradicals resulting from radial bond fission, if cyclopropyl radical inversion is substantially slower than bond rotation in and ring closure of these diradicals. The structure of the cyclopropyl radical has been the focus of a number of recent investigations,[36–39] and the evidence is unequivocal that it is pyramidal but rapidly inverting. Esr measurements place the lower limit for this inversion of 10^8/sec at liquid nitrogen temperatures.[36] A simple calculation then suggests that the free energy barrier to inversion of the cyclopropyl radical is no higher than 2 kcal/mol. Successful trapping of a cyclopropyl radical before configurational equilibration has been accomplished only within a solvent cage[37] or in experiments involving electron transfer where alternative mechanistic pathways could be involved,[38] and even in these instances only 50% or less retention of configuration was observed. Tin hydride reagents have been incapable of trapping cyclopropyl radicals[39a] without loss of configurational integrity except when an α fluorine is present.[39b] In the instance of an α-methylcyclopropyl radical, a slight amount of inversion has been noted.[39c] In an elegant study of tin hydride reductions, Carlsson and Ingold[40] found that the rate constant for hydrogen transfer from triphenyl tin hydride to the relatively hindered *t*-butyl radical is $3 \times 10^6\ M^{-1}$ sec^{-1} at room temperature. Thus, any process involving complete configuration in equilibration of radical in *ca.* 1 *M* Ph_3SnH must have a rate constant in excess of 10^8/sec. Using Altman's data,[39a,c] the activation free energy for conformational equilibration of the α-methyl- and α-trifluoromethylcyclopropyl radicals is less than 7 kcal/mol at 300°K. If these data can be extended to the system under present consideration, then it is not un-

(35) This process is just the first step in a vinylcyclopropane rearrangement, namely reversible cleavage of an allylic cyclopropyl bond; however, completion of the reaction in the usual sense would lead to a $\Delta^{1,7}$-bicyclo[2.2.1]heptene.

(36) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(37) H. M. Walborsky and C.-J. Chen, *J. Amer. Chem. Soc.*, **89**, 5499 (1967).

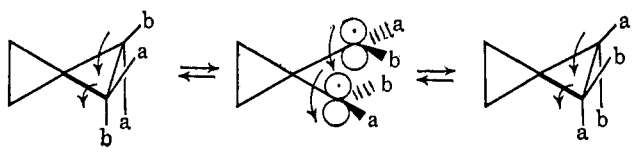
(38) J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969).

(39) (a) L. J. Altman and J. C. Vederas, *ibid.*, 895 (1969); (b) T. Ando, F. Namigata, H. Yammanaha, and W. Funssaka, *J. Amer. Chem. Soc.*, **89**, 5719 (1967); (c) L. T. Altman and B. W. Nelson, *ibid.*, **91**, 5163 (1969).

(40) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

reasonable to expect the barrier for inversion of the cyclopropyl radical in **48c** and **t** to be 5 kcal/mol or less. The question then is how fast is diradical ring closure to starting materials? Recombination of radicals has been demonstrated to be very fast, diffusion controlled in some cases.[41] However, reclosure of trimethylene diradicals may be a relatively slow process. By estimating the heat of formation of the trimethylene diradical and using kinetic data, O'Neal and Benson found that k^C is $10^{13.6}\exp\{9300/RT\}$.[42] The explanation for this relatively high barrier considers that reclosure requires eclipsing of all substituents on the species and the possibility of encountering some angle strain in order to bring the two half-filled p orbitals close enough to interact to ultimately slide down the energy surface. If this numerical estimate is correct even to a half an order of magnitude, the rates of diradical ring closure and cyclopropyl radical inversion are competitive, and complete equilibration of **18–21** should have been detected if radial bond fission occurred. Thus, it is unlikely that radial bond fission in the spiropentane thermolyses is competitive with peripheral bond fission.

Alternative Mechanistic Pathways. Scheme I is predicted on the intermediacy of diradical species, and while the system responded affirmatively to the classical tests for diradicals, alternative, concerted pathways are imaginable, particularly in light of recent theoretical speculations. Foremost among these is the possibility that a concerted interconversion of **18** and **19** or of **20** and **21** occurs *via* a conrotatory pathway with a π cyclopropane as an intermediate or transition state,[43] and this process (eq 14) could conceivably be independent of

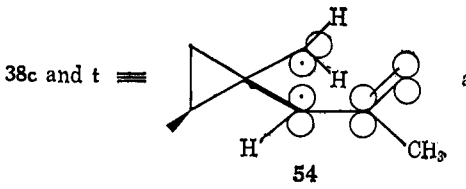


(14)

the skeletal rearrangements observed. This pathway has been excluded on experimental grounds in the pyrolyses of alkyl-substituted cyclopropanes[44] and in vinylcyclopropane itself,[31a] but the spiropentane system may be more favorable for these electronic and nuclear motions.

A second possibility is one raised previously, namely that epimerization could proceed *via* diradicals, but the rearrangement products are derived by independent, concerted but nearly equienergetic processes. Further, complete rotation about bonds in the diradicals **38c** and **t** and **40c** and **t** does not appear to be necessary to account for the observations. In fact, orthogonal species such as **54** and **55** would be responsible for the interconversion of **18** and **19**[45] and could also give rise to **22** as well as **44** (Scheme I). The point here, then, is that all events observed can occur without ever requiring more than one 90° rotation about one bond in the formation of the diradical intermediates.

(41) S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 90, 1659 (1968), and references contained therein.
(42) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).
(43) R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).
(44) (a) J. A. Berson and J. M. Balquist, *ibid.*, 90, 7343 (1968); (b) W. L. Carter and R. G. Bergman, *ibid.*, 90, 7345 (1968).
(45) (a) This proposal is similar to if not identical with Smith's[45b] explanation for the geometric isomerization in cyclopropane; (b) F. T. Smith, *J. Chem. Phys.*, 29, 235 (1958).



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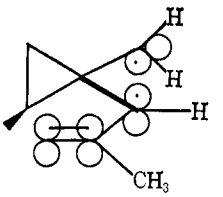

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Finally, it should be noted that conversion of the diradicals to the methylenecyclobutanes may be a single or a multistep reaction as indicated in the introduction. No experiment reported here bears on this question, but recent experiments with the *cis*- and *trans*-4,5-dimethyl-1-carbethoxyspiropentane pyrolysis indicate that there is partial specificity in the thermal rearrangement to the *cis*- and *trans*-2,3-dimethyl-1-carbethoxymethylidenecyclobutanes.[46] Studies are currently in progress to establish the limits of stereochemical control in the vicinal alkyl shift and its dependence on the rotations about bonds in the cyclopropane ring suffering initial cleavage.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian A-60 and HA-100 spectrometers. Carbon tetrachloride was used as a solvent with chloroform as an internal lock in frequency sweep mode; chemical shifts are reported as δ values in parts per million downfield from TMS. Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G spectrophotometers in the indicated solvent. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using the indicated columns. Analyses were performed by Spang Microanalytical Laboratory.

Isopropenylspiropentane (6). To an ethereal methyl Grignard solution prepared from 0.52 g (0.021 g-atom) of magnesium and 3.2 g (0.0225 mol) of methyl iodide was added at room temperature 1.0 g (0.0072 mol) of ethyl spiropentanecarboxylate.[15] The solution was stirred for 3 hr, then decomposed with a freshly prepared, saturated aqueous solution of anhydrous sodium sulfate. After decantation and drying, the solution was concentrated by removal of the solvent at atmospheric pressure. The tertiary alcohol was dehydrated immediately by passage of the vapor through a horizontal glass tube half filled with basic alumina at 170° (0.5 Torr); the products were trapped in a Dry Ice–acetone trap downstream from the oven. The olefinic product was purified by preparation vpc on a 10 in. × 3/8 in. XF 1150 column operated at 90° and 100 ml/min helium flow rate. Despite losses in collecting off the chromatograph, the yield of 99+% pure isopropenylspiropentane (**6**) ranged between 20 and 45% based on starting ester. Analyses were conducted on 200-ft UCON 50HB2000 and 200-ft didecyl phthalate (DDP) capillary columns (i.d. = 0.01 in.): ir (neat) 3070, 3000, 1635, 1000, 988, 970, and 875 cm^{-1}; nmr (60 MHz) singlet at δ 0.77 (4 H), multiplet from 0.77 to 1.2 (2 H), triplet, J = 1.1 Hz, at 1.62 (3 H), doublet of doublets, J = 7.5 and 5.0 Hz, at 1.75 (1 H), multiplet at 4.65 (2 H); *m/e* 108.0937 (calcd for C_8H_{12}, 108.0940).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.10; H, 10.91.

Pyrolyses of Isopropenylspiropentane in Sealed Tubes. Pyrolyses were conducted in the gas phase in tubes prepared and sealed as follows: clean Pyrex tubes were rinsed with dilute ammonium hydroxide solution, dried in an oven at 100° for 2 hr, then evacuated with a vacuum pump to remove the last traces of water; the tubes were then flushed with dry nitrogen. A small tube containing iso-

(46) J. J. Gajewski, unpublished observations.

propenylspiropentane was placed in the pyrolysis tube; the pyrolysis tube and contents were then immersed in a Dry Ice–acetone bath, and the tube was evacuated to 0.5 mm and sealed with a torch. After warming to room temperature the tube was placed in an oven (temperature fluctuation was ±10°). After reaction the pyrolysate was condensed in the narrow end of the tube, and the tube was broken open.

A. Pyrolysis of Isopropenylspiropentane at 245°. In a 25-ml tube, 7 μl of isopropenylspiropentane was heated at 245° for 70 min. No tars or residue were present on the inner surface of the reaction vessel, and about 7 μl of pyrolysate was obtained. Vpc analysis on a 10 ft × 1/16 in. SE-30 column indicated that 55% of starting material remained, and two other peaks constituting 2 and 42% of the product, respectively, were also present. These latter two peaks were subsequently identified in 2-isopropenyl-1-methylenecyclobutane (**9**) and 5-methylspiro[2.4]hept-4-ene (**7**), respectively.

B. Pyrolysis of Isopropenylspiropentane at 285° and Product Isolation. In a 25-ml tube, 60 μl of isopropenylspiropentane was heated at 285° for 2.5 hr, and 55 μl of clear, colorless material was obtained. Vpc on a 200-ft UCON Polar 50HB2000 capillary column indicated that little, if any, starting material was present. The pyrolysate consisted of 5.4% **9** and 87.5% **7**, and the remainder of the material consisted of 13 peaks, the largest of which constituted 1.6% of the reaction mixture. These latter materials were not identified. Subsequent pyrolyses of two 80-μl samples of isopropenylspiropentane under these conditions gave enough material for preparative vpc separation on a 10 ft × 3/8 in. XF 1150 column operated at 90° and 200 ml/min helium flow. A substantial amount of the major product was isolated as well as a small amount of the next most abundant material.

1. Physical Constants of Major Product Isolated above (7). Nmr (100 MHz)[11d] showed a symmetrical multiplet at δ 0.5 (4 H), quartet, J = 1.3 Hz, at 1.7 (3 H), unsymmetrical triplet with fine structure, J = 7 Hz, at 1.85 (2 H), unsymmetrical triplet with fine structure, J = 7 Hz, at δ 2.35 (2 H), sextet, J = 1.3 Hz, at 4.74 (1 H); ir (neat) 3075, 3040, 3000, 1655, 1030, 1005, 990, 955, 855, and 820 cm^{-1}; λ_{max} (EtOH) 212 nm (ε 5500); m/e 108.0937 (calcd for C_8H_{12}, 108.0940).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.08; H, 10.88.

2. Physical Constants of Minor Product Isolated above (9). Nmr (60 MHz) showed a triplet, J = 1 Hz, at δ 1.7 (3 H), broad multiplet from 1.7 to 2.8 (4 H), broad multiplet from 3.3 to 3.8 (1 H), multiplet at 4.75 (4 H); ir (neat) 3080, 2980, 2930, 1670, 1640, 1450, 1375, and broad, intense 880 cm^{-1}.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 89.02; H, 11.17.

Pyrolysis of 6 in a Static Phase Reactor. Kinetic Runs. A 5-μl sample of **6** was expanded into a well-conditioned 200-ml flask which was immersed in a thermostat at 254.7°.[47] After a certain time the material was condensed out of the bulb and analyzed on a didecyl phthalate capillary column. The first-order rate constant for disappearance of **6** was $3.38 \times 10^{-4} \pm 2\%$ (average deviation of five points), and the ratio of **7** to **9** was 16.7 ± 3.6. A second kinetic run at 237.8° allowed calculation of a first-order rate constant for loss of **6** of $7.8 \times 10^{-5} \pm 2\%$, and the ratio of **7** to **9** was 26.3 ± 0.4.

5-Methylspiro[2.4]heptan-4-one (11). To 0.323 g (0.0134 mol) of sodium hydride in 8 ml of dimethylformamide under nitrogen at room temperature was added 1.48 g (0.0134 mol) of spiro[2.4]heptan-4-one.[48] After stirring for 3 hr the suspension was a deep lime green color, and it was poured into 30 ml of methyl iodide. The resultant mixture was poured into water and the lower layer was collected. The aqueous layer was extracted with ethyl ether, and the combined organic layers were washed many times with water and dried over anhydrous sodium sulfate. Evaporation of the solvent left 1.36 g of a light yellow clear oil. Vpc indicated three peaks in the ratio 1:7:1. The major peak, 5-methylspiro[2.4]-heptan-4-one (**11**), was collected from a 20 ft × 3/8 in. Carbowax 20M column: ir of **11** (neat) 3090 and 1725 cm^{-1}; nmr (60 MHz) of **11** (CCl_4) triplet, J = 3 Hz, at δ 0.78 (2 H), multiplet at 1.1 (5 H), multiplet from 1.5 to 2.5 (5 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.30; H, 9.73. Found: C, 77.56; H, 9.81.

The *p*-toluenesulfonylhydrazone (mp 142–143°) was prepared by addition of *p*-toluenesulfonylhydrazine to a boiling methanol solution of the ketone. White crystals deposited upon cooling, and these were recrystallized from methanol.

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.55; H, 6.89; N, 9.62; S, 10.97. Found: C, 61.37; H, 6.98; N, 9.60; S, 11.11.

Authentic 5-Methylspiro[2.4]hept-4-ene (7). To 0.112 g (0.384 mmol) of 5-methylspiro[2.4]heptan-4-one tosylhydrazone suspended in 1 ml of ethyl ether at room temperature was added 0.5 ml of 1.6 *M* methyllithium in ethyl ether.[12] A gas was evolved and the solution turned orange immediately. Water was then added, and the organic layer was collected and dried over anhydrous sodium sulfate. Vpc indicated the presence of only one peak besides solvent. The product was collected on a 20 ft × 3/8 in. XF 1150 column. The spectral and physical properties of the material were identical with those of the major product from pyrolysis of **6**.

Methyl 2-Methylenecyclobutanecarboxylate (13). To a −10°, stirred solution of 4.45 g (0.045 mol) of 2-methylenecyclobutylcarbinol[13] in 18 ml of acetone was added dropwise 10 ml of Jones reagent. After addition of saturated brine and water the solution was extracted with ethyl ether. The ether solution was then extracted with excess 10% sodium bicarbonate solution. After acidification with 10% hydrochloric acid and saturation with sodium chloride, the aqueous solution was extracted with ethyl ether. The ether solution was dried over anhydrous sodium sulfate and evaporated giving 1.8 g of a yellow oil whose nmr spectrum was identical with that of 2-methylenecyclobutanecarboxylic acid.[49]

The entire residue was treated with diazomethane in ethyl ether, and the resulting ester, methyl 2-methylenecyclobutanecarboxylate (**13**), was purified by preparative vpc on a 10 ft × 3/8 in. XF 1150 column: ir of **13** (neat) 1735, 1680, and 890 cm^{-1}; nmr (60 MHz) of **13** (CCl_4) broad multiplet from δ 2.0 to 3.0 (4 H), singlet at 3.7 (4 H), quartet, J = 2.5 Hz, at 4.8 (1 H), quartet, J = 2.5 Hz, at 4.94 (1 H).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.68; H, 7.97.

Authentic 1-Isopropenyl-2-methylenecyclobutane (9). Methyl 2-methylenecyclobutanecarboxylate was treated with excess methylmagnesium iodide, and the resultant tertiary alcohol was immediately dehydrated as described above for the preparation of isopropenylspiropentane except that the alumina-filled tube was heated at 210°. From 400 μl of the ester, 250 μl of a yellow oil was obtained which by vpc was a complex mixture with one major peak representing 50% of the volatile material. The major peak, 1-isopropenyl-2-methylenecyclobutane (**9**), was collected from a 20 ft × 3/8 in. XF 1150 column and found to be 99.9% pure by capillary vpc. The spectral and physical properties of this material were identical with those of the minor product from pyrolysis of **6**.

1-Carbomethoxy-3-methylenecyclobutane (16). To 3.0 g (0.075 mol) of sodium hydroxide dissolved in 10 ml of water was added 1.1 g (0.0105 mol) of 1-cyano-3-methylenecyclobutane.[14] After being heated at reflux for 5 hr under nitrogen, the reaction mixture was cooled, acidified, saturated with sodium chloride, and extracted with diethyl ether. After drying over anhydrous sodium sulfate the solvent was evaporated giving 1.4 g of a clear oil which was redissolved in ether and treated with an excess of an ethereal diazomethane solution. Evaporation of the solvent gave a colorless oil which was 97% homogeneous by capillary vpc. An analytical sample was collected from an SE-30 vpc column: nmr (60 MHz) of **16** (CCl_4) broad singlet at δ 2.90 (5 H), singlet at 3.72 (3 H), broad singlet at 4.78 (2 H).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.51; H, 7.90.

1-Isopropenyl-3-methylenecyclobutane (14). To an ethereal solution of methyl Grignard prepared from 0.34 g (0.014 g-atom) of magnesium and 2.0 g (0.014 mol) of methyl iodide was added 0.5 g (0.004 mol) of **16**. After stirring at room temperature for 1 hr a saturated aqueous solution of anhydrous sodium sulfate was used to decompose the addition complex. The ether layer was decanted, dried over anhydrous sodium sulfate, and was evaporated through a Vigreux column giving 400 μl of a clear oil which was subjected to vapor phase dehydration over basic alumina

(47) The temperature recorded is that of the bath using an uncalibrated copper–constantan thermocouple. These data were not used to determine activation parameters since the capillary inlet lines were of sufficient relative volume and erratically heated to cause a small uncertainty in the actual temperature of the reacting material.

(48) R. Mayer and E. Alder, *Chem. Ber.*, **88**, 1866 (1955).

(49) "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., Spectrum No. 128; there appears to be no literature on the preparation of this material, and Varian Associates is not aware of the source of their material or the spectrum.

at 240° and 0.5 Torr. A yellow oil (250 μl) was collected which consisted of two materials in the approximate ratio of 4:1. This mixture was separated by vpc on a 20 ft × 3/8 in. XF 1150 column operated at 90° and 60 ml/min helium flow. The major product which also had the shorter retention time was 1-isopropenyl-3-methylenecyclobutane, **14**: nmr of **14** (100 MHz) singlet at δ 1.70 (3 H), multiplet centered at 2.80 (5 H), broad singlet at 4.7 (4 H); ir (CCl_4) of **14** 3100, etc., 1770, 1620, 1450, 1435, 1380, 960, and 885 cm^{-1}.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.92; H, 11.08.

The material with longer retention time formed in the reaction had ir absorptions at 3100, 1620, 960, and 880 cm^{-1} and nmr singlets at δ 1.85 (6 H), 4.95 (4 H), and 5.2 (2 H).

Pyrolysis of 14. 1-Methyl-4-methylenecyclohexene (17). A 10-μl sample of **14** was heated in the vapor phase at 240° for 1 hr in a neutralized 25-ml tube sealed under vacuum. Upon cooling, 6.5 μl of liquid material, 1-methyl-4-methylenecyclohexene (**17**), was obtained which was homogeneous on capillary vpc. An analytical sample was collected from an SE-30 vpc column. Ir of **17** (CCl_4) showed 3090, 3050, 3020, etc., 1650, 1450, 1435, 1375, etc., and 890 cm^{-1}; nmr (100 MHz) of **17** (CCl_4) singlet at δ 1.68 (3 H), multiplet centered at 1.1 (2 H), multiplet centered at 2.25 (2 H), broad singlet at 2.70 (2 H), singlet at 4.65 (2 H), broad singlet at 5.30 (1 H).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.83; H, 11.25.

***medial,anti*-1-Isopropenyl-4-methylspiropentane (18).** *medial,anti*-1-Isopropenyl-4-methylspiropentane (**18**) was prepared from *medial,anti*-1-carbethoxy-4-methylspiropentane[15] as described above for the preparation of **6** from 1-carbethoxyspiropentane. After vpc purification on a 20 ft × 3/8 in. XF 1150 column operated at 100° and 60 ml/min helium flow, the pure hydrocarbon was obtained in 30% yield: ir (CCl_4) of **18** 3090, 3075, etc., 1635, 1455, 1440, 1373, 1280, 1135, 1010, and 875 cm^{-1}; nmr (100 MHz) of **18** broad singlet at δ 0.36 (1 H) broad singlet centered at 1.0 (7 H), broad singlet at 1.61 (4 H), broad singlet at 4.60 (2 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.22; H, 11.74.

***proximal*-1-Isopropenyl-4-methylspiropentane (19).** *proximal*-1-Isopropenyl-4-methylspiropentane (**19**) was prepared from *proximal*-1-carbethoxy-4-methylspiropentane[15] and purified in the same manner as preparation and purification of **6** from carbethoxyspiropentane: ir (CCl_4) of **19** 3090, 3075, etc., 1635, 1460, 1375, 1140, 1035, 1010, and 880 cm^{-1}; nmr (100 MHz) of **19** unsymmetrical triplet, J = 4 Hz, at δ 0.32 (1 H), multiplet from 0.6 to 1.45 (7 H), singlet at 1.62 (3 H), doublet of doublets, J = 8 Hz and 4 Hz, at 1.75 (1 H), broad singlet at 4.64 (1 H), broad singlet at 4.75 (1 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.35; H, 11.57.

***distal*-1-Isopropenyl-4-methylspiropentane (20).** *distal*-1-Isopropenyl-4-methylspiropentane (**20**) was prepared from *distal*-1-carbethoxy-4-methylspiropentane[15] and purified in the same manner as preparation and purification of **6** from carbethoxyspiropentane: ir (CCl_4) of **20** 3090, 3070, etc., 1635, broad 1450, 1380, 1370, 1070, and 870 cm^{-1}; nmr (100 MHz) of **20** singlet at δ 0.42 (1 H), multiplet from 0.65 to 1.30 (7 H), singlet at 1.60 (3 H), doublet of doublets, J = 7.5 and 4.5 Hz, at 1.73 (1 H), broad singlet at 4.64 (2 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.59.

***medial,syn*-1-Isopropenyl-4-methylspiropentane (21).** *medial,syn*-1-Isopropenyl-4-methylspiropentane (**21**) was prepared from *medial,syn*-1-carbethoxy-4-methylspiropentane[15] and purified in the same manner as preparation and purification of **6** from carbethoxyspiropentane: ir (CCl_4) of **21** 3095, 3075, etc., 1635, 1455, 1440, 1380, 1370, 1140, 1010, and 880 cm^{-1}; nmr (100 MHz) of **21** broad singlet at δ 0.35 (1 H), multiplet from 0.75 to 1.20 (7 H), singlet at 1.57 (3 H), doublet of doublets, J = 7.5 and 5 Hz, at 1.77 (1 H), singlet at 4.52 (2 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.88; H, 11.20.

Pyrolyses of 18–21. In 15-ml carefully neutralized, sealed Pyrex tubes were pyrolyzed 3–5 μl of each 1-isopropenyl-4-methylspiropentane **18–21** at approximately 245° for 1.25 hr. The procedure was the same as described for the pyrolysis of **6**. The product distributions from each are given in Table I.

Preparative Pyrolysis of 21. In two separate 40-ml tubes were pyrolyzed a total of 53 μl of **21** at approximately 275° for 1.25 hr. Under these conditions the two major products corresponding to **22** and **23** were formed and separated by vpc on a 20 ft × 3/8 in. XF 1150 column; **22** and **23** were each obtained with approximately 10% of other contaminants: nmr of **22** (60 MHz) singlet at δ 0.18 (relative area, 0.75), multiplet centered at 0.75 (relative area, 2), broad singlet at 1.0 (relative area, 3.5), broad singlet at 1.70 with additional peaks on the downfield side (relative area, 6.5), unsymmetrical triplet with fine structure at 2.25, J = 6 Hz (relative area, 2), broad singlet with fine structure at 4.92 (relative area, 1); nmr (60 MHz) of **23** multiplet centered at δ 0.75 (relative area, 3.5), broad singlet at 1.0 (relative area, 3.7), singlet at 1.68 (relative area, 4), multiplet at 1.85 (relative area, 1), unsymmetrical triplet, J = 7 Hz, at 2.3 (relative area, 2), broad singlet with fine structure at 4.68 (relative area, 1).

Stability of 23 under Thermolysis Conditions. In a 15-ml tube was pyrolyzed a 2-μl sample of **23** obtained above at 275° for 1.25 hr. Vpc on a didecyl phthalate capillary column revealed that a 1:1 mixture of **22** and **23** was present.

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