Dominant Double Rotation in the Thermally Induced 1,2,4-Trimethylspiropentane Geometric Isomerization

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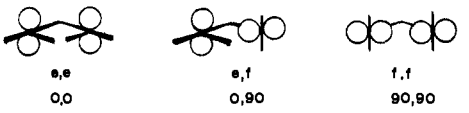
Abstract: The four 1,2,4-trimethylspiropentanes interconvert at 561.7 K with first-order rate constants by reversible C_1–C_2 bond fission. Double inversion occurs as fast as the two single-inversion processes in all cases. A factor analysis reveals that a correction for generation or destruction of 1,4-proximal methyl relationships allows deduction of a substantial preference for double over single inversion. Specifically, if there is no kinetic preference for generating cis over trans 1,2-dimethyl relationships, double inversion is favored over single inversion by a factor of 2.95 ± 0.10 in every case. Since the cis compounds should undergo double inversion slower than trans compounds if conrotation is the dominant stereorotation mode and vice versa if disrotation is dominant, it is concluded that the two trans isomers undergo conrotatory double inversion and the cis isomers undergo disrotatory double inversion. This is attributed to dynamical effects and not simply to the energy surface since the same biradical species is common to both the trans and cis reactants. The product distribution is unaffected by changes in pressure from 15 Torr to the liquid phase.

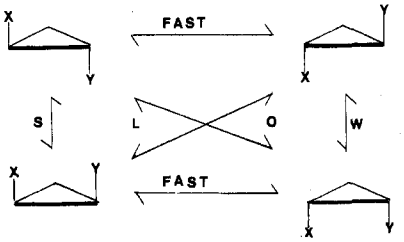
In 1968 Hoffmann[1] published the results of extended Hückel calculations on the stereomutation of cyclopropane. Three geometries were considered for the transition state (or intermediate): 0,0 (edge to edge), 0,90 (edge to face), and 90,90 (face to face). The EHT result is that the 0,0 geometry



is the most stable at large C–C–C angles and, most surprisingly, that the lowest energy path for reclosure to cyclopropane (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-

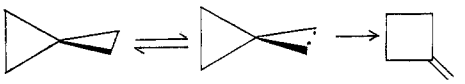
cyclopropane) by interaction with the C–H orbitals at the central carbon.

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 cause racemization faster than formation of its geometrical isomer.



However, optically active *trans*-1,2-diphenylcyclopropane,[4] 1-methyl-2-ethylcyclopropane,[5] 1-cyano-2-isopropenylcyclopropane,[6] 1,2-diphenyl-1-carbomethoxycyclopropane,[7] and 1,2-dimethyl-1,2-bis(trideuteriomethyl)cyclopropane[8] do not undergo preferential double rotation. But later Berson and co-workers[9] provided evidence from the pyrolysis of optically active 1,2-dideuterio- and 2-phenyldeuteriocyclopropane 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.[11,12] With alkyl- and alkenylspiropentanes, reversible cleavage of a peripheral bond, and not a radial bond, occurs initially.[11]

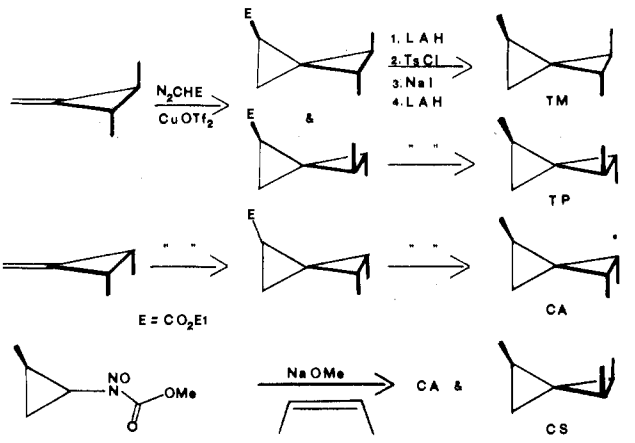


Whether there is preferential double inversion possibly via a π-spiropentane in the geometric isomerization is the subject of this paper. Consideration of the interactions of the π-type Walsh oribtals of the intact cyclopropane ring[13] at the central carbon of the π biradical reveals that the symmetric biradical should be more highly destabilized relative to the antisymmetric one here than in the cyclopropane case. Thus double inversion via conrotatory motions should be more highly favored in the spiropentane geometric isomerization than in the cyclopropane one.

The findings with 1,2,4-trimethylspiropentane indicate that double inversion is indeed favored by a factor of 3 over single inversion but that the mutual rotation direction is dependent on steric and dynamical effects rather than on electronic ones.

Results

Synthesis and Stereochemistry of the 1,2,4-Trimethylspiropentanes. In order to examine the possibility of preferential double inversion in the spiropentane thermolysis the four di-



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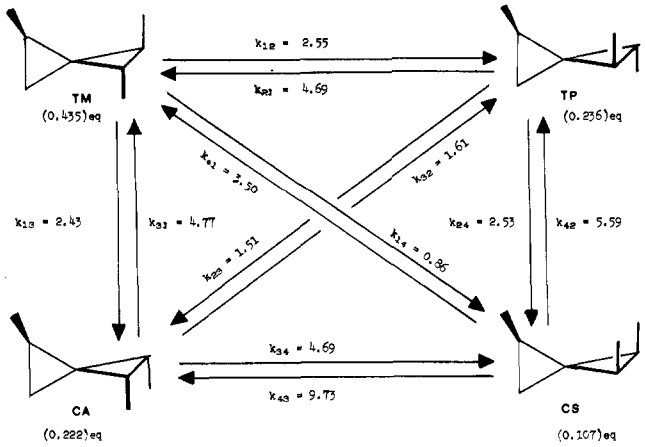
Scheme I. Rate Constants for the Pyrolysis of the Four Isomeric 1,2,4-Trimethylspiropentanes (Rate Constants $\times 10^6$)[a]



[a] The equilibrium concentrations are calculated values.

astereomeric 1,2,4-trimethylspiropentanes were prepared. The trans, medial (TM) and trans, proximal (TP) isomers were derived from the two adducts of *trans*-2,3-dimethylmethylenecyclopropanes and carbethoxycarbene derived from copper-catalyzed decomposition of ethyl diazoacetate.[14,15] The stereochemical assignments follow from steric considerations[16] in such additions as well as NMR chemical shifts.[14] Confirmation of steric effects directing the orientation of such additions follows from the observation of only one adduct from the carbene and *cis*-2,3-dimethylmethylenecyclopropane, which was assumed to be *cis,anti*-4,5-dimethyl-1-carbethoxyspiropentane; *cis,anti*-trimethylspiropentane (CA) was prepared by the same reduction, activation, displacement, and reduction sequence as with the trans isomers. The *cis,syn*-1,2,4-trimethylspiropentane isomer (CS) was prepared as part of a mixture resulting from base-induced decomposition of methyl *N*-(2-methylcyclopropyl)-*N*-nitrosourethane in neat *cis*-2-butene. CA and CS were formed in a 3:2 ratio in this reaction but as a minor products.

Pyrolysis of the 1,2,4-Trimethylspiropentanes. Small quantities (1-5 μL) of each of the four diastereomeric 1,2,4-trimethylspiropentanes were pyrolyzed in a well-conditioned 2-L bulb at 561.7 K with ca. 150 Torr of added nitrogen. The reactions were carried out to 8-35% conversion and were analyzed by GC with electronic integration. The experimental mole fractions are listed in Table V. Rate constants were obtained by the best fit of a Runge-Kutta numerical integration of the differential rate expressions of Scheme I to the GC-determined mole fractions. Important constraints on the rate constants are the three independent microscopic reversibility conditions,[18] namely, that

$$k_{12}k_{24}k_{31}k_{43} = k_{13}k_{21}k_{34}k_{42}$$

$$k_{12}k_{23}k_{34}k_{41} = k_{14}k_{21}k_{32}k_{43}$$

$$k_{13}k_{24}k_{32}k_{41} = k_{14}k_{23}k_{31}k_{42}$$

The calculated concentrations vs. time are presented graphically in Figures 1-4 along with the experimental data. The fits are excellent except at short reaction times where, though the ratio of products is reproduced, the amount of starting material is analyzed to be less than that calculated suggesting a systematic error in the integrations perhaps due to large differences in relative amounts of material. Moreover, no fit to the short reaction time data could be achieved without violating the microscopic reversibility conditions.

At the longest reaction times, small amounts (1-4%) of structural isomers were observed. They were identified by comparison to authentic samples of the expected isomers, *trans*- and *cis*-2,3-dimethyl-*syn*- and *anti*-ethylidenecyclobutane, which were synthesized from the cyclobutanones (see Experimental Section). The formation of these should not dramatically affect the rate constants with the possible ex-

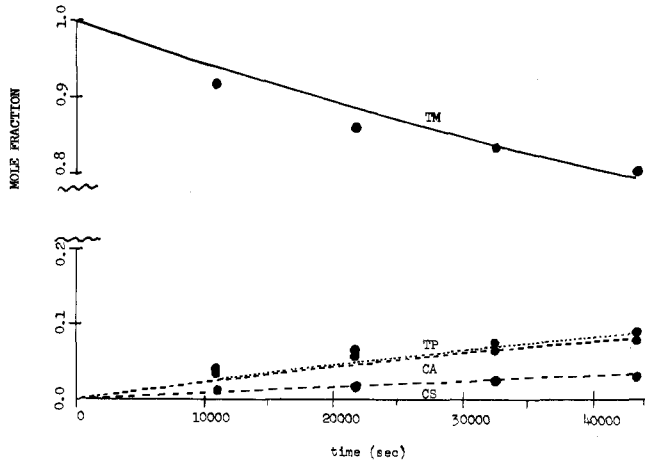


Figure 1. Calculated and experimental data for the pyrolysis of TM.

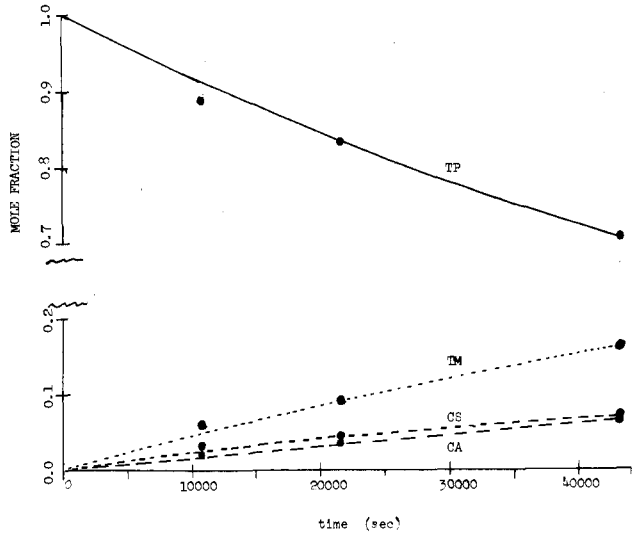


Figure 2. Calculated and experimental data for the pyrolysis of TP.

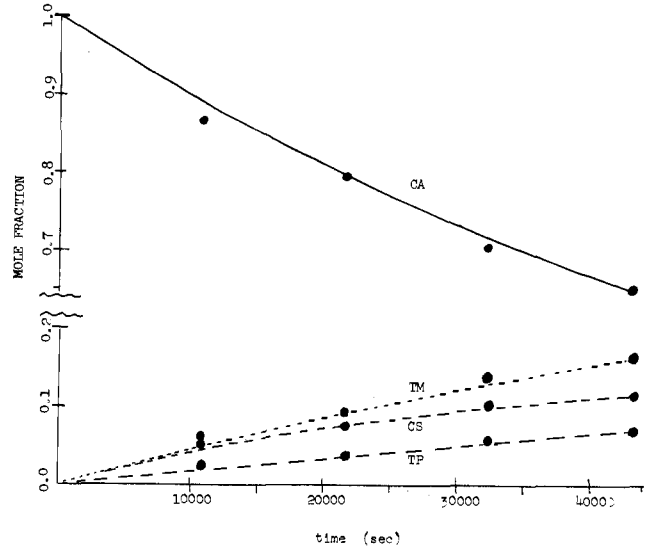


Figure 3. Calculated and experimental data for the pyrolysis of CA.

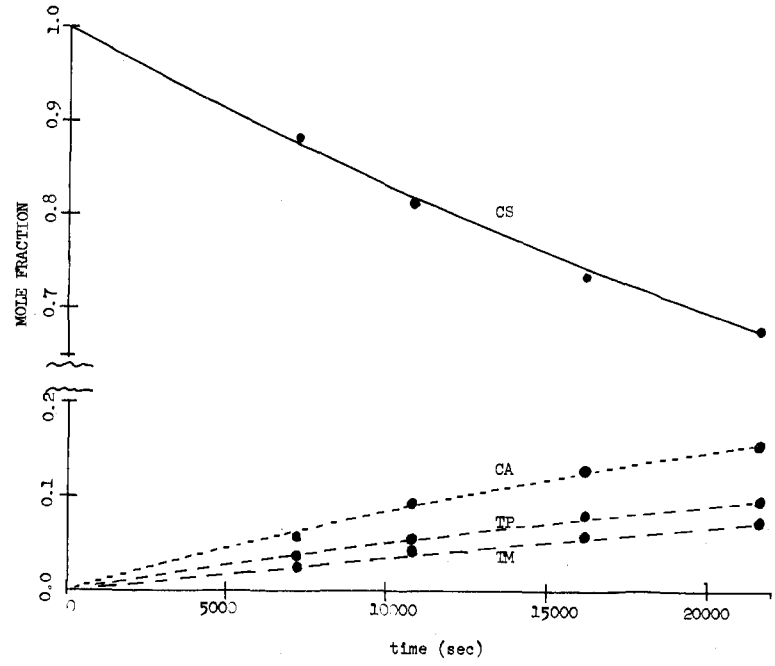


Figure 4. Calculated and experimental data for the pyrolysis of CS.

ception that the calculated amount of each starting material might be a little higher than is observed since more structural isomerization would come from the starting spiropentane isomer. In any event, an uncertainty of 10% in the rate constants might be possible, although it is unlikely to be so high since the number of observations far exceeds the number of unknowns; moreover, adherence to microscopic reversibility is a strong boundary condition.

Finally, to examine the question of pressure effects on the product distribution, CA was pyrolyzed at 289.3 °C for 9 h without added gas (total pressure < 0.7 Torr) and with 480 Torr added nitrogen. The product distribution was identical. Moreover, a pyrolysis of CA in toluene at 289 ± 3 °C gave a product distribution that coincided with that observed from CA at 150 Torr at a similar extent of conversion.

Discussion

Since peripheral bond fission has been demonstrated in previous spiropentane thermolyses,[11,12] an analysis of the results of the trimethylspiropentane isomerization depends only on which of the two peripheral bonds ruptures in the reaction, although it is important to note that exclusive reversible C_4C_5 fission cannot be responsible for any of the diastereomerizations except that interconverting TM and TP. It is reasonable to expect fission between C_1 and C_2 to occur faster than between C_4 and C_5 owing to greater alkyl substitution at the former bond. Methyl substitution for hydrogen lowers bond dissociation energies by 2-2.5 kcal/mol, and a comparison of the activation energies of cyclopropane and cyclobutane geometric isomerizations confirms this.[19] At 562 K, 2.5 kcal/mol corresponds to a rate factor of nearly 10 and so C_4-C_5 fission should occur only to a small extent.

With each isomer the rate constant for double inversion can be compared with that for each of the two single-inversion reactions, and these ratios are given in Table I. No pattern emerges other than a possible varying preference for double inversion. Significant for an analysis of these results are the ratios of the two single inversion reactions from each isomer given in Table II.

Factor Analysis. The variation in the double to single inversion rate ratios of Table I and the regularity in the ratios of single inversion of Table II suggest that a correction for steric factors might allow deduction of an intrinsic double to single inversion rate ratio which by definition would be identical from all isomers. Analysis of the single inversion rate ratios of Table II indicates a difficulty in generating a proximal relative to a medial or distal 1,4-dimethyl relationship.[15] Thus, k_{14}/k_{13} equals k_{32}/k_{31} equals 0.338, and this can be defined as a rate factor, f_{+p}. The calculated equilibrium concentrations suggest that a 1,4-proximal dimethyl interaction is destabilizing in the ground states, and it is not unreasonable that a transition state that generates this relationship would be destabilized relative to one that generates a medial or distal 1,4-dimethyl relationship. Table II also reveals that there is a factor retarding conversion of a proximal 1,4-dimethyl relationship to either a medial or distal one;[3] thus, k_{23}/k_{24} and

Table I. Ratios of Double to Single Inversion

starting material	products	rate constant ratio
TM	TP/CA	$k_{12}/k_{13} = 1.04$
TM	TP/CS	$k_{12}/k_{14} = 2.96$
TP	TM/CA	$k_{21}/k_{23} = 3.11$
TP	TM/CS	$k_{21}/k_{24} = 1.85$
CA	CS/TM	$k_{34}/k_{31} = 0.985$
CA	CS/TP	$k_{34}/k_{32} = 2.92$
CS	CA/TM	$k_{43}/k_{41} = 2.81$
CS	CA/TP	$k_{43}/k_{42} = 1.76$

Table II. Ratios of Single Inversion

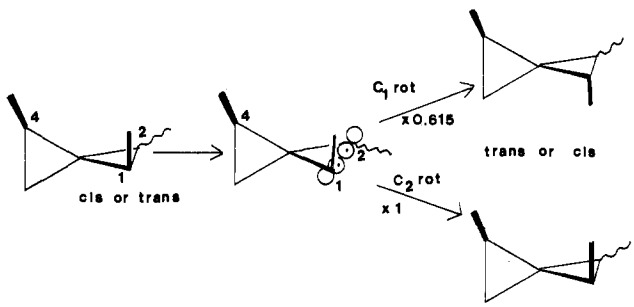
starting material	product	rate constant, $\times 10^6$/s	ratio
TM	CS	$k_{14} = 0.82$	0.338
TM	CA	$k_{13} = 2.43$	
TP	CA	$k_{23} = 1.51$	0.596
TP	CS	$k_{24} = 2.53$	
CA	TP	$k_{32} = 1.61$	0.338
CA	TM	$k_{31} = 4.77$	
CS	TM	$k_{41} = 3.50$	0.635
CS	TP	$k_{42} = 5.59$	

Table III. Intrinsic Ratios of Double to Single Inversion

starting isomer	rate constant ratio = contributing rate factors[a]	(D/S)[b]
TM	$k_{12}/k_{13} = \frac{f_{+p}(D/S)_{TM}}{f_{+c}}$	2.99 (f_{+c})
TM	$k_{12}/k_{14} = \frac{f_{+p}(D/S)_{TM}}{(f_{+p})(f_{+c})}$	2.96 (f_{+c})
TP	$k_{21}/k_{23} = \frac{f_{-p}(D/S)_{TP}}{(f_{+c})(f_{-p})}$	3.11 (f_{+c})
TP	$k_{21}/k_{24} = \frac{f_{-p}(D/S)_{TP}}{f_{+c}}$	3.01(f_{+c})
CA	$k_{34}/k_{31} = (f_{+p})(f_{+c})(D/S)_{CA}$	2.92(1/(f_{+c}))
CA	$k_{34}/k_{32} = \frac{(f_{+p})(f_{+c})(D/S)_{CA}}{f_{-p}}$	2.92(1/(f_{+c}))
CS	$k_{43}/k_{41} = \frac{(f_{-p})(f_{+c})(D/S)_{CA}}{f_{-p}}$	2.81(1/(f_{+c}))
CS	$k_{43}/k_{42} = (f_{-p})(f_{+c})(D/S)_{CS}$	2.86(1/(f_{+c}))

[a] See Discussion. [b] Calculated from the data of Table II with f_{+p} = 0.338 and f_{-p} = 0.615.

k_{41}/k_{42} average 0.615. This rate retardation factor is defined as f_{-p}. The origin of f_{-p} might be rationalizable in terms of initial generation of a face to face biradical in which the subsequent outward rotation of a C_1 proximal methyl past the C_4 methyl is retarded relative to outward rotation of a medial or distal methyl at C_2.



For any of these trimethylspiropentane isomers, the intrinsic ratio of double to single inversion, defined here as *D/S*, might be expected to be modified by the factors f_{+p} and f_{-p} as well as a factor, f_{+c}, that represents the potential difficulty in generating a cis 1,2-dimethyl relationship relative to a trans one. After each transformation is examined for involvement of the three rate factors and these are used to modify the *D/S* ratio the observed rate ratios of Table I should result. In turn, the *D/S* ratio can be calculated, but only in terms of f_{+c} since this cannot be determined independently from data. The complete dissection is provided in Table III.

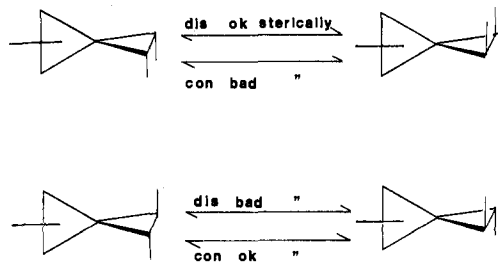
Remarkably, the four *D/S* ratios from the trans isomers are the same within experimental error provided f_{+c} is a constant. Moreover, the four *D/S* ratios from the cis isomers are the same within experimental error. Such consistency is difficult to attribute to fortuitous cancellation of unknown factors and provides support for the magnitudes of f_{+p} and f_{-p} and their interplay in modifying the intrinsic ratio of double to single inversion. Most importantly, this apparently proper analysis reveals that there is a preference for double over single inversion for any reasonable value of f_{+c} (0.5–2.0; see next section).

***D/S* as a Function of f_{+c}.** Table IV lists the *D/S* ratio as a fraction of various f_{+c}'s. For a value that is constant from all

Table IV. *D/S* Ratios as a Function of f_{+c}

reaction	*D/S* (f_{+c} = 0.5)	*D/S* (f_{+c} = 0.98)	*D/S* (f_{+c} = 2)
TM → TP/CA	1.49	2.93	5.89
TM → TP/CS	1.48	2.90	5.92
TM → TM/CA	1.56	3.04	6.22
TM → TM/CS	1.50	2.95	6.02
	av 1.51	2.96	6.04
CA → CS/TM	5.84	2.98	1.46
CA → CS/TP	5.84	2.98	1.46
CS → CA/TM	5.62	2.87	1.40
CS → CA/TP	5.72	2.92	1.43
	av 5.75	2.91	1.43

isomers but one that favors generation of trans over cis isomers ($f_{+c} < 1$), double inversion is more favored than single inversion with cis isomers than with trans isomers. This would suggest that the double-inversion process involves disrotatory motions since the methyls of the cis isomer can rotate outward in a sterically unhindered manner[20] but one of the methyls of the trans isomers must rotate inward in a sterically hindered pathway[20] all relative to single inversion reactions of each isomer.



If the double-inversion reaction were a conrotatory process as expected by analogy to the calculations for cyclopropane ring opening[1-3] and to EHT calculations on the edge to edge diradical from spiropentane,[21] the *D/S* ratio from trans isomers should be higher than that from cis isomers.[20] But this is possible only if $f_{+c} > 1$; that is, there must be a kinetic preference for generation of cis isomers over trans isomers. While such a steric attraction has been justified in highly exothermic reactions,[22] Bergman's work with the thermal interconversions of 1,2-dialkylcyclopropanes indicates little preference for generation of cis or trans isomers in ring closure of nearly stereorandom biradicals.[5]

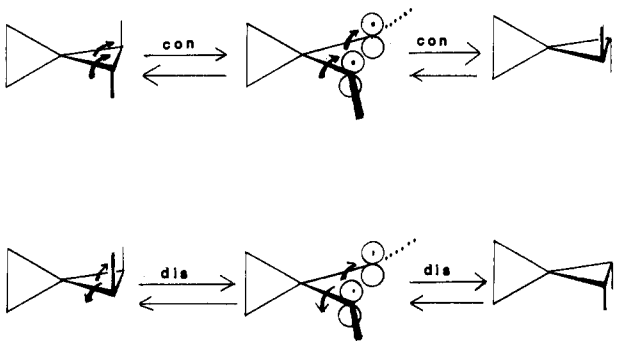
Interestingly, using Bergman's result, which suggests that f_{+c} is near unity, the *D/S* ratios from all isomers are the same and near the value 3.

Pathway for Double Inversion. If f_{+c} is 0.98, implying that the transition state for closure of an intermediate reflects the ground-state stabilities of products only to a small extent, as has been demonstrated,[5] then the *D/S* ratio is 2.9 and is the same for all starting isomers. Thus, double inversion is equally preferred over single inversion in all isomers, which is at odds with expectations based on either conrotatory and disrotatory double inversion. It suggests that trans isomers undergo conrotatory double inversion while cis undergo disrotatory double inversion all so to avoid the rate-retarding effect of an "inward" methyl rotation.[20]

Such a postulate must recognize that the transition state or intermediate structure in the conrotatory double inversion of the trans isomers is identical with that in the disrotatory double inversion of the cis isomers, yet this species, if involved, must give different products depending on its origins.

In the context of absolute rate theory this is impossible since the transition state is in thermal equilibrium with its environ-

ment and must give the same product no matter how it is formed. If the species were an intermediate in thermal equilibrium with its environment this is also true. Thus this species is neither an intermediate nor a transition state of absolute rate theory. However, the reaction coordinate motions for the two pathways are clearly not identical, and so the reaction dynamics might be responsible for the observations provided that the species generated by the two paths are different due to different internal rotation directions which are unaltered throughout the isomerization.[23]



The suggestion here then is that the double-inversion process is favored over single rotation but its stereo pathway is dictated by steric effects; once the rotational motion is initiated it continues without (much) hesitation into the product manifold.

If this is true, not much information about the energy surface in the region of the π-spiropentane is obtained by these experiments. The π-spiropentane implicated here is not vibrationally relaxed and therefore is not free to explore a surface. Perhaps the π-spiropentane in equilibrium with its environment is a potential energy minimum, as is suggested by heats of formation calculations by group additivities,[19] but the experiments neither support nor deny this possibility.

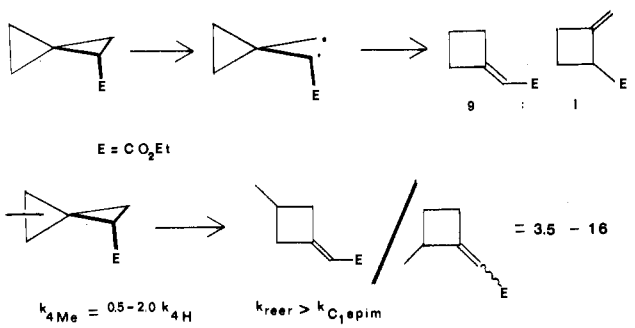
Spiropentane and Cyclopropane Geometric Isomerizations. The pathway for the 1,2,4-trimethylspiropentane double inversion discussed above has no analogy in cyclopropane pyrolyses since double inversion does not dominate over single inversion in 1,2-dialkylcyclopropane geometric isomerization,[5] and where substantial double inversion is observed, namely, with 1,2-dideuteriocyclopropane and 2-deuteriophenylcyclopropane, steric effects of the type discussed here cannot play a role.[9] Nevertheless in the cyclopropane double inversions the question should be raised as to whether it is due to conrotatory opening to one antisymmetric diradical which is stabilized relative to a symmetric one or whether double rotation occurs by both conrotatory and disrotatory motions each proceeding independently simply because once the rotations are initiated they continue irrespective of the energy surface.

A further concern with cyclopropane geometric isomerization is the inconsistency in the extent of double inversion as a function of substituents. Cyclopropane undergoes almost exclusive (>90%) double inversion as does phenylcyclopropane, yet vinylcyclopropane undergoes geometric isomerization with a statistical ratio of double to single inversion,[24] and the results with the 1-methyl-2-ethylcyclopropanes also suggest near-random amounts of double and single inversion.[5] No simple pattern emerges from these results, but, if the spiropentane geometric isomerization has any bearing on the cyclopropane isomerization, then expections based on electronic effects may not be appropriate to rationalize the diverse behavior of variously substituted cyclopropanes.

Pressure Effects. It is well recognized and generally understood that unimolecular thermal reactions involve a preequilibrium collisional activation process that requires a minimal sample (or added gas) pressure. For most organic molecules of C_4 or higher, the minimum pressure is 100 Torr, and, since pressure is required for activation and deactivation, first-order rate constants characterizing loss of starting material are indeed constant and independent of pressure above 100 Torr. However, product distributions can be a function of pressure when a sequential series of reactions is possible where the subsequent steps take place as a result of inefficient collisional deactivation of a primary product which is formed vibrationally hot with sufficient energy to traverse a secondary barrier that the vibrationally deactivated product could not surmount at the temperature of the primary reaction.[25]

In the case of the spiropentane double inversion where the rotations apparently proceed above the energy surface, it might be asked if increasing the pressure of added gas might increase the deactivation rate of a particular reacting molecule to bring it closer to the energy surface so as to explore other avenues of reaction. This, however, depends on the time it takes the activated molecule with the energy localized in the correct bond to actually react. Since collisional encounters even in the liquid phase occur at 10^9–10/s, any reaction with a rate constant greater than 10^{10}/s cannot be intercepted. This appears to be true in the spiropentane isomerization since the relative amounts of these products are independent of pressure.

Comparison to Other Spiropentane Pyrolyses. The hypothesis that face to face biradicals are involved in the 1,2,4-trimethylspiropentane thermal geometric isomerization coincides with that for the structural isomerization of carbethoxyspiropentanes.[11b] In the pyrolysis of carbethoxyspiropentanes, peripheral bond fission again occurs to give 1-carbethoxymethylidenecyclobutane, but structural isomerization is faster than geometric isomerization which allows deduction of the stereochemistry of the structural isomerization using 2,4- and 4,5-dimethyl-1-carbethoxyspiropentanes. In these cases roughly two-thirds of the reaction proceeds with retention of configuration at C_2, the migration terminus, and at C_4, the migrating carbon, and with rotation of C_1 in the Woodward–Hoffmann "allowed" sense. However, the reaction is not concerted since methyl substitution at C_4 and C_5 affects the rate of reaction only to a small extent but has a profound effect on the distribution of products. Thus, the diyl appears to be an intermediate with a face to face geometry having residual interaction between the originally bound carbons to permit orbital symmetry control in the product-determining step.



The similarity in the mechanistic hypotheses that are most likely for geometric and structural isomerization of spiropentanes suggest an energy surface that responds to substituents in a reasonable way. A unified hypothesis would have ring opening to a face to face biradical (as a potential energy intermediate) which, with 1,2,4-trimethyl substitution, undergoes double or single rotation slower than reclosure,[26] but in the carbethoxy substituted system it undergoes rearrangement faster than closure possibly as a result of favorable polar factors.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian HR-220, HA-100, and EM-360 spectrometers with carbon

tetrachloride as the solvent and the chemical shifts are reported as δ values in parts per million relative to internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer. Preparative and analytical vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using the indicated columns. High-resolution mass spectra were recorded on an A.E.I. Model MS-9.

***trans*-1,2-Dimethyl-*medial*-4-methylspiropentane (TM).** Ethyl *trans*-4,5-dimethyl-*medial*-spiropentanecarboxylate[14] (0.421 g, 2.51 mmol) was added to a slurry of 1.05 g (27.8 mmol) of lithium aluminum hydride in 50 mL of ether and was refluxed for 1 h. The excess hydride was quenched with a freshly prepared saturated sodium sulfate solution. The mixture was filtered, and the salts were washed with several portions of ether. The ether from the combined filtrate and washings was distilled, and the residue was purified by gas chromatography (5 ft × ¼ in. 30% SE-30, 125 °C) to yield 0.323 g (95%) of *trans*-4,5-dimethyl-*medial*-spiropentanemethanol: IR (neat, film) 2.95 (broad), 3.25–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.54 (t, J = 4 Hz, 1 H), 0.65 (m, 2 H), 0.79 (m, 1 H), 1.04 (m, 6 H), 1.19–1.35 (multiplet superimposed on a broad resonance, total 2 H), 3.28–3.5 (m, 2 H).

The *trans*-4,5-dimethyl-*medial*-spiropentanemethanol (0.300 g, 2.21 mmol) was added to a solution of 0.480 g (2.51 mmol) of *p*-toluenesulfonyl chloride dissolved in 3 mL of dry pyridine at 0 °C and stirred for 3.5 h. The mixture was taken up in 50 mL of ether, washed with 2 × 50 mL of 5% hydrochloric acid, 50 mL of saturated sodium bicarbonate, and 50 mL of saturated sodium chloride, and dried over magnesium sulfate. The ether was removed in vacuo to yield 0.477 g (74%) of a pale yellow oil, *trans*-4,5-dimethyl-*medial*-spiropentanemethanol *p*-toluenesulfonate: IR (neat, film) 3.25–3.5, 6.25 μ; NMR (CCl_4, 220 MHz) δ 0.60 (m, 2 H), 0.89 (m, 1 H), 0.95 (t, J = 5 Hz, 6 H), 1.35 (m, 1 H), 2.43 (s, 3 H), 3.67 (q, J = 2 and 8 Hz, 1 H), 4.00 (q, J = 4 and 7 Hz, 1 H), 7.18 (d, J = 7 Hz, 2 H), 7.66 (d, J = 7 Hz, 2 H).

The tosylate (0.450 g, 1.55 mmol) was added to a solution of 0.500 g (3.33 mmol) of sodium iodide dissolved in 4 mL of dry acetone and stirred for 4 h. The solution was filtered and the solvent was distilled. The residue was taken up in 25 mL of ether, washed with 25 mL of saturated sodium bisulfite, 25 mL of saturated sodium bicarbonate, and 25 mL of saturated sodium chloride, and dried over magnesium sulfate. The solvent was distilled to yield a dark yellow, unstable liquid that was immediately injected into a slurry of excess lithium aluminum hydride in bis-2-(2-methoxyethoxy)ethane. A vacuum was applied and the volatiles were collected in a cold trap (liquid N_2). The 150 μL of liquid that was collected was purified by gas chromatography (5 ft × ¼ in. 30% SE-30, 70 °C) to yield approximately 30 μL of *trans*-1,2-dimethyl-*medial*-4-methylspiropentane (TM): IR (CCl_4) 3.35–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.26 (m, 1 H), 0.45–0.65 (m, 2 H), 0.72 (m, 1 H), 0.95–1.05 (m, 10 H); *m/e* 110.1090 (calcd for C_8H_{14}, 110.1096).

***trans*-1,2-Dimethyl-*proximal*-4-methylspiropentane (TP):** IR 2.76, 3.27–3.48 μ; NMR (CCl_4, 220 MHz) δ 0.38 (t, J = 4 Hz, 1 H), 0.66 (m, 2 H), 0.78 (q, J = 4 Hz, 1 H), 1.01 (d, J = 6 Hz, 3 H), 1.08 (d, J = 6 Hz, 3 H), 1.37 (m, 1 H), 3.34 (q, J = 4 and 7 Hz, 1 H), 3.57 (q, J = 4 and 7 Hz, 1 H).

***trans*-4,5-Dimethyl-*proximal*-spiropentanemethanol *p*-Toluenesulfonate:** IR (CCl_4) 3.27–3.48, 6.25 μ; NMR (CCl_4, 220 MHz) δ 0.47 (t, J = 4 Hz, 1 H), 0.68 (m, 2 H), 0.87 (q, J = 4 Hz, 1 H), 0.98 (d, J = 6 Hz, 3 H), 1.04 (d, J = 6 Hz, 3 H), 1.43 (m, 1 H), 2.43 (s, 1 H), 3.90 (m, 2 H), 7.26 (d, J = 8 Hz, 2 H), 7.70 (d, J = 8 Hz, 2 H).

***trans*-1,2-Dimethyl-*proximal*-4-methylspiropentane (TP):** IR (CCl_4) 3.35–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.17 (m, 1 H), 0.55 (m, 1 H), 0.60–0.75 (m, 2 H), 0.97 (d, J = 6 Hz, 3 H), 1.05–1.12 (m, 7 H); *m/e* 110.1091 (calcd for C_8H_{14}, 110.1096).

***cis*-1,2-Dimethyl-*anti*-4-methylspiropentane (CA):** IR (CCl_4) 2.76, 3.28–3.48 μ; NMR (CCl_4, 220 MHz) 0.32 (t, J = 4 Hz, 1 H), 0.66 (q, J = 4 Hz, 1 H), 0.94 (m, 6 H), 1.01–1.13 (m, 1 H), 1.37 (m, 2 H), 3.40 (d, J = 6 Hz, 2 H).

***cis*-4,5-Dimethyl-*anti*-spiropentanemethanol *p*-Toluenesulfonate:** IR (CCl_4) 3.27–3.48, 6.25 μ; NMR (CCl_4, 220 MHz) δ 0.37 (t, J = 4 Hz, 1 H), 0.74 (q, J = 4 Hz, 1 H), 0.88 (t, J = 6 Hz, 1 H), 0.97–1.07 (m, 1 H), 1.40 (m, 1 H), 2.44 (s, 3 H), 3.73 (1, J = 8 Hz, 2 H), 7.68 (d, J = 8 Hz, 2 H).

***cis*-1,2-Dimethyl-*anti*-4-methylspiropentane:** IR (CCl_4) 3.35–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.04 (t, J = 4 Hz, 1 H), 0.60 (m, 1 H), 0.87–1.00 (m, 12 H); *m/e* 110.1090 (calcd for C_8H_{14}, 110.1096).

***cis*-1,2-Dimethyl-*syn*- and *cis*-1,2-dimethyl-*anti*-4-methylspiropentane (CS and CA).** *cis*-2-Butene (15 mL) was condensed into a flask cooled to 0 °C containing 1.50 g (27.8 mmol) of sodium methoxide. To this was added 2.75 g (17.4 mmol) of *N*-nitroso-*N*-(2-methylcyclopropyl)carbamate (see below) via a syringe driver over a period of 1.5 h. At the end of this time the excess 2-butene was allowed to evaporate and the remaining volatiles were collected in a cold trap cooled in liquid nitrogen while applying a vacuum. Collection of the two least volatile peaks off the gas chromatograph (30% SE-30, 100 °C) gave ca. 15 μL of fraction 1 (shortest retention time) and ca. 10 μL of fraction 2.

Fraction 2: IR (CCl_4) 3.28–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.62 (m, 1 H), 1.14 (d, J = 6 Hz, 3 H), 1.24 (broad quartet, J = 6 and 8 Hz, 1 H), 1.32–1.51 (m, 1 H); *m/e* 108.0949 (calcd for C_8H_{12}, 108.0940). This material was assigned as at least one of the four possible 1,1-dimethylbicyclopropylidenes.

Fraction 1 was actually two overlapping peaks in the ratio 3:4 which were separated on a 6 ft × ¼ in. DBTCP column at 90 °C. The fastest eluting material was identical with *cis*-1,2-dimethyl-*anti*-4-methylspiropentane (CA) prepared previously. The other peak was identified as *cis*-1,2-dimethyl-*syn*-4-methylspiropentane: IR (CCl_4) 3.35–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.33 (t, J = 4 Hz, 1 H), 0.76 (d of d, J = 4 + 2 Hz, 1 H), 0.92 (s, J = 2 Hz), 1.02 (d, J = 6 Hz), 1.08 (d, J = 4 Hz) superimposed upon a broad resonance, total 12 H; *m/e* 110.1087 (calcd for C_8H_{14}, 110.1096).

Static Gas-Phase Pyrolysis. The reaction vessel was a 2-L Pyrex bulb conditioned by the injection of 200 μL of dimethylchlorosilane at 370 °C. This was allowed to stand for 10–20 h and evacuated, and the treatment was repeated twice. After this, 100 μL of diethylamine was injected and allowed to stand for several hours, the bulb was evacuated, and the process was repeated. The vacuum line was fitted with Teflon stopcocks, had a five-way splitter/collector, and had a value arrangement that allowed direct injection of the samples onto the capillary gas chromatograph. The gas chromatographic output was digitalized with a Vidar Autolab integrator. The bulb was immersed in a molten potassium nitrate–sodium nitrite bath heated by a 500-W Vycor immersion heater and fine temperature control was accomplished with a Bayley Controller Model 76-8 in connection with a 125-W Vycor immersion heater. Stirring was provided by a "Lightening stirrer". The temperature was measured with copper–constantan thermocouples (referenced to 0 °C) and read-out was performed with a Leeds and Northrup Type K-3 potentiometer and galvanometer. In a typical experiment 2 μL of liquid was allowed to expand into the bulb (start time) followed by enough nitrogen to bring the pressure up to 150 Torr. The vertical temperature gradient across the bulb was approximately 0.5 °C and the average was usually the same as that taken at the midpoint of the bulb. The temperature variation at one point varied only ±0.10 °C. The temperature reported is the average of three readings taken in equal increments from the bottom of top of the bulb. Each starting material was checked for contaminants before use on a 200 ft × 0.1 in. i.d. stainless steel capillary column packed with dibutyl tetrachlorophthalate. The interconversions were studied in the range of 8–35% conversion at 561.7 K, and each kinetic run was analyzed from three to five times on the DBTCP column. The average of these values is reported. The pyrolysis results are presented graphically in Figures 1–4 in the Results section and in tabular form in Table V. Retention times (in minutes) for the four isomeric spiropentanes on a 200 ft × 0.01 in. i.d. DBTCP gas chromatography column operated at 15 psi and 30 °C follow: trans, medial, 16.5; trans, proximal, 22.5 cis, anti, 24.0; cis, syn, 29.5

Pyrolyses as a Function of Pressure. In a separate experiment performed by Mr. Ming Jing Chang, CA was pyrolyzed in the gas phase at 289.3 °C for 9 h at various pressures of added nitrogen. In addition, a pyrolysis of CA was conducted at 289 ± 3 °C in a sealed tube with toluene solvent for 9 h. The product distributions are given in Table VI.

***cis*-2,3-Dimethyl-*syn*- and -*anti*-ethylidenecyclobutane.** Ethyltriphenylphosphonium bromide was suspended in 5 mL of dry ether and 1.20 mL (2.52 mmol) of butyllithium in hexane was added under nitrogen. After 1 h 250 mg (2.55 mmol) of *cis*-2,3-dimethylcyclobutanone[14] was added in a small amount of ether. This was allowed to stir for 1 h at room temperature and then refluxed for 3 h. Most of the ether was distilled and the remaining volatiles were collected in a cold trap (liquid N_2) at 25 Torr. The volatiles were separated on a 10 ft × ¼ in. 20% DBTCP (on Chromosorb P) at 100 °C. The two least vol-

Table V. Mole Percent of the Isomers from Pyrolysis of the Four 1,2,4-Trimethylspiropentanes[a]

time, s	TM	TP	CA	CS
		Starting Material: TM		
10 800	91.72 (0.44)	3.29 (0.23)	3.98 (0.15)	1.01 (0.11)
21 600	85.98 (1.03)	5.84 (0.60)	6.53 (0.48)	1.56 (0.08)
32 400	83.47 (0.74)	7.38 (0.43)	6.87 (0.43)	2.28 (0.34)
43 200	80.48 (1.12)	8.71 (0.45)	7.98 (0.42)	2.83 (0.26)
		Starting Material: TP		
10 800	5.68 (1.12)	88.75 (1.69)	2.27 (0.30)	3.12 (0.27)
21 600	9.04 (0.42)	83.30 (0.51)	3.62 (0.11)	4.04 (0.29)
43 200	16.11 (0.45)	70.69 (0.77)	6.44 (0.28)	6.77 (0.48)
		Starting Material: TM		
10 800	5.06 (0.09)	2.31 (0.22)	86.67 (0.20)	5.97 (0.29)
21 600	9.28 (0.38)	3.53 (0.13)	79.72 (0.40)	7.47 (0.18)
32 400	13.64 (0.51)	5.59 (0.20)	70.83 (0.60)	10.20 (0.21)
43 200	16.25 (0.92)	6.80 (0.41)	65.62 (0.88)	11.32 (0.42)
		Starting Material: CS		
7200	2.41 (0.09)	3.61 (0.22)	5.89 (0.24)	88.09 (0.38)
10 800	4.15 (0.16)	5.47 (0.11)	9.32 (0.03)	81.00 (0.26)
16 200	5.63 (0.19)	7.97 (0.21)	12.90 (0.14)	73.60 (0.13)
21 600	7.23 (0.25)	9.43 (0.31)	15.61 (0.38)	67.73 (0.60)

Table VI

	0.7 Torr	12 Torr	480 Torr	liq[a]
TM	0.151 ± 0.002	0.148 ± 0.06	0.151 ± 0.002	0.071 ± 0.002
TP	0.058 ± 0.001	0.059 ± 0.01	0.058 ± 0.004	0.028 ± 0.001
CA	0.686 ± 0.004	0.686 ± 0.004	0.687 ± 0.004	0.837 ± 0.003
CS	0.105 ± 0.002	0.016 ± 0.001	0.103 ± 0.002	0.063 ± 0.002

[a] The poor temperature control must be responsible for net lower conversion but the product distribution should be compared to those of Figure 3.

atile peaks were collected to yield approximately 5 μL each.

cis-2,3-Dimethyl-*syn*-ethylidenecyclobutane (first off column): IR (CCl_4) 3.28–3.53, 5.88 μ; NMR (CCl_4, 220 MHz) δ 0.94 (t, J = 6 Hz, 6 H), 1.45 (d with fine coupling, J = 6 Hz, 3 H), 2.01 (d with fine coupling, J = 14 Hz, 1 H), 2.35 (m, 1 H), 2.66 (m, 1 H), 2.91 (m, 1 H), and 5.04 (m, 1 H); IR (CCl_4) 3.29–3.52 and 5.88 μ; *m/e* 110.1100 (calcd for C_8H_{14}, 110.1096).

***cis*-2,3-Dimethyl-*anti*-ethylidenecyclobutane:** IR 3.28–3.53, 5.89 μ; NMR (CCl_4, 220 MHz) δ 0.98 (d, J = 7 Hz, 3 H), 1.06 (d, J = 7 Hz, 3 H), 1.50 (d of t, J = 7 and 2 Hz, 3 H), 2.03–2.18 (m, 1 H), 2.36 (septet, J = 8 Hz, 1 H), 2.62 (m, 1 H), 2.98 (m, 1 H), and 4.86 (m, 1 H); IR (CCl_4) 3.29–3.54 and 5.90 μ; *m/e* 110.1102 (calcd for C_8H_{14}, 110.1096).

***trans*-2,3-Dimethyl-*syn*- and -*anti*-ethylidenecyclobutane.** The two compounds were synthesized in the same manner as the cis isomers except that during the vacuum transfer the pot was heated. From 146 mg of *trans*-2,3-dimethylcyclobutanone[14] was obtained approximately 100 μL of liquid that was two overlapping peaks on a 10 ft × ¼ in. DBTCP column (100 °C): IR (CCl_4) 3.28–3.55, 5.90 μ; NMR (CCl_4, 22 MHz) δ 1.00–1.18 (8 lines, 6 H), 1.42–1.54 (m, 3 H), 1.77 (m, 1 H), 1.97 (m, 1 H), 2.37 (broad doublet, J = 26 Hz, 1 H), 2.66 (m, 1 H), and 5.00 (m, 1 H); *m/e* 110.1102 (calcd for C_8H_{14}, 110.1096).

2-Methylcyclopropylamine. Methyl 2-methylcyclopropylamine oxime (5.76 g, 51.0 mmol) was prepared from the corresponding ketone[17] and was placed in 10 mL of dry dimethoxyethane under nitrogen; 8.0 mL (12 g, 57 mmol) of trifluoroacetic anhydride was added over a period of 1 h, the mixture was refluxed for 1.5 h,[17] and then most of the dimethoxyethane was distilled away. The mixture was cooled in an ice bath and a solution of 11 g of KOH in 20 mL of ethylene glycol and 10 mL of water was added slowly. Careful distillation of this mixture through a 30-cm column packed with Pyrex helices yielded 2.73 g of material, bp 65–70 °C, that was contaminated with a small amount of dimethoxyethane: IR (CCl_4) 2.95, 3.35–3.5 μ; NMR (CCl_4, 220 MHz) δ 0.18 (q, J = 4 Hz, 1 H), 0.10 (9, J = 4 Hz, 1 H), 0.38 (p, J = 4 Hz, 1 H), 0.49–0.66 (m, 3 H), 0.95 (d, J = 6 Hz, 3 H), 1.07 (d, J = 6 Hz, superimposed on a broad multiplet, 5 H), 1.89 (p, J = 1 Hz, 1 H), 2.22 (sextet, J = 4 Hz, 1 H); *m/e* 71.0731 (calcd for C_4H_9H, 71.0735). From the NMR two isomers were formed in the ratio of 3:2 by integration of the signals at δ 1.89 and 2.22.

Methyl *N*-(2-Methylcyclopropyl)carbamate. Crude 2-methylcyclopropylamine (2.35 g) was added to an ice-cold slurry of 2.25 g of potassium carbonate (16.3 mmol) in 10 mL of ether and to this mixture was added 3.0 mL (3.7 g, 39 mmol) of methyl chloroformate. The mixture was allowed to warm and stirred for 1 h. Water was added cautiously (30 mL) and the mixture was extracted with 2 × 30 mL of ether and dried over magnesium sulfate. The solvent was removed in vacuo to yield 2.18 g of clear, mobile liquid: IR (CCl_4) 2.9, 3.0 (broad), 3.35–3.5, 5.78 μ; NMR (CCl_4, 220 MHz) δ 0.40 (q, J = 6 Hz, 1 H), 0.61 (septet, J = 2 and 4 Hz, 1 H), 0.73–0.89 (m, 1 H), 1.07 (d, J = 6 Hz, 3 H), 2.08–2.20 (m, 1 H), 3.56 (broad singlet, 3 H), 4.72–5.18 (broad singlet, 1 H); *m/e* 129.0792 (calcd for $C_6H_{14}NO_2$, 129.0790).

Methyl *N*-Nitroso-*N*-(2-methylcyclopropyl)carbamate.[29] Methyl *N*-(2-methylcyclopropyl)carbamate (1.29 g, 10.0 mmol) was placed in 70 mL of dry methylene chloride with 5.0 g of anhydrous sodium acetate and 3.5 g of anhydrous sodium sulfate. The mixture was cooled in an ice bath and an ice-cold solution of dinitrogen tetroxide (ca. 1 M in ether) was added in portions via a cannula.[29] The addition was discontinued when the blue-green color persisted for more than 5 min. The mixture was then evaporated for several minutes at room temperature to remove excess dinitrogen tetroxide. The mixture was then poured into 50 mL of ice water, and the organic layer was separated, washed with 2 × 50 mL of ice-cold 1:1 saturated sodium chloride–saturated sodium bicarbonate and once with ice-cold saturated sodium chloride, and dried over sodium sulfate in the cold. The solvent was removed in vacuo at room temperature to yield 1.58 g of bright yellow liquid; IR (neat, film) 3.35–3.5, 5.68, 6.53 μ; NMR (CCl_4, 220 MHz) δ 0.68–0.90 (m, 3 H), 1.17 (d, J = 6 Hz, 3 H), 1.89 (q, J = 4 and 6 Hz, 1 H), 3.97 (s, 1 H). The material gave no molecular ion and was too unstable to analyze.

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Syn Stereospecificity in the S_N2' Reaction of an Acyclic Allylic Chloride with Secondary Amines

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Abstract: Previous theoretical and experimental investigations of the stereochemistry of the S_N2' reaction (bimolecular nucleophilic substitution with allylic rearrangement) are inconclusive and often contradictory. The reaction of isotopically labeled α-methylallyl chloride with three secondary amines is now shown to be stereospecifically syn. (*R*)-(−)-3-Chloro-(*Z*)-1-butene-*1-d* (**5**) reacts with diethylamine to give a 95:5 mixture of (*R*)-(*E*)- and (*S*)-(*Z*)-allylic amines **14** which is reduced by diimide to (*R*)-(+)- and (*S*)-(−)-*N,N*-diethyl-1-aminobutane-*1-d* (**9**). An authentic sample of (*R*)-(+)-**9** from yeast reduction of butanal-*1-d* shows an unusually large specific rotation, $[\alpha]^{25}_D$ +5.66° (ether). Comparison of the specific rotation of **9** from reduction of the S_N2' product with that of optically pure material reveals that the substitution process is stereospecific: nucleophile attacks the allylic system on the face bearing the leaving group. Similarly, reaction of the enantiomeric chloride (*S*)-(+)-**6** with both dimethylamine and piperidine proceeds with syn stereospecificity.

The S_N2' reaction (bimolecular nucleophilic substitution with allylic rearrangement) has been of synthetic and mechanistic interest for years.[1] Since the first reported example,[2] numerous instances of the process have been documented. Bordwell[1a,3] has argued that a concerted S_N2' process never occurs; rather, all such reactions proceed stepwise, often via ion-pair intermediates of the type postulated by Sneen[4] for S_N reactions in general. On the other hand, Georgoulis and Ville[5] have presented convincing evidence for direct attack by nucleophilic solvents on either the neutral substrate or a polarized species which is less ionized than an intimate ion pair.

Regardless of the precise timing of the bond-making and bond-breaking steps, one can still inquire into the stereochemistry of the reaction. Most theoretical analyses have led to a predicted preference for syn attack[6,8] (in which the nucleophile and leaving group are on the same face of the allylic system), while allowing the possibility of anti stereochemistry for certain combinations of entering and leaving groups.[8c,e]

Until recently, the definitive experimental investigation of the stereochemistry was that by Stork and White[9] who showed that *trans*-6-alkyl-2-cyclohexen-1-yl 2,6-dichlorobenzoates underwent exclusive syn attack by piperidine and malonate. Stork and Kreft[10] have now reinvestigated this system (and the related mesitoate esters of the cis and trans isomers) and have demonstrated that the stereochemistry can vary from predominantly syn to largely anti as the nucleophile is changed; a similar conclusion in support of syn attack on a closely related system was reached by Dobbie and Overton.[11] One can argue, however, that a cyclohexenyl system has certain built-in conformational biases which force syn attack, independent of any stereoelectronic requirements of the S_N2' reaction.[12]

An acyclic case, free of such complications, has been re-

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