Dominant Disrotatory Double Rotation in the Thermally Induced 1,2-Dimethylspiropentane Geometric Isomerization

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Abstract: Pyrolysis of optically active *trans*-1,2-dimethylspiropentane and *syn*-4,4-dideuterio-*cis*-1,2-dimethylspiropentane at 290.0 °C in the vapor-phase allowed determination of $k_{T\rightarrow C} + k_{C\rightarrow T} = 3.43 \times 10^{-5}$/s, $K_{eq}(T/C) = 2.41$, $k_{Tact\rightarrow Trac} = 1.36 \times 10^{-5}$/s, and $k_{CS\rightarrow CS+CA} = 8.76 \times 10^{-5}$/s. This data indicates preferred double over single rotation in the cleavage of the C-1,C-2 bond, particularly with the cis isomer. The greater preference for double inversion over single inversion from the cis relative to the trans isomer suggests that the double inversion occurs by a disrotatory pathway. Pyrolysis of optically active *trans,medial-* and *trans,proximal*-1,2,4-trimethylspiropentanes at low conversions revealed that the previously observed interconversions of these isomers occur predominantly by C-4,C-5 bond cleavage and not by double rotation after C-1,C-2 bond fission. These observations reinforce the conclusion above that the dominant pathway for double rotation in spiropentane isomers is disrotatory.

In 1968 Hoffmann[1] published the results of extended Hückel calculations on the stereomutation of cyclopropane. Three geometries were considered for the transition state (or intermediate): 0,0 (edge to edge), 0,90 (edge to face), and 90,90 (face to face) (Chart I). The EHT result is that the 0,0 geometry is the most stable at large C–C–C angles and, most surprisingly, that the lowest energy path for reclosure to cyclopropane (by 1 kcal/mol) is via a conrotatory motion. The last result was attributed to the fact that the symmetric, 0,0 MO (π_g-cyclopropane) is destabilized relative to the antisymmetric (π_u-cyclopropane) by interaction with the C–H orbitals at the central carbon (Chart II).

Other, more sophisticated calculations have been performed (most notably by Salem[2a] and Goddard[2b] and recently by Jean[3]), and, although they do not show the π-cyclopropane as an intermediate, they do persist in predicting that the energetically most favorable pathway is a conrotatory double rotation by 0.5–1 kcal/mol. The implication of these predictions is that pyrolysis of an optically active, 1,2-disubstituted cyclopropane should result in racemization faster than formation of the geometrical isomer (Scheme I).

However, optically active *trans*-1,2-diphenylcyclopropane,[4] 1-methyl-2-ethylcyclopropane,[5] 1-cyano-2-isopropenylcyclopropane,[6] 1,2-diphenyl-1-(carbomethoxy)cyclopropane,[7] and 1,2-dimethyl-1,2-bis(trideuteriomethyl)cyclopropane[8] do not undergo preferential double rotation. But later Berson and coworkers[9] provided evidence from the pyrolysis of optically active 1,2-dideuterio- and 1-phenyl-2-deuteriocyclopropane that indicates a substantial preference for double rotation. Unfortunately, no experimental distinction between conrotatory or disrotatory double rotation could be made.

Spiropentanes undergo thermal reactions analogous to those of cyclopropane, namely, structural rearrangement to methylenecyclobutane[10,11] and geometric isomerization (Scheme II).[11,12]

Chart I

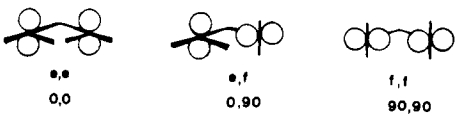
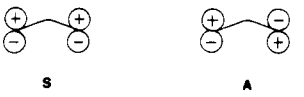
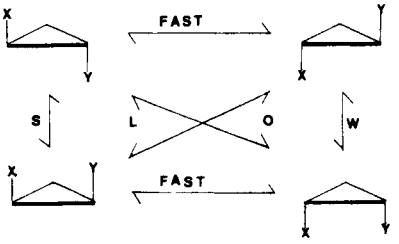


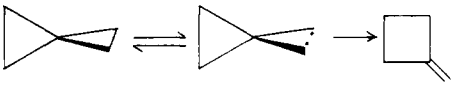
Chart II



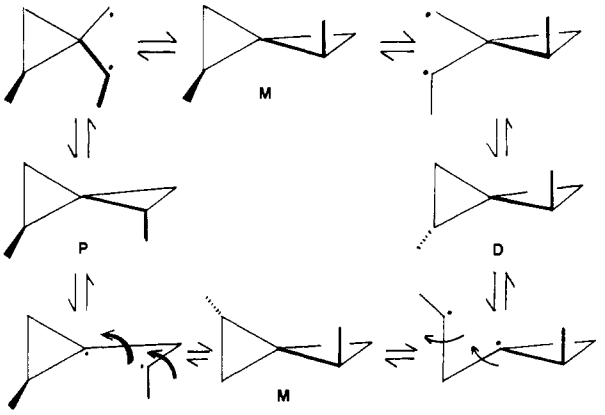
Scheme I



Scheme II



Scheme III



In the structural isomerization of monosubstituted spiropentanes, the product distribution appears to be derived via peripheral bond fission followed by migration. In the geometric isomerization of 1,4-disubstituted spiropentanes there is sequential interconversion

(1) Hoffman, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.
(2) (a) Horseley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279. (b) Hay, P. J.; Hunt, W. J.; Goddard, W. A. *Ibid.* **1972**, *94*, 638.
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(6) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168; for work with 2-phenylcyanocyclopropane see: Baldwin, J. E.; Carter, C. G. *J. Am. Chem. Soc.* **1979**, *101*, 1325.
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(9) (a) Berson, J. A.; Pedersen, L. D. *J. Am. Chem. Soc.* **1975**, *97*, 238. (b) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *Ibid.* **1975**, *97*, 240. (c) *Ibid.* **1976**, *98*, 122.
(10) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 5550. Flowers, M. C.; Gibbons, A. R. *J. Chem. Soc. B* **1971**, 612. Burkhardt, P. J. *Diss. Abstr.* **1962**, *23*, 1524.
(11) (a) Gajewski, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 3688. (b) Gajewski, J. J.; Burka, L. T. *Ibid.* **1972**, *94*, 8865.
(12) (a) Gilbert, J. C. *Tetrahedron* **1969**, *25*, 1459; (b) Gajewski, J. J.; Burka, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 8857.

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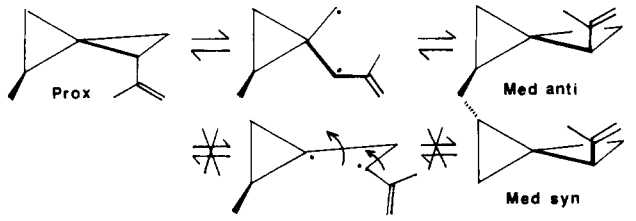
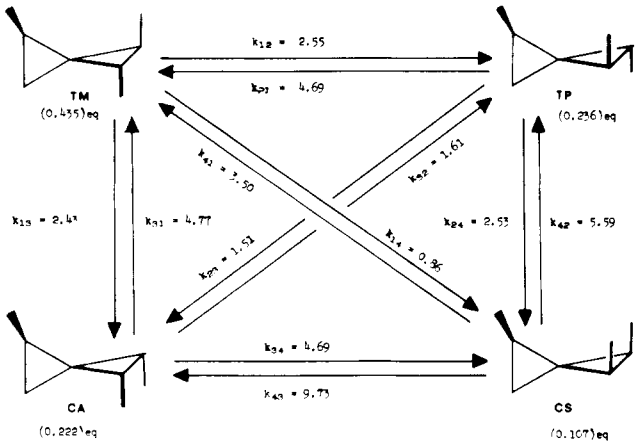
Scheme IV



Scheme V. Rate Constants for the Pyrolysis of the Four Isomeric 1,2,4-Trimethylspiropentanes (Rate Constants × 10^6)



of proximal (P), medial (M), and distal (D) isomers suggestive of reversible peripheral bond fission (Scheme III).[11] Although specific double rotation accompanying radial bond fission could account for the observations in the dimethyl system, in the geometric isomerization of 4-methyl-1-isopropenylspiropentanes, this is not the case (Scheme IV).[11a]

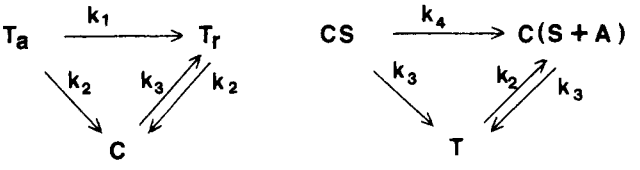
In an attempt to find double rotation via a π-spiropentane the 1,2,4-trimethylspiropentanes were prepared and pyrolyzed.[13] Here single rotation after C-1,C-2 peripheral bond fission leads to cis-trans isomerization, but double rotation leads to trans-medial, trans-proximal interconversion and to cis-anti, cis-syn interconversion. After application of a factor analysis which involved reasonable and consistent consideration of the effects of the 4-methyl group with the assumption that only C-1,C-2 bond fission occurs, it was found that double rotation is favored over a single rotation by a factor of 3 starting with any of the four isomers (Scheme V). It was surprising that double rotation was preferred by the same factor in each case since steric retardation of "inward" methyl rotation in one or the other of the isomers should have been observed if the double rotation were exclusively conrotatory or exclusively disrotatory. This led to speculation of dynamical effects in the geometric isomerization as well as to the further experimental work reported here.

In summary the results of pyrolysis of the 1,2-dimethylspiropentanes and of optically active *trans*-1,2,4-trimethylspiropentanes make clear that double rotation is favored over single rotation by a factor of 3–4 in cis to cis interconversions, but there is little preference for double rotation in trans to trans interconversions, suggesting that double rotation is a disrotatory process. Further, the previously observed product of double rotation in the *trans*-trimethylspiropentanes is actually the result of mostly C-4,C-5 bond fission.

Results

Optically active Feist's acid was converted to *trans*-2,3-dimethylmethylenecyclopropane as previously reported.[14] Methylenation by the Gaspar–Roth procedure gave (+)-*trans*-1,2-dimethylspiropentane, T_{act}. After pyrolysis at 290.0 °C for various lengths of time, the product distribution was determined by repeated GC analysis, and after VPC separation the rotation of recovered T was determined. The results are given in Table I.

Scheme VI

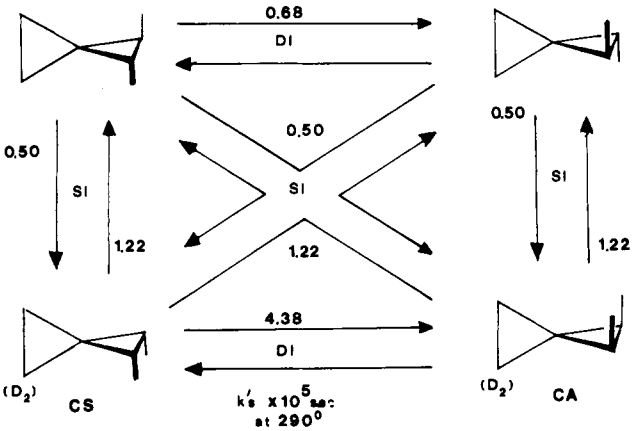


$$\ln \frac{T - T_{eq}}{T_o - T_{eq}} = -(k_2 + k_3)t = \ln \frac{C - C_e}{C_o - C_e}$$

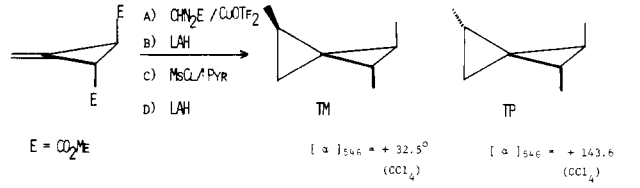
$$\ln T_a = \ln(T * OP_T) = -(k_1 + k_2)t$$

$$\ln CS = \ln(C * \frac{CS - CA}{CS + CA}) = -(k_3 + k_4)t$$

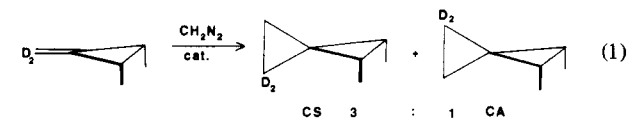
Scheme VII



Scheme VIII



cis-2,3-Dimethyl-1-(dideuteriomethylene)cyclopropane[15] was methylenated by the Gaspar–Roth procedure, giving a 3:1 ratio of *cis,syn*- and *cis,anti*-4,4-dideuterio-1,2-dimethylspiropentane, CS and CA, respectively (eq 1). After pyrolysis at 290.0 °C for various lengths of time, the product distribution was determined by repeated GC analysis, and after VPC separation, the deuterium distribution in recovered C was determined by 220-MHz NMR. The results are given in Table I.



(1)

A determination of rate constants follows from Scheme VI. Thus, $k_2 + k_3 = 3.43 \times 10^{-5}$/s, $k_1 + k_2 = 2.37 \times 10^{-5}$/s, $k_3 + k_4 = 1.12 \times 10^{-4}$/s, and $K_{eq} = k_3/k_2 = 2.41$. From the precision of the analyses (typically ±1%) a random error of ~3% in each rate constant might be expected. The rate constants are summarized in Scheme VII, where the rate constants are recalculated for the individual steps by using symmetry and ignoring long-range

(13) Gajewski, J. J.; Weber, R. J.; Chang, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2100.
(14) Gajewski, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 4450.
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Table I. Pyrolysis of T_{act} and CS at 290.0 °C

T_{act}

time, s	$[\alpha]_D$, deg[a]	OP_t^{rel}	T/T_0[c]	(ln OP_t^{rel})T/T_0
0	+117.53	1.0	1.00	0
10 800	+98.8	0.840	0.922[e]	−0.255
16 200	+87.5	0.745	0.877	−0.426
21 600	+81.5	0.694	0.846	−0.533
27 000	+75.1	0.639	0.823	−0.643
32 400	+67.4	0.573	0.794	−0.787
249 300	racemic compound used		0.707	

CS

time, s	CS/(CS + CA)[b]	(CS − CA)/(CS + CA)	C/C_0[c]	ln [(CS − CA)/(CS + CA)]C/C_0
0	0.763	0.526	1.00	0
7 200	0.642	0.284	0.842	−1.431
10 800	0.605	0.218	0.776[e]	−1.814
21 600	0.538	0.076	0.628	−3.04
27 000[d]	0.517[d]	0.034	0.569	−3.945
32 400[d]	0.507[d]	0.041	0.523	−4.896

[a] Optical rotation of GC separated trans isomer. [b] Ratio determined by HA-220 integration of the ^{1}H NMR signals at δ 0.45 and δ 0.71 of the GC separated cis isomer. [c] Capillary GC analysis. [d] These points are so close to the equilibrium value that they were not included in the least-squares fit to determine $k_3 + k_4$. [e] Calculated from $k_2 + k_3 = 3.43 \times 10^{-5}$/s.

isotope effects, e.g., $[CA]_{eq}/[CS]_{eq} = 1.0$.

Optically active (−) Feist's acid was esterified and treated with ethyl diazoacetate in the presence of copper triflate. The resulting mixture of triesters was converted to the optically active *trans,-medial-* and *trans,proximal*-1,2,4-trimethylspiropentanes, TM and TP, of necessarily equivalent optical purities which were separated by preparative GC. The rotations and absolute configurations are given in Scheme VIII.

Pyrolysis of (+)-TM at 289 °C for 3 h gave roughly 10% conversion to the other isomers in a distribution similar to that obtained previously.[13] The rotation of TP formed in the pyrolysis was $[\alpha]_{546} = +98.04°$ (CCl_4). Thus, the major enantiomer of TP has the same configuration at C-1 and C-2 as starting TM which indicates that 84.1% of the TM to TP isomerization preceeds via C-4,C-5 fission and epimerization at C-4. Only 15.9% of the TM to TP isomerization proceeds by double rotation of C-1 and C-2.

Similarly, TP was pyrolyzed at 289 °C for 3 h to give roughly 10% conversion to the other isomers. The rotation of TM from the pyrolysis was $[\alpha] = +24.0°$. Thus, the major enantiomer of TM formed (86.9%) also has the opposite configuration to that expected by double rotation at C-1 and C-2. Thus, the major pathway for TP to TM conversion occurs via cleavage at C-4 and C-5 and rotation at C-4.

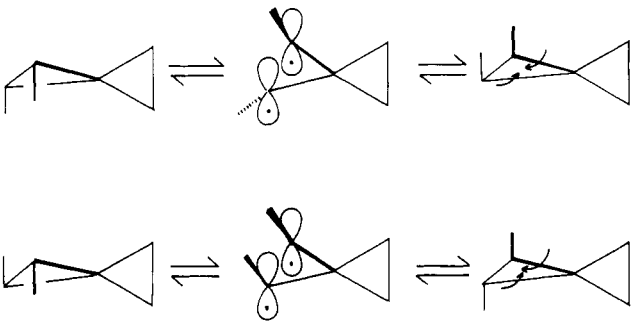
In the pyrolyses of (+)-TM and (+)-TP starting material was recovered with no change in rotation.

Discussion

1,2-Dimethylspiropentane. Despite the fact that double rotation is not observed with 1,2-disubstituted cyclopropanes, the data of Scheme VII and that previously obtained reveal a threefold preference for double rotation with *cis*-1,2-dimethylspiropentanes. That double rotation might be expected to be more facile in spiropentane thermolyses compared to that in cyclopropane pyrolyses follows from consideration of the greater potential interaction of the π-type Walsh orbitals on the second cyclopropane in the π-spiropentane.[2] However, these considerations also imply that ring opening and reformation should be conrotatory as predicted for cyclopropane.

Steric considerations would suggest that conrotatory opening of a *trans*-1,2-dimethylspiropentane should be more facile than conrotatory opening of a *cis*-1,2-dimethylspiropentane relative to a single rotation in each case. This is because one methyl is forced to rotate inward from the cis isomer via conrotation. Yet in the pyrolyses of *trans*-1,2-dimethylspiropentane and of the *trans*-1,2,4-trimethylspiropentane isomers discussed below, there is little preference for double rotation after C-1,C-2 bond fission. All of the data is far easier to rationalize on the basis of preferred disrotatory ring opening and closure—a conclusion opposite to the predictions of quantum chemistry.[2]

Scheme IX



Disrotatory opening of *cis*-1,2-dimethylspiropentane isomers is unimpeded by steric effects, but disrotatory opening of *trans*-1,2-dimethylspiropentanes would be expected to suffer from an inward methyl rotation, and this is consistent with the facts (Scheme IX).

Why disrotatory opening and reclosure is preferred with spiropentane (and perhaps with cyclopropane though no data bears on this point in cyclopropane cases that do undergo double rotation) is difficult to rationalize. One possibility is that through space interactions are stronger than through bond interactions despite all the calculations.[2] The through space interactions favor the symmetrical π-cyclopropane, therefore promoting disrotatory opening and reclosure.

An alternative suggestion is that bond homolysis may occur to preserve as much overlap between the originally bonded centers as is possible regardless of the stability of the biradical generated.[16,17] If this notion has any validity then disrotatory opening should be kinetically favored over conrotatory motions in cyclopropane ring opening. In cyclobutane and cyclopentane ring-opening conrotatory motions are favored over disrotatory ones perhaps for the same reason.[17]

The conclusion of preferred disrotatory double rotation might appear to assume that a potential random biradical does not preferentially close to a *cis*-1,2-dimethylspiropentane. For instance, if there were a 1.62-fold preference for formation of the cis isomer from a biradical common to the pyrolyses of both the *trans*- and *cis*-1,2-dimethylspiropentanes, then the double to single rotation preference from both isomers would be the same and equal to 2.21. But this implies that a common random biradical cannot be involved in both reactions since the double rotation preference would be expected to be unity after this correction.

1,2,4-Trimethylspiropentane. It must be recognized that the conclusion of disrotatory double rotation in the 1,2-dimethylspiropentane isomerization is contrary to the previous conclusions on the basis of the interconversions of the 1,2,4-trimethylspiropentanes.[13] In these cases the double to single rotation preferences were identical for the trans and cis isomers on the basis of pyrolyses of racemic materials where it was assumed that the interconversions of the trans diastereomers occurred exclusively through cleavage of the most substituted bond, namely, that between C-1 and C-2. However, pyrolysis of optically active materials reported here clearly reveals that the major pathway for this diastereomerization is actually cleavage of the less substituted C-4,C-5 bond.

It is appropriate to note that epimerization at C-4 is actually faster than epimerization of either C-1 or C-2 in both TM and TP. Thus, C-4,C-5 bond fission appears to occur faster than

(16) Wilcox, C. F., Jr.; Carpenter, B. K. *J. Am. Chem. Soc.* **1979**, *101*, 3897.

(17) Gajewski, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 5254. Gajewski, J. J.; Salazar, J. *Ibid.* **1979**, *101*, 2739, 2740.

cleavage of the more substituted C-1,C-2 bond.

Experimental Section

General Data. Nuclear magnetic resonance spectra were recorded on Varian HR-220 and T-60A spectrometers with carbon tetrachloride or deuteriochloroform as solvent, and the chemical shifts are reported in δ values in parts per million relative to internal tetramethylsilane. Infrared spectra were obtained with Perkin-Elmer Model 137 and 437 spectrometers. Purification and separation of mixtures were accomplished on a Varian Aerograph Model A90-P3 gas chromatograph by using the indicated columns. Quantitative analysis of mixtures was performed with a Varian Aerograph Model 1220-2 gas chromatograph with a flame ionization detector using a 200-ft capillary di-*n*-butyl tetrachlorophthalate (DBTCP) column. Relative areas were determined with a Vidar autolab integrator. Optical rotations were determined on a Rudolph Research Model 26202 automatic polarimeter.

Optically Active *trans*-1,2-Dimelthylspiropentane. Optically active (−)-*trans*-2,3-dimethylmethylenecyclopropane, 84% optically pure, was prepared as described previously and was subjected to the Gaspar–Roth methylenation. Thus, a 15-mL test tube, fitted with a side arm which was sealed to a dry ice condenser, was connected to the side arm of a 250-mL Erlenmeyer flask with a drying tube filled with pellets of potassium hydroxide in between. The flask was filled with 100 mL of 50% aqueous potassium hydroxide and 25 mL of decalin, and nitrogen was allowed to bubble through the solution through a glass tube. A magnetic stirrer was put in the test tube, and the tube was charged with 900 μL of the optically active *trans*-2,3-dimethylmethylenecyclopropane, 1.5 mL of pentane, and 100 mg of cuprous chloride. The test tube was cooled in an ice bath, and the contents were stirred. A 15-g sample of *N*-methyl-*N*-nitrosourea was added to the flask containing potassium hydroxide at a rate of 1 g every 10 min. When the addition was completed, the dark reaction mixture was filtered. The filtrate was chromatographed on a 5 ft × $^1/_4$ in. 25% SE 30 column at 60 °C. A 350-μL sample of the optically active *trans*-1,2-dimethylspiropentane together with 100 μL of the starting material was collected. NMR (CCl_4): 0.59 (m, 6 H), 1.02 (d, 6 H). The optical rotation of the dimethylspiropentane was measured: $[\alpha]_{589}^{22}$ +145° (heptane), +138.16 (CCl_4). Mass spectrum: *m/e* (relative intensity) 96 (M^+, 2.5), 95 (3.4), 91 (1.1), 82 (6.2), 81 ($M^+ - CH_3$, 96.6), 79 (31.4), 77 (7.3), 69 (1.3), 68 (48.8), 67 (base peak), 66 (10.5), 65 (14.8).

***cis*-1,2-Dimethylspiropentane and *cis*-1,2-Dimethyl-4,4-Dideuteriospiropentane.** These materials were prepared from *cis*-2,3-dimethylmethylenecyclopropane and *cis*-2,3-dimethyl(dideuteriomethylene)-cyclopropane (87% D by NMR), respectively,[15] by the same procedure used for the preparation of *trans*-1,2-dimethylspiropentane. NMR (CCl_4): 0.45 (m, 2 H), 0.71 (m, 2 H), 0.93 (unsymmetrical d, 6 H), 1.02 (m, 2 H). In the deuterio compound, multiplet 0.71 becomes a broad singlet and that at 0.45 is reduced in intensity. The integration showed the ratio of *cis,syn*- to *cis,anti*-1,2-dimethyl-4,4-dideuteriospiropentane to be 3:1.

Optically Active *trans,medial*- and *trans,proximal*-1,2,4-Trimethylspiropentane. To 70 g (0.41 mol) of 77.6% optically pure (−)-trans Feist's methyl ester in 175 mL of cyclohexane was added 5 g of cupric triflate. Enough anhydrous benzene was added to make a homogeneous solution. A 130-mL (140-g, 1.23-mol) sample of ethyl diazoacetate was added to the mixture in 20 h through a syringe with the syringe needle immersed in the solution. When the addition was completed, the reaction mixture was diluted with 500 mL of ether, and 300 mL of saturated ammonium chloride solution was added. The organic layer was separated and the aqueous solution was extracted with 3 × 100 mL of ether. The combined organic solutions were dried over magnesium sulfate. Evaporation of the solvent gave a brown liquid which was fractionally distilled at 0.5mmHg. A 11.7-g sample of the starting material was recovered (bp 50 °C) together with some diethyl fumarate and maleate. The major product was collected (bp 150–160 °C) to give 53 g (60% yield) of spiropentane triester. The NMR spectrum showed it to be a mixture of isomers.

The triester (26 g, 0.1 mol) was dissolved in 100 mL of tetrahydrofuran and the solution added to a mixture of 12.5 g of lithium aluminum hydride (0.33 mol) and 0.7 g of lithium hydride (0.09 mol) in 400 mL of tetrahydrofuran. After workup with saturated sodium sulfate solution 24.7 g of yellow triol was obtained. The triol was treated with excess methanesulfonyl chloride in pyridine, and the trimesylate was then converted to the hydrocarbon by reduction with a large excess lithium aluminum hydride in bis[2-(2-methoxyethoxy)ethyl] ether at 70 °C under a nitrogen stream with the hydrocarbon being collected in a dry ice–acetone trap. The hydrocarbon obtained was preparatively chromatographed on a 6 ft × $^1/_4$ in. 25% di-*n*-butyl tetrachlorophthalate (DBTCP) column at 60 °C. The two major products were collected to give 5 mL each of optically active *trans,medial*- (TM) and *trans,proximal*- trimethylspiropentane (TP). Optical rotations: TM, $[\alpha]^{25}_{546}$ +32.5° (CCl_4); TP $[\alpha]^{25}_{546}$ +143.6° (CCl_4).

Pyrolyses. All pyrolyses were done in a well-conditioned 2-L bulb immersed in a potassium nitrate–sodium nitrite bath with nitrogen as inert gas at the temperature indicated. The products were analyzed on a capillary DBTCP column at room temperature, and the product ratio was determined with a Vidar Autolab integrator. The pyrolysis products were then separated on a preparative column, and the optical rotations of the products were measured. A 5 ft × $^1/_4$ in. 25% SE30 column was used for dimethylspiropentane and an 18 in. × $^1/_4$ in. 25% DBTCP column was used for trimethylspiropentane. See Results section and Table I.

Acknowledgment. We thank the National Science Foundation for generous financial support.