(30) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, Chapter 1.
(31) J. H. Exner and E. C. Steiner, *J. Am. Chem. Soc.*, **96**, 1782 (1974).
(32) T. C. Moriarity, Ph.D. Thesis, University of Pittsburgh, 1973.
(33) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).
(34) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).
(35) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).
(36) I. M. Kolthoff and T. B. Reddy, *Inorg. Chem.*, **1**, 189 (1962).
(37) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **90**, 2821 (1968).
(38) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 6561 (1968).
(39) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970); **93**, 4315 (1971).
(40) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974).
(41) G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).
(42) S. Takahashi, L. A. Cohen, H. K. Miller, and E. G. Peake, *J. Org. Chem.*, **36**, 1205 (1971).
(43) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).
(44) R. W. Taft Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1962, Chapter 13.
(45) W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCallum, and N. R. Vanier, *J. Am. Chem. Soc.*, **97**, 7006 (1975).
(46) C. D. Ritchie and R. E. Uschold, *J. Am. Chem. Soc.*, **89**, 2960 (1967).
(47) I. V. Zuika and Y. A. Bankovskii, *Russ. Chem. Rev. (Engl. Transl.)*, **42**, 22 (1973).
(48) F. Bernardi, I. G. Czimadia, A. Mangini, H. B. Schlegel, M. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **97**, 2209 (1975).
(49) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1973.
(50) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(51) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960.
(52) T. C. Waddington, *Trans. Faraday Soc.*, **54**, 25 (1958).
(53) H. Arm, K. Hochstrasser, and P. W. Schindler, *Chimia*, **28**, 237 (1974).
(54) R. G. Pearson in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, London and New York, 1972.
(55) A. P. Marks and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 3324 (1975), and previous literature cited therein.
(56) B. G. Cox, *Annu. Rep. Prog. Chem., Sect. A*, **70**, 249 (1973).

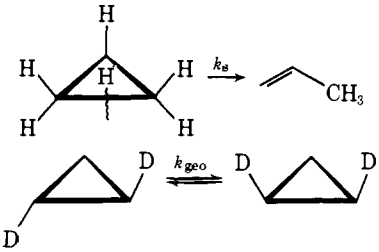
Pyrolyses of Alkyl 2-Methyl- and 2,3-Dimethylcyclopropanecarboxylates and 2-Methylcyanocyclopropane. Effect of Substitution on Geometric and Structural Isomerization. Evidence for Cyclopropane Double Inversion via Reversible Formation of Enols Resulting from Homo-1,5-Hydrogen Shifts

Joseph J. Gajewski,* Robert J. Weber, Richard Braun, Marcia L. Manion, and Brad Hymen

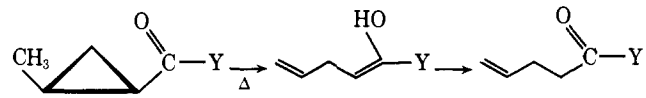
Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received September 2, 1975*

Abstract: Substitution of a carboalkoxy group on cyclopropane reduces the thermal geometric to structural isomerization rate ratio from 20–50 to 5–14, while cyano substitution gives a ratio of 33. Pyrolysis of methyl *cis*-2-methylcyclopropanecarboxylate did not lead to methyl 4-pentenoate, the product reported from homo-1,5-hydrogen shift and ester enol to ester tautomerization. Since ethyl *cis*, *syn*- and *trans*-2,3-dimethylcyclopropanecarboxylates interconverted at 230–275 °C with $\log k_f\,(s^{-1}) = 11.86 - (39\,900 \pm 700)/2.3\,RT$ and $\log k_b\,(s^{-1}) = 11.86 - (42\,800 \pm 700)/2.3\,RT$, while ethyl *cis*,*anti*-2,3-dimethylcyclopropanecarboxylate was stable at 275 °C, it is proposed that the cyclopropane double inversion occurs by reversible homo-1,5-hydrogen shift to a γ,δ-unsaturated ester enol which has at least a 45 kcal/mol barrier to undergo the 1,3-hydrogen shift to produce the γ,δ-unsaturated ester.

Structural and geometric isomerization of cyclopropane upon thermolysis is well known, with geometric isomerization being 10–20 times faster than structural rearrangement.[1] Recently, Berson showed that geometric isomerization occurred with stereospecific double inversion with unsubstituted and phenyl-substituted cyclopropanes.[2]



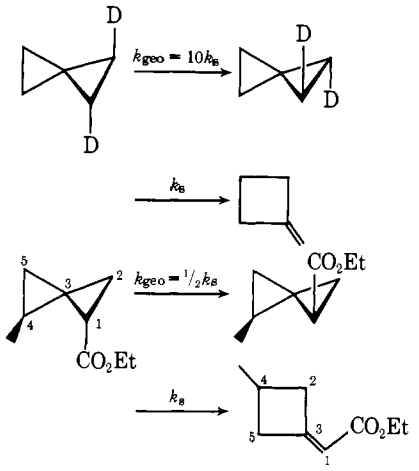
Alkyl,[3a,b] phenyl,[2b] or vinyl[3c] substitution on cyclopropane actually increases the k_{geo}/k_s ratio and, except for monophenyl substitution,[2b] retards double inversion to favor a randomized or "continuous" biradical intermediate.[3d-f] In addition, polar substituents enhance k_{geo} at the expense of k_s—witness Cram's work with geometric and optical isomerization of methyl 2-phenyl-1-cyanocyclopropane-1-carboxylate.[4] With simple carbonyl-substituted cyclopropanes no reactions have been reported save homo-1,5-hydrogen shift and subsequent tautomerization in *cis*-2-alkyl cases to γ,δ-unsaturated carbonyl derivatives.[5]



Y = alkyl or alkoxy

Our interest in alkyl cyclopropanecarboxylates stems from the observation that ethyl spiropentanecarboxylate undergoes structural rearrangement to ethyl methylenecyclobutanecarboxylate faster than geometric isomerization[6] despite the fact that unsubstituted and alkyl-substituted spiropentanes isom-

erize geometrically ten times faster than structural isomerization to methylenecyclobutanes.[7] The dramatic effect of the carbethoxy group made it possible to study the stereochemistry of the structural rearrangement, which was roughly 50% concerted in a $2\sigma s + 2\sigma a$ manner with retention at C(2) and C(4).[6] With the hope that the structural rearrangement of



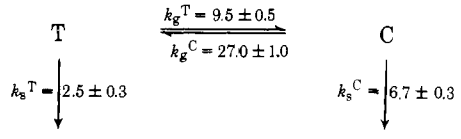
methyl cyclopropanecarboxylate would similarly be enhanced to allow study of the stereochemistry of the cyclopropane structural isomerization as well as isotope effects, the present work was initiated. While the objective was not totally accomplished, the effect of ester and cyano substitution was examined, and evidence bearing on the mechanism of the homo-1,5-hydrogen shift was obtained as a result of observation of a double inversion geometric isomerization of alkyl 2-methyl- and 2,3-dimethylcyclopropanecarboxylate.

Results

Methyl *cis*- and *trans*-2-methylcyclopropanecarboxylate, C and T, respectively, were prepared[3d] and pyrolyzed in a carefully conditioned static gas-phase reactor at 370 °C. Geometric isomerization (cis-trans interconversion) and structural isomerization to the methyl 2- and 3-pentenoates[8] occurred (Table I).

In order to quantitate the reactions, Runge-Kutta numerical integration[9] of the differential equations appropriate to kinetic Scheme I was performed using various values for the rate

Scheme I (all k's $\times 10^{-6}$ /s)

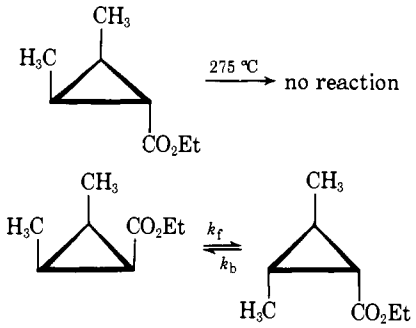


constants. Those providing the best fit to the data of Table I are shown in Scheme I. The distribution of pentenoates from C and T were determined from pyrolyses to only 18% reaction and are recorded in Table II. The 2- and 4-pentenoates were shown to be stable to short-term pyrolysis conditions.

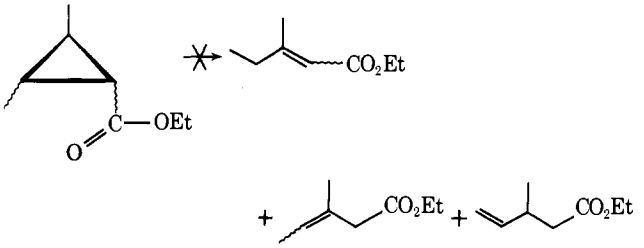
Because it had previously been reported that C gave only methyl 4-pentenoate at 250 °C,[5a] it was surmised that the tautomerization that followed the homo-1,5-hydrogen shift was not occurring in the well-conditioned reactor, and so evidence for the 1,5-hydrogen shift was sought by pyrolyzing the ethyl *cis,syn*-, the *cis,anti*-, and the *trans*-2,3-dimethylcyclopropanecarboxylates. In the temperature range 230-275 °C, the cis,anti compound was stable, but the *cis,syn*- and *trans*-2,3-dimethyl materials interconverted with $\log k_f\ (s^{-1}) = 11.86 - (39\,000 \pm 700)/2.3\,RT$ and $\log k_b\ (s^{-1}) = 11.86 - (42\,800 \pm 700)/2.3\,RT$.

Table I. Pyrolysis of C and T at 370 °C

	Time, s	% C	% T	% methyl 2- and 3-pentenoates
Methyl *cis*-2-methylcyclopropanecarboxylate (C)	4 200	83.2	12.0	4.4
	10 800	69.4	24.3	6.0
	18 000	56.3	34.0	9.8
	55 200	27.1	47.3	25.2
Methyl *trans*-2-methylcyclopropanecarboxylate (T)	7 200	5.8	92.0	2.1
	18 000	10.2	82.3	6.9
	25 200	12.3	79.7	7.6
	55 200	17.2	68.0	14.8



Five VPC analyses of each of three reaction times at a single temperature allowed calculation of a rate constant for reversible first-order interconversion using an equilibrium constant calculated from the value at 275 °C assuming $\Delta S = 0$. Thus the rate constant at a given temperature was the result of 15 analyses. All analyses at the three temperatures were used in the determination of the Arrhenius activation parameters, which was accomplished by an uncorrected least-squares program. The error in the rate constants is the standard deviation as is that for ΔG. The error in E_a is the standard error (Table III). Under the conditions at 275 °C none of the hydrogen-shifted products were formed.



Finally, *cis*- and *trans*-2-methylcyanocyclopropane[3d] were pyrolyzed in the gold flow system at 500 °C and found to undergo geometric isomerization to a nearly 1:1 mixture roughly 33 times faster than structural isomerization to a 6:4 mixture of *cis*- and *trans*-2-pentenonitrile.[10]

Discussion

Geometric vs. Structural Isomerization of Substituted Cyclopropanes. Unsubstituted, monoalkyl-, and dialkyl-substituted cyclopropanes undergo geometric isomerization 20, 34, and 74 times faster than structural isomerization, respectively, as judged by 1,2-dideuterio-,[1b,c] 2,3-dideuterio-1-methyl-,[3a] and 1,2-dimethylcyclopropane,[3b] respectively. Substitution of vinyl[3c] or phenyl[2b] on cyclopropane enhances geometric

Table II. Pyrolysis of Products From C and T at 370 °C

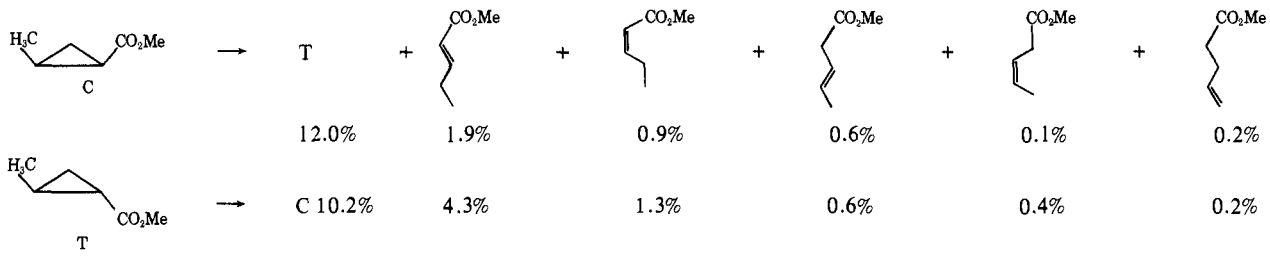


Table III. Rate Constants For The Interconversion of Ethyl *cis,syn-* and *trans*-2,3-Dimethylcyclopropanecarboxylate

Temp	K_{eq}	k_f	k_b
275.27 °C	13.73	9.098×10^{-5}	6.624×10^{-6}
Std deviation	±0.6	(±0.278)	(±0.203)
% error		3.06	3.06
249.97 °C	15.59	1.525×10^{-5}	9.783×10^{-7}
Std deviation	±0.7	(±0.058)	(±0.369)
% error		3.80	3.77
229.84 °C	17.40	3.334×10^{-6}	1.916×10^{-7}
Std deviation	±0.8	(±0.108)	(±0.062)
% error		3.24	3.24

isomerization by a factor of 600 and >100, respectively, over structural isomerization via the same type of vicinal hydrogen shift as in the parent compound.

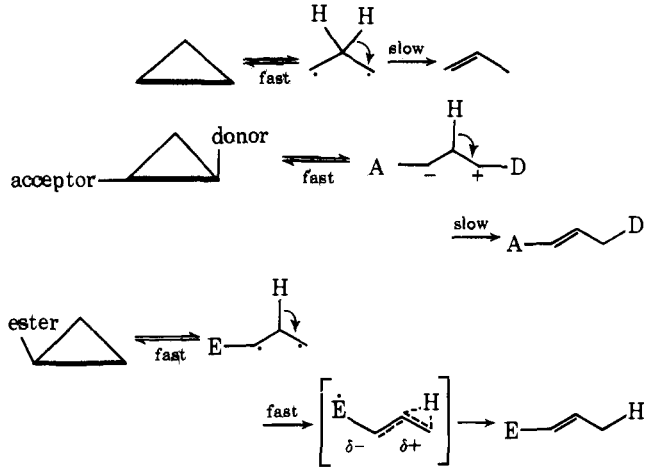
The present work reveals that geometric isomerization of methyl *cis*- and *trans*-2-methylcyclopropanecarboxylate occurs with $k_f + k_b = 3.65 \times 10^{-5}$/s at 370 °C (Scheme I). Geometric isomerization of C and T is only 5.5 and 14 times as fast, respectively, as structural isomerization. Thus, carbomethoxy substitution either increases the rate of structural isomerization relative to geometric isomerization or lowers the rate of geometric isomerization relative to structural isomerization.

Comparison of the rate constants of 1,2-dimethylcyclopropane and C and T at 370 °C reveals that k_{geo} for the ester is only four times faster than for the hydrocarbon, but k_s is 20–50 times faster for the ester than for the hydrocarbon. Thus, ester substitution facilitates structural rearrangement more than geometric isomerizaion. While it is tempting to attribute this to a polar effect on the structural rearrangement transition state, it must be recognized that polar substituents such as cyano do not imbue the cyclopropane with the same behavior as the carbomethoxy substituent (vide infra).

It is possible that polarization of trimethylene biradicals may be a graded continuum, with the nonpolar and very polar biradicals (zwitterions) preferring ring closure, but substitution of weakly electron withdrawing groups may simply polarize the hydrogen shift transition state and, therefore, facilitate that process.

Further evidence that the ester group has the effect of increasing the rate of structural isomerization and not retarding geometric isomerization follows from the relative amounts of 2- and 3-pentenoates formed: 4:1 from C and 5.6:1 from T. To the extent that formation of 3-pentenoate reflects the usual "unpolarized" biradical reactions, the factor of 4–5 increase in the amount of the 2-olefin reflects a rate enhancement by the ester group.

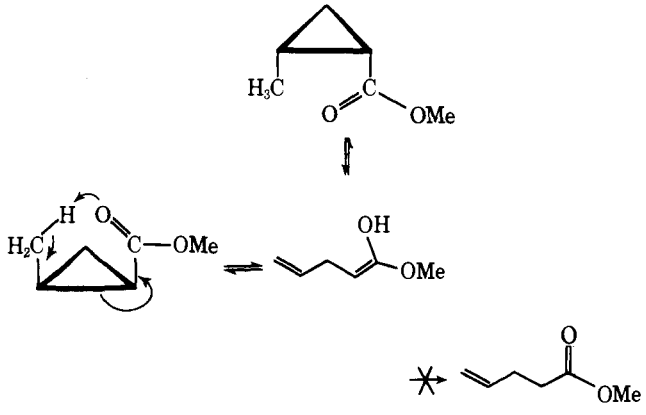
On the other hand, the small factor of 4 increase in k_{geo} upon ester substitution may reflect retardation of geometric isomerization, since ester substitution usually increases ring cleavage rates by factors of 10–20 over methyl.[11] Perhaps the sheer mass of the ester group prevents rapid rotation around



the carbon-bearing ester relative to methyl. If this were true, however, phenyl-bearing carbon should also rotate slower, but k_{geo} is high relative to k_s with 1,2-diphenylcyclopropanes.[3e]

Another correlation that seems to exist is that the more stable the radicals resulting from cyclopropane bond fission, the greater is k_{geo} over k_s. This may be due to rotation becoming more competitive with ring closure, while k_s may be "normal".

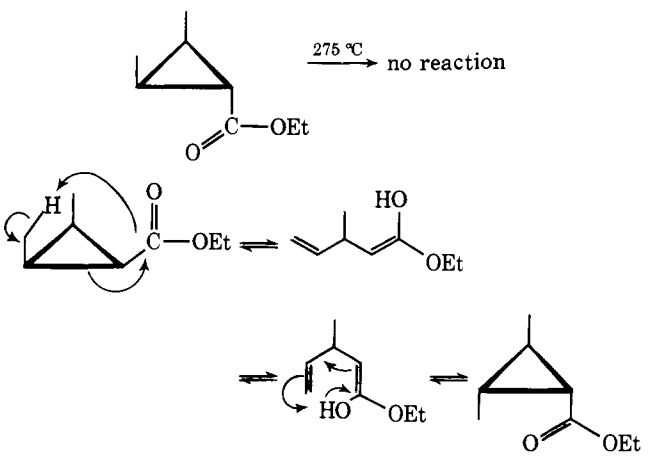
Absence of Methyl 4-Pentenoate from Pyrolysis of C. Contrary to published reports, methyl *cis*-2-methylcyclopropanecarboxylate does not give methyl 4-pentenoate[5a] at high temperatures provided the reaction vessel is well conditioned or if it is a gold flow reactor. One likely possibility recognizes that the previously reported reaction was run at high concentrations in base-washed tubes. The mechanism of formation of the γ,δ-unsaturated ester requires the well-established homo-1,5-hydrogen shift[12a] followed by tautomerization of the resulting ester enol to the ester. Our hypothesis is that enol to ester tautomerization cannot occur in the gas phase in a well-conditioned reactor and, instead, the enol merely reverts to starting *cis*-methylcyclopropane ester.[12b]



Demonstration of this hypothesis could be provided if the optically active cis ester would racemize long before geometric

isomerization to the trans ester could occur; i.e., double inversion of the cis ester should be fast relative to single inversion. However, double inversion of cyclopropanes has been demonstrated without appendaged carbonyl and *cis*-methyl groups to allow the homo-1,5-hydrogen shift,[2] so optically active trans material must also be pyrolyzed to distinguish between the two mechanisms, recognizing that the trans compound cannot double invert by the homo-1,5-hydrogen shift pathway.

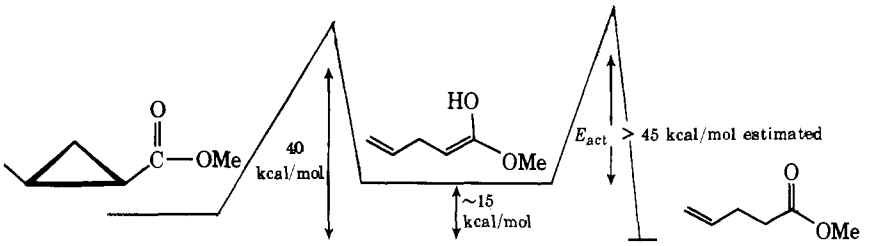
Forsaking the elegance of enantiomerization studies for the convenience of diastereomerization experiments, the carbethoxycarbene adducts of *cis*- and *trans*-2-butene were pyrolyzed with the result that double inversion did indeed occur at low temperatures <275 °C in the well-conditioned reactor when a 2-methyl group was cis to the ester group, but not when the 2-methyl group was trans to the ester. Thus, double inversion occurs via reversible homo-1,5-hydrogen shifts in alkyl *cis*-2-methylcyclopropanecarboxylates.



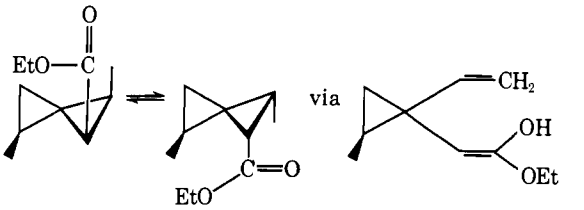
The kinetics of the double inversion also reveal a negative entropy of activation (−7 eu) consistent with the proposed mechanism. Furthermore, the activation energy is 23 kcal/mol less than expected for cyclopropane ring cleavage[1] and ester substitution should not lessen this by more than 5 kcal/mol.[11]

The previously reported conversion of C to methyl 4-pentenoate must have been the result of catalysis of the ester enol tautomerization to the γ,δ-unsaturated ester; therefore, the reported activation parameters for the overall reaction could also be those of a catalyzed reaction. Indeed, the conversion of C to the γ,δ-unsaturated ester was reported to have $\Delta H^{\ddagger}$ of 35.9 kcal/mol and $\Delta S^{\ddagger}$ of −17 eu. The relatively low enthalpy and entropy of activation compared with that in the present work suggests wall catalysis in the rate determining step of the conversion of C to the γ,δ-unsaturated ester.[5]

Energetics of Enol to Ester Tautomerization. It is interesting to note that the tautomerizaion of an enol to an ester can occur by a Woodward-Hoffmann "allowed", but sterically unfavorable 1,3-antarafacial hydrogen shift or by a Woodward-Hoffmann "forbidden", but sterically good 1,3-suprafacial reaction.[13] The suprafacial reaction could be electronically allowed by Berson-Salem subjacent orbital control,[14] and the observations here set the minimum activation energy for this process at 45 kcal/mol. Thus, the enol is about 15 kcal/mol higher in energy than the cyclopropane ester, considering the difference in C-H and O-H bond energies as well as C-O π and C-C cyclopropane bond energies. At 370 °C the enol is in equilibrium with the starting ester. But the ester is being exposed to thermal conditions that easily allow the molecule to traverse a 60-kcal/mol barrier. Thus, the enol has at least a 45-kcal/mol barrier to tautomerize to the γ,δ-unsaturated ester.



Comparison to Other 2-Methylcyclopropanecarboxylate Systems. Double inversion in the pyrolysis of ethyl *cis*-2-methylspiropentanecarboxylate systems in a gold flow reactor was noted previously without explanation in our laboratory.[6] These are now understandable.



R. M. Roberts has examined the kinetics of *cis*-2-methylacetylcyclopropanes always obtaining γ,δ-unsaturated ketones.[5b] This observation requires a catalytic surface which will, no doubt, be demonstrated.[5b]

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on a Varian HR-220 spectrometer. Carbon tetrachloride was used as a solvent; chemical shifts are reported as δ values in parts per million relative to internal Me_4Si. Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrophotometer. 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.

Static Gas-Phase Pyrolyses. The pyrolysis apparatus has been described previously,[7b] but has been modified to allow direct injection of samples from the vacuum line onto a capillary analytical GC. The pyrolysis vessel itself was a 2 l. bulb which was conditioned by injection of 200 μl of dimethyldichlorosilane at 370 °C. After standing for 10-20 h the vessel was evacuated and the treatment was repeated twice more. Then two separate injections of 100 μl each of diethylamine were made. In a typical pyrolysis, 2-5 μl of sample was flushed into the evacuated bulb with sufficient nitrogen gas to bring the pressure to 50-100 Torr.

Flow System Pyrolyses. Flow system pyrolyses in a helium stream were carried out on a Chemical Data Systems Model 1100 Pyrochrom whose reactor output was injected directly into a capillary GC. The reactor is a gold capillary tube with a volume of 3.89 ml. A typical pyrolysis was initiated by injection of the residual sample in a 10-μl syringe, which was flushed in the liquid.

Pyrolysis of methyl *cis*- and *trans*-2-methylcyclopropanecarboxylate in the static reactor was conducted at 370 °C and analyzed by a 200 ft × 0.01 in. i.d. stainless steel capillary column packed with DEGA (LAC-2-R-446). The results are shown in Tables I and II. Flow system pyrolyses were performed at 550 °C with a flow rate of 25 ml/min resulting in 33% reaction to the methyl 2- and 3-pentenoates in the same distribution as from the static reactor pyrolysis.

Preparation and Characterization of Products from Pyrolyses of Methyl *cis*- and *trans*-2-Methylcyclopropanecarboxylate. Methyl 5-methyl-Δ^2-pyrazoline-3-carboxylate was prepared and pyrolyzed by the method of McGreer.[8] In addition to methyl acrylate, four peaks were observed on a 10 ft × ¼ in. 20% Carbowax column. These were separated preparatively and identified.

Peak 1: Methyl *cis*-2-Pentenoate. IR (neat) 1715 (C=O), 1640 cm^{-1} (C=C); NMR (220 MHz) δ 1.05 (t, J = 8 Hz, 3 H), 2.64 (quintet of d, J = 8 and 1.5 Hz, 2 H), 3.63 (s, 3 H), 4.65 (d with fine splitting, J = 11 Hz, 1 H), 5.14 (d of t, J = 11 and 8 Hz, 1 H); *m/e* 114.0687 (calcd for $C_6H_{10}O_2$, 114.0681).

Peak 2: Methyl *trans*-2-Methylcyclopropanecarboxylate. Spectral data were identical with that from a previously isolated sample of methyl *trans*-2-methylcyclopropanecarboxylate. A trace of methyl *cis*-2-methylcyclopropanecarboxylate was also present in this sample.

Peak 3. Both methyl *cis*- and *trans*-3-pentenoate were collected from this peak by separate collection of the front and back sides of the peak.

Front Side of Peak 3: Methyl *cis*-3-Pentenoate. NMR (220 MHz) δ 1.68 (br s, 3 H), 2.91 (br s, 2 H), 3.60 (s, 3 H), 5.04 (m, 2 H).

Back Side of Peak 3: Methyl *trans*-3-Pentenoate. IR (neat) 1740 (C=O), 970 cm^{-1} (*trans*-C-H); NMR (220 MHz) δ 1.64 (d, J = 5 Hz, 3 H), 2.98 (d, J = 6 Hz, 2 H), 3.61 (s, 3 H), 5.50 (m, 2 H); *m/e* 114.0677 (calcd for $C_6H_{10}O_2$, 114.0681).

Peak 4: Methyl *trans*-2-Pentenoate. IR (neat) 1715 (C=O), 1650 (C=C), 978 cm^{-1} (*trans*-C-H); NMR (220 MHz) δ 1.09 (t, J = 7 Hz, 3 H), 2.22 (quintet of d, J = 7 and 1 Hz, 2 H), 3.64 (s, 3 H), 5.71 (d of t, J = 16 and 1 Hz, 1 H), 6.90 (d of t, J = 16 and 7 Hz, 1 H); *m/e* 114.0685 (calcd for $C_6H_{10}O_2$, 114.0681).

Methyl *trans*-2-Pentenoate. In a three-necked flask fitted with reflux condenser, mechanical stirrer, and dropping funnel was placed 0.89 g (57% suspension in mineral oil, 0.021 mol) of sodium hydride in 10 ml of benzene. To the suspension was added 5 g (0.024 mol) of methyl diethylphosphonoacetate in 5 ml of benzene and the stirring continued until hydrogen evolution ceased. To the ylide solution, 1.2 g (0.021 mol) of propionaldehyde in benzene was added dropwise. Stirring was continued at room temperature for 1.5 h and at 100 °C for 2 h. The solution was diluted with water and extracted with diethyl ether. After removal of the ether, the oil was distilled to yield 2 g (83%) of methyl *trans*-2-pentenoate, bp 55 °C (2.5 mm). The spectral data were identical with those of methyl *trans*-2-pentenoate isolated from the pyrolysis of methyl 5-methyl-Δ^2-pyrazoline-3-carboxylate.[8]

Methyl-4-pentenoate was prepared by the method of Kuwajima and Doi.[15] To 0.505 g (5 mmol) of diisopropylamine in tetrahydrofuran was added slowly with cooling 4.18 ml of 1.18 M *n*-butyllithium in hexane under a nitrogen atmosphere. The tetrahydrofuran solution of lithium diisopropylamide was added slowly dropwise to 0.35 g (4 mmol) of methyl acetate and 1.52 g (8 mmol) of cuprous iodide in tetrahydrofuran at −110 °C under nitrogen. The stirring was continued until the cooling bath reached −30 °C. To the solution was added 0.242 g (2 mmol) of allyl bromide in tetrahydrofuran and the stirring continued at −30 °C for 1 h. Saturated ammonium chloride was added to the reaction mixture, the aqueous layer discarded, and the solvent removed under aspirator vacuum. The product was purified by GLC on a 10 ft × ¼ in. 20% Carbowax on Chromosorb W column operated at 90 °C to give 0.1 g (45%) of methyl 4-pentenoate: IR (neat) 1725 (C=O), 1625 (C=C), 985 (C-H), 915 cm^{-1} (C-H); NMR (220 MHz) δ 2.32 (br s, 4 H), 3.60 (s, 3 H), 4.97 (m, apparently t of d with 18, 10, and 1 Hz spacing of lines, 2 H), 6.35 (m, 1 H); *m/e* 114.0664 (calcd for $C_6H_{10}O_2$, 114.0681).

***cis*- and *trans*-2-methylcyanocyclopropane** were synthesized from 2-methyl-3-chlorobutyronitrile by the method of Bergman.[3d]

Pyrolysis of *cis*- and *trans*-2-Methylcyanocyclopropane. *cis*- and *trans*-2-methylcyanocyclopropane were pyrolyzed in the flow system at 475–500 °C and a flow rate of 15 ml/min. Starting with the *cis*-cyclopropanenitrile, 34% of the trans isomer, 2% of the *cis*-2-pentenonitrile, 1% of *trans*-2-pentenonitrile, and 1% of an unknown were formed at 475 °C. At 500 °C the percentage of the products were 41, 1.6, 3.5, and 2.8, respectively. At 500 °C the products from *trans*-2-methylcyclopropanenitrile were the cis isomer (43%), the *cis*-α,β-unsaturated nitrile (7%), the *trans*-α,β-unsaturated nitrile (4%), and unknown (3%).

***trans*- and *cis*-2-pentenonitrile** were synthesized by the method of Jones and Marsey[16] except that THF was used as the solvent. The two components were separated on a 20 ft × ⅜ in. 20% Carbowax (125 °C, 100 ml/min): cis/trans = 1.1.

***cis*-2-Pentenonitrile:** IR (neat, film) 3.25–3.5, 4.51, 6.18, 13.55 μm; NMR (CCl_4, 220 MHz) 1.12 (t, J = 7.5 Hz, 3 H), 2.42 (d of p, J = 7.5 and 1 Hz, 2 H), 5.22 (d of t, J = 11 and 1 Hz, 1 H), 6.38 (d of t, J = 11 and 7.5 Hz, 1 H); *m/e* 81.05790 (calcd for C_5H_7N, 81.05785).

***trans*-2-Pentenonitrile:** IR (neat, film) 3.25–3.5, 4.49, 6.14, 10.32 μm; NMR (CCl_4, 220 MHz) 1.04 (t, J = 7 Hz, 3 H), 2.26 (d of p, J = 7 and 1.75 Hz with fine structure, 2 H), 5.27 (d of t, J = 16.5 and 6.5 Hz, 1 H), 7.04 (d of t, J = 16.5 and 1.75 with fine structure, 1 H); *m/e* 81.05187 (calcd for C_5H_7N, 81.05785).

Ethyl *cis,syn*-, *cis,anti*-, and *trans*-2,3-Dimethylcyclopropanecarboxylates. The syntheses of ethyl *cis,syn*- and *cis,anti*-2,3-dimethylcyclopropanecarboxylates and the trans isomer were accomplished in a manner similar to that described by Kochi[17] and were obtained in approximately 20% yield (based on ethyl diazoacetate). The anti and syn isomers (1.5:1) were separated on a 20 ft × ⅜ in. DEGS on Chromosorb W column at 110 °C, 100 ml/min He. The trans isomer was also purified on this column.

Cis,Syn: IR (CCl_4) 3.3–3.5, 5.80, 8.69 μm; NMR (CCl_4, 220 MHz) 1.16 (d, J = 6 Hz) and 1.32 (t, J = 7 Hz) superimposed on a broad multiplet (total, 11 H), 1.50 (d of d, J = 4 and 5 Hz, 1 H), 4.00 (q, J = 7, 2 H); *m/e* 142.0989 (calcd for $C_8H_{14}O_2$, 142.0994).

Cis,Anti: IR (CCl_4) 3.3–3.5, 5.81, 8.50 μm; NMR (CCl_4, 220 MHz) 0.87 (t, J = 4 Hz, 1 H), 1.09 (unsymmetrical 4 lines, 6 H), 1.22 (t, J = 7 Hz, 3 H), 1.38 (m, 2 H), 3.99 (q, J = 7 Hz, 2 H); *m/e* 142.1000 (calcd for $C_8H_{14}O_2$, 142.0994).

Trans: The NMR agreed with the literature:[18] IR (CCl_4) 3.3–3.5, 5.82, 8.49, 8.61 μm; NMR (CCl_4, 220 MHz) 1.10 (d of d, J = 8 and 6 Hz) and 1.23 (t, J = 7 Hz) superimposed on other resonances (total, 12 H), 4.02 (q, J = 7 Hz, 2 H); *m/e* 142.1000 (calcd for $C_8H_{14}O_2$, 142.0994).

Ethyl *trans*- and *cis*-3-methyl-2-pentenoate were synthesized according to the method of Wadsworth and Emmons[19] and the NMR and IR are consistent with the two components separated by VPC (cis/trans = 2.8:1) on a 20 ft × ⅜ in. 30% DEGS column at 115 °C, 120 ml/min.[20,21]

Ethyl 3-methyl-4-pentenoate was produced by the pyrolysis of ethyl *trans*-2,3-dimethylcyclopropanecarboxylate in an acid washed sealed tube for 42 h at 282 °C. Spectral data were consistent with the literature.[5a]

Kinetics of Interconversion of Ethyl *cis,syn*- and *trans*-2,3-Dimethylcyclopropanecarboxylate. The kinetics of interconversion of these compounds were studied in the static reactor at 230–275 °C and analyzed by a 200 ft × 0.1 in. i.d. stainless steel capillary column packed with DEGA (LAC-2-R-446). The results are presented in Table III. The homo-1,5-hydrogen shift product from ethyl *cis,anti*-2,3-dimethylcyclopropanecarboxylate was stable for 13 h at 275 °C.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

References and Notes

(1) (a) T. S. Chambers and G. B. Kistiakowski, *J. Am. Chem. Soc.*, **56**, 399 (1934); (b) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); (c) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).
(2) (a) J. A. Berson and L. D. Pedersen, *J. Am. Chem. Soc.*, **97**, 238 (1975); (b) J. A. Berson, L. D. Pedersen, and B. K. Carpenter, *Ibid.*, **97**, 240 (1975); **98**, 122 (1976).
(3) (a) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); (b) M. C. Flowers and H. M. Frey, *Proc. R. Soc. London, Ser. A*, **257**, 122 (1960); **260**, 424 (1960); (c) C. A. Wellington, *J. Phys. Chem.*, **66**, 1671 (1962); (d) W. L. Carter and R. G. Bergman, *J. Am. Chem. Soc.*, **90**, 7344 (1968); **91**, 7411 (1969); (e) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968); (f) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **96**, 1168 (1974).
(4) (a) E. W. Yankee, B. Spencer, N. E. Howe, and D. J. Cram, *J. Am. Chem. Soc.*, **95**, 4220 (1973); (b) N. E. Howe, E. W. Yankee, and D. J. Cram, *Ibid.*, **95**, 4230 (1973); see also (c) A. Chmurny and D. J. Cram, *Ibid.*, **95**, 4237 (1973).
(5) (a) D. E. McGreer and N. W. K. Chiu, *Can. J. Chem.*, **46**, 2217, 2225 (1968); (b) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, **87**, 2281 (1965).
(6) J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8865 (1972); C. R. Johnson, et al., *Ibid.*, **93**, 3771 (1971).
(7) (a) J. C. Gilbert, *Tetrahedron*, **25**, 1459 (1969); (b) J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8857 (1972).

(8) D. E. McGreer, W. Wai, and G. Carmichael, *Can. J. Chem.*, **38**, 2410 (1960).
(9) We thank Professor Martin Saunders for giving us a copy of this program.
(10) Also formed was an unknown roughly equivalent in quantities to the trans-α,β-unsaturated nitrile and surmised to be one of the β,γ-isomers.
(11) (a) E. W. Cain and R. G. Solly, *J. Am. Chem. Soc.*, **95**, 4791 (1973); (b) D. C. Owsley and J. J. Bloomfield, *J. Org. Chem.*, **36**, 3768 (1971).
(12) (a) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964) report log k (s^{-1}) = 11.03 − (31,200/2.3 RT) for the conversion of *cis*-2-methylvinylcyclopropane to *cis*-1,4-hexadiene. (b) This hypothesis is a logical extension of the observations of W. R. Roth, *Justus Liebigs Ann. Chem.*, **671**, 10 (1964); W. R. Roth and J. Konig, *ibid.*, **688**, 28 (1965); and of W. Grimme, *Chem. Ber.*, **98**, 756 (1965), which deal with *cis*-1,4-hexadienes reforming *cis*-2-methylvinylcyclopropanes.
(13) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(14) (a) J. A. Berson and L. Salem, *J. Am. Chem. Soc.*, **94**, 8917 (1972); (b) L. Salem and W. T. Borden, *ibid.*, **95**, 932 (1973).
(15) I. Kuwajima and Y. Doi, *Tetrahedron Lett.*, 1163 (1972).
(16) G. Jones and R. F. Marsey, *Chem. Commun.*, 543 (1968).
(17) J. K. Kochi and R. G. Salomon, *J. Am. Chem. Soc.*, **95**, 3300 (1973).
(18) J. A. Landgrebe and J. D. Shoemaker, *J. Am. Chem. Soc.*, **89**, 4465 (1967).
(19) W. S. Wadsworth and W. D. Emmons, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, p 547.
(20) H. Vieregge, H. M. Schmidt, J. Renema, H. J. T. Bos, and J. Garens, *Recl. Trav. Chim. Pays-Bas*, **85**, 929 (1966).
(21) L. Decaux and K. Vessiere, *C. R. Acad. Sci., Ser. C*, **267**, 738 (1968).

Stereocontrolled Synthesis, Conformational Features, and Response to Thermal Activation of the Seven Possible Bis- and Trishomocycloheptatrienes

Michael R. Detty[1] and Leo A. Paquette*

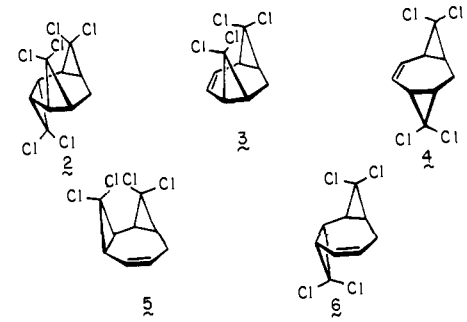
Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received July 27, 1976*

Abstract: The stereocontrolled synthesis of the seven possible bis- and trishomocycloheptatrienes is detailed. Reaction of cycloheptatriene with dichlorocarbene and subsequent reductive dechlorination has afforded *syn*- (**8**) and *anti*-1,5-bishomocycloheptadienes (**9**) together with the anti,anti-trishomo derivative **7**. Sequential treatment of **9** with dibromocarbene and sodium in *tert*-butyl alcohol/tetrahydrofuran provided exclusively the anti,syn-trishomo framework (**11**). Preparation of the stereoisomeric 1,3-bishomocycloheptadienes **20** and **23** began by exhaustive cyclopropanation of 3,5-cycloheptadienol. Following Collins oxidation to the derived ketones, the requisite olefinic units were introduced by lithium–ammonia reduction of the enol phosphates. The remaining trishomo derivative **24** was obtained by cyclopropanation of **20** with methylene iodide and zinc–silver couple. The conformational populations of these tri- and tetracyclic systems were revealed by detailed NMR examination which included variable-temperature studies. The most interesting compound proved to be **9** which undergoes facile degenerate ring inversion with E_a = 8.13 kcal/mol and $\Delta H^{\ddagger}$ = 7.74 kcal/mol. A decrease in conformational flexibility relative to cycloheptatriene (by ca. 2.3 kcal/mol) was thereby revealed. Lastly, the susceptibility of all seven hydrocarbons to thermal rearrangement was assessed.

Although the concepts of homoconjugation and homoaromaticity have elicited much interest in recent times,[2] the interactions which are so strikingly manifested in monohomo examples have less frequently been sought in systems having the intrinsic structural capability for more extended electronic delocalization.[3] Bis- and trishomocycloheptatrienes, for example, potentially bring this dimension to the chemistry of the familiar tropylium ion. Yet, none of the seven possible hydrocarbons which belong to this series have been reported to this time.[4] The primary goal of the present study was to devise unequivocal routes to these molecules such that all possible stereoisomers were fully characterized. Ancillary objectives were examination of the conformational characteristics of the title hydrocarbons and determination of their susceptibility to thermal bond reorganization. The success of the synthetic schemes to be described has provided substrates directly relevant to mechanistic studies of long-range cyclopropyl interaction,[5a,b] photoelectron spectroscopic analysis of extended cyclopropane interaction,[6] and the general question of stereochemical requirements for trishomoaromaticity.[5c]

Synthetic Considerations

The consequences of adding dichlorocarbene to cycloheptatriene (**1**) under conditions of phase transfer catalysis were first examined. Contrary to the report of Sasaki and coworkers,[7] one tricyclopropanated (**2**) and two biscyclopropanated compounds (**3** and **4**) were produced and readily separated by a combination of column chromatography on silica gel and fractional crystallization. Rigorous stereochemical assignments to these adducts could, of course, not be made on the basis of their ^{1}H NMR spectra. However, because the cyclopropyl protons in **2** appear as a narrow signal at δ 1.80 and the pair of methylene protons gives rise to multiplets centered at 2.36 and 1.18, a symmetrical structure is seemingly implicated for this product. The level of anisotropic shielding operating on the latter of these hydrogens is particularly noteworthy. The spectra of **3** and **4** also reveal symmetrical patterns consistent with molecular frameworks having either C_s or C_2 symmetry (see Experimental Section).



From the demonstrated absence of **5** and **6** (vide infra), the preferred initial site of dichlorocarbene attack on cycloheptatriene is inferred to be the C(1)–C(2) double bond. Subse-