Table I. Ratio of Methyl-Shifted to Non-Methyl-Shifted Cyclopentadiene at 50°

Bath gas[a]	Reactant[b]	Pressure			
		<2 Torr	100 Torr	465 Torr	900 Torr
Pentane	**2**		0.88 ± 0.03	0.70 ± 0.03	0.65 ± 0.03
	1		0.76 ± 0.10	0.54 ± 0.10	
Nitrogen	**2**		0.97 ± 0.03	1.01 ± 0.05	
	1		0.85 ± 0.10	0.85 ± 0.10	
None	**2**	0.91 ± 0.03			
	1	0.85 ± 0.10			

[a] Bicyclopentene + cyclopentadiene pressure <2 Torr in all experiments. [b] **1**, 1-methylbicyclopent-2-ene; **2**, 2-methylbicyclopent-2-ene.

less rearranged product. Our experimental results at 50° are in good agreement with the calculations of Flowers and Frey[5] which are based on the scheme in eq 1. Finally, experiments carried out at 30° were qualitatively similar to those shown in the table. These results, taken together, require that at least the predominant pathway for production of the rearranged isomer must be hydrogen shifts in the chemically activated cyclopentadiene produced by central bond cleavage.

The isomerization of methylbicyclopentenes in solution was studied in order to clarify previous controversy and for comparison with gas-phase results. The products were not trapped but analyzed directly.[8] By determining rate constants for disappearance of **2** ($k = 1.28 \times 10^{-4}$ sec^{-1}, 50°) as well as those for the interconversion of **3** and **4** ($k_{3\rightarrow4} = 3.65 \times 10^{-5}$, $k_{4\rightarrow3} = 2.78 \times 10^{-5}$ sec^{-1}, 50°) and measuring the amounts of **3** and **4** at various times, we could determine[9a] the ratio of **4**/**3** at zero time to be[9b] *ca.* 10. The kinetic data at 30° were not amenable to treatment at the same level of sensitivity. However, results were similar to those at 50°, implicating an unequivocal amount of rearranged isomer arising directly from starting methylbicyclopentene. As noted previously, the amount of rearranged product observed in solution is of the order predicted by consideration of the gas-phase pressure dependence and the mechanism outlined in eq 1. This suggests a virtually unprecedented chemically activated reaction in solution.[10]

The original work[1] in the bicyclopentene system assumed cleavage of the central bond; the activation parameters for this process were shown to be completely consistent with similar processes in other larger, bicyclic systems. It thus seemed to us highly unlikely that such a process was not operative for bicyclopentene itself. Subsequently, the energetics were shown to be consistent with the comparable, formally disrotatory process in monocyclic cyclobutenes.[11] In none of this work was a biradical mechanism assumed. An empirical biradical *model* for estimating energetics was utilized,[1b] but no mechanistic inferences were drawn as to whether the reaction was actually stepwise, involving a discrete intermediate.

It now seems clear that the evidence presented in support of concerted bond switching reactions[2b,4] is neither conclusive nor persuasive. Presently available data lead to the conclusion that the major course of the reaction involves cleavage of the central bond to give the unrearranged cyclopentadiene, followed by hydrogen shifts.

Finally, we reemphasize that secondary products arising from chemical activation may be important (and misleading) in mechanistic investigations. Work is underway to examine their importance in other systems.

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(8) Rates of disappearance of 2-methylbicyclopentene and of interconversion of the cyclopentadienes in dry tetrahydrofuran were measured in sealed tubes which had previously been washed with 5% EDTA solution. Reactant and product mixtures were analyzed as above. Addition of crushed glass to the reaction tubes had no effect upon the course of the reactions.

(9) (a) Determined by finding the relative rate constants for "direct" production of 3 and 4 which give (by numerical integration) the best least-squares fit to all of the data, making use of the independently measured rate constants for disappearance of 2 and interconversion of 3 and 4. (b) Within the reproducibility of our rate constants the ratio is 10 ± 1. If we permit ±20% variation in the interconversion rate constants for 3 and 4, the ratio varies from approximately 5 to 18. However, all combinations of reasonable values of the rate constants require some "direct" formation of 3 from 2.

(10) However, note that the intermediacy of chemically activated cyclobutene has been proposed in the solution phase decomposition of the Grignard reagent from 4-bromo-1-chloro-1-butene: E. A. Hill, *J. Amer. Chem. Soc.*, **94**, 7462 (1972). Also, "hot atom" chemistry has been observed in rigid media; see, for example, W. B. DeMore and N. Davidson, *ibid.*, 81, 5869 (1959).

(11) J. I. Brauman and W. C. Archie, Jr., *ibid.*, **94**, 4262 (1972).

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Kinetics of the Thermal Isomerization of 2-Methylbicyclo[2.1.0]pent-2-ene in Hexane[1]

Sir:

At 50° in the presence of 1 atm of nitrogen, 2-methylbicyclo[2.1.0]pent-2-ene (A) is isomerized to both 2-methylcyclopentadiene (B) and 1-methyl cyclic diene (C).[2] The kinetic data for the three-component, four rate constant reaction scheme, analyzed in terms of the appropriate integrated rate expressions, give the partitioning ratio $k_{ab}/k_{ac} = 1.3$.[2]

Two rationales have been advanced for the appearance of the "crossover product" as a major component of the kinetically controlled isomerization mixture. In one, the isomerizations are viewed as competitive ${}_\sigma 2_s + {}_\sigma 2_a$ intramolecular cycloreactions in which either bonds 12,54 or 43,51 of the bicyclopentene are utilized.[2] In the second and more recently proposed mechanistic interpretation,[3] rate-determining cleavage of the 14 bond gives vibrationally excited 2-methylcyclopenta-

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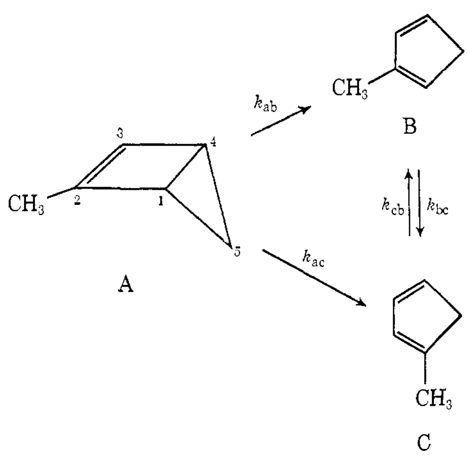
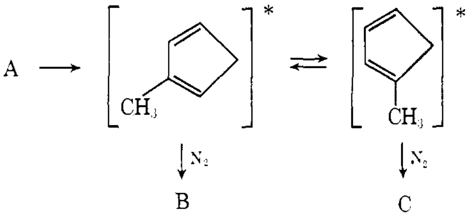
(1) Support from the National Science Foundation and the Hoffmann-La Roche Co. is gratefully acknowledged.

(2) J. E. Baldwin and G. D. Andrews, *J. Amer. Chem. Soc.*, **94**, 1775 (1972).

(3) M. C. Flowers and H. M. Frey, *ibid.*, **94**, 8636 (1972).



diene: this chemically activated species rearranges through 1,5-hydrogen shifts[4] faster than it can be collisionally deactivated.[3] Indeed, calculations suggested that the isomerization of A should give nearly the same product ratios at pressures from 100 to 1000 Torr—collisional deactivation in the gas phase, according to the model and parameters used, is that inefficient.[3]



Chemical activation effects in thermal hydrocarbon rearrangements, while well known, are ordinarily totally suppressed at pressures of 10–100 Torr.[5] The isomerization of 2-methylbicyclo[2.1.0]pent-2-ene, however, may be particularly susceptible to chemical activation effects; the reaction is quite exothermic and the secondary rearrangement relatively facile.

To challenge these conflicting hypotheses with new and relevant data, the kinetics of the isomerizations of A in hexane at 30.0–89.7° have been measured.

After simpler routes from experimental data to rate constants, including plots of [B] and [C] against $1 - \exp(-kt)$, where k measures the first-order disappearance of A,[6] and visual best-fit efforts matching theoretical curves based on estimated parameters with experimental points,[7] were tried and recognized as unreliable, we turned to a method obviating subjective judgments: a computer-accomplished least-squares fit using all data points for the linear function appropriate to the kinetic scheme.[8,9] Here $k' = k_{bc} + k_{cb}$ and $k = k_{ab} + k_{ac}$.

$$([B]_\infty - [B]_t)/[A]_0 + (([B]_0 - [B]_\infty)/[A]_0)\exp(-k't) = ((k_{ab} - k_{cb})/(k' - k))(\exp(-k't) - \exp(-kt))$$

All rate constants in the expression except k_{ab} are relatively easy to measure independently and may then be combined with initial concentrations and $[B]_t$ data in the linear least-squares treatment to give k_{ab} as the single derived parameter. A similar equation uses $[C]_t$ data and provides k_{ac}. The results obtained are summarized in Table I,[10] while the methylcyclopentadiene equilibration kinetics are reported in Table II.

Table I. Kinetics of the Thermal Isomerizations of 2-Methylbicyclo[2.1.0]pent-2-ene in Hexane

Temp, °C	$k = k_{ab} + k_{ac}$, sec^{-1}	k_{ab}/k_{ac}
30.0	$(1.07 \pm 0.1) \times 10^{-5a}$	13.9 ± 4.2
50.0	$(1.01 \pm 0.07) \times 10^{-4a}$	13.0 ± 5.1
70.0	$(10.41 \pm 0.05) \times 10^{-4b}$	10.7 ± 2.3
80.3	$(3.14 \pm 0.03) \times 10^{-3b}$	11.5 ± 2.7
89.7	$(7.68 \pm 0.08) \times 10^{-3b}$	12.0 ± 3.9

[a] Data averaged over four runs; in each, five–ten aliquots from a single reaction mixture were analyzed. [b] Data from analysis of eight–ten separate sealed ampoules.

Table II. Kinetics of Thermal Equilibration of 1- and 2-Methylcyclopentadiene in Hexane

Temp, °C	$k' = k_{bc} + k_{cb}$, sec^{-1}	k_{cb}/k'
30.0	$(3.2 \pm 0.3) \times 10^{-6}$	0.593^b
50.0	$(3.59 \pm 0.08) \times 10^{-5}$	0.583
70.0	3.43×10^{-4a}	0.574^b
80.3	$(1.05 \pm 0.04) \times 10^{-3}$	0.570
89.7	2.76×10^{-3a}	0.567^b

[a] Estimated from an Arrhenius plot. [b] Interpolated or extrapolated from measured values at 50 and 80°.

Arrhenius plots for $\ln k$ and $\ln k'$ as functions of T^{-1} give $E_a = 24.7 \pm 0.6$ kcal mol^{-1} and $\log A = 12.7 \pm 0.4$ for the isomerizations of 2-methylbicyclopentene, and $E_a = 24.7 \pm 0.5$ kcal mol^{-1} and $\log A = 12.2 \pm 0.3$ for the interconversion of 1-methyl- and 2-methylcyclopentadienes.

The rate constants k_{ab} and k_{ac} in Table I are obtained with comparable absolute precision, and taking the ratio of the larger to the smaller inevitably leads to a substantial standard deviation. Taken as a whole, the ratios k_{ab}/k_{ac} over the temperature range studied *give a 95% confidence interval of 12.2 ± 3.5.* Thus, the partitioning ratio is quite different in hexane and in the gas phase, but there is a clearly recognizable component of 1-methylcyclopentadiene in the kinetically controlled product mixture in hexane.[11]

In terms of a chemical activation model with rate-determining 14-bond cleavage, these results may be explained by assuming that even in solution and to a constant extent over a 60° temperature range, collisional deactivation and further isomerization of vibrationally excited 2-methylcyclopentadiene are kinetically competitive.

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[4] D. S. Glass, R. S. Boikess, and S. Winstein, *Tetrahedron Lett.*, 999 (1966).

[5] *Inter alia* (a) B. S. Rabinovitch and M. C. Flowers, *Quart. Rev., Chem. Soc.*, 18, 122 (1964); (b) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, 49 (1972); (c) J. E. Baldwin and J. Ollerenshaw, *Tetrahedron Lett.*, 3757 (1972).

[6] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 160–162.

[7] J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, in press.

[8] The expression for this kinetic system with boundary conditions $[A] = [A_0]$, $[B] = [B_0]$, and $[C] = [C_0]$ at $t = 0$ published by R. A. Alberty and W. G. Miller (*J. Chem. Phys.*, 26, 1231 (1957)) is in error.

[9] The apparent singularity in the integrated rate equations for the case $k = k'$ may be handled; as k approaches k', the right side of the equation approaches a finite limit, which through application of l'Hospital's rule is found to be $(k_{ac} - k_{ab})t \exp(-kt)$; *cf.* C. L. Perrin, "Mathematics for Chemists," Wiley, New York, N. Y., 1970, p 24.

[10] Referees and Editors were provided with a detailed account of the numerical analysis and sample kinetic plots.

[11] S. McLean, D. M. Findlay, and G. I. Dmitrienko (*J. Amer. Chem. Soc.*, 94, 1380 (1972)) found no more than 5% of 1-methylcyclopentadiene when A was isomerized in chloroform-*d* at 43°, correcting earlier mistaken reports (S. McLean and D. M. Findlay, *Can. J. Chem.*, 48, 3107 (1970); J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

In terms of a direct partitioning model the rate ratio variation between vapor and condensed phase isomerizations may be explained by assuming that $\Delta\Delta \bar{V}^{\ddagger}$ for the two competitive processes and differences in solvent organization at the transition states may combine to cause the observed change.[12]

Either model may yet be demonstrated experimentally as the more correct, or each may be appropriate to some fraction of the total process. At present the issue remains unresolved, for neither the gas phase nor the solution phase kinetic findings are uniquely interpretable by a single mechanistic postulate.

(12) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 131.

(13) National Science Foundation Predoctoral Trainee, 1972–1973.

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The Chemistry of Alkyl Thiolsulfinate Esters. IV. A Mechanistic Study of the Disproportionation Reaction[1]

Sir:

Thiolsulfinate esters are an unusually unstable class of compounds known to disproportionate readily to disulfides and thiolsulfonate esters (eq 1); this reaction

$$2RS(O)SR \longrightarrow RSO_2SR + RSSR \qquad (1)$$

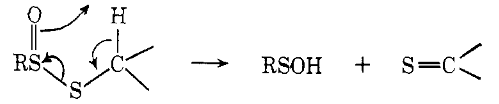
displays acid and sulfide catalysis and may be thermally as well as photochemically initiated.[2–4] Detailed studies of the mechanism of the thermal[2a] and catalyzed[4] disproportionation of diaryl thiolsulfinates have recently appeared; similar studies with dialkyl thiolsulfinates have not hitherto been described. We now report the preliminary results of a study of the thermal and photochemical disproportionation of a variety of symmetrical and unsymmetrical dialkyl thiolsulfinates and contrast these findings with those previously described for the diaryl esters. In a study of the disproportionation reaction, the dialkyl esters possess the advantage that they (and their decomposition products) are amenable to detailed gas chromatographic (gc) and coupled gas chromatographic–mass spectrometric (gc–ms) analysis under mild conditions. Furthermore the possibility exists for the diversion of intermediates through reactions involving the alkyl groups; the synthetic exploitation of this latter possibility is the subject of the accompanying communication.[5]

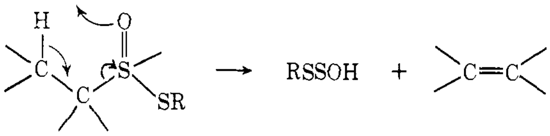
Table I. Relative Thermal Stability of Neat Dialkyl Thiolsulfinate Esters

Thiolsulfinate esters	Time for 50% decomposition at 96° (min)[a]
MeS(O)SMe	7
MeS(O)SEt[6]	11
MeS(O)S-*i*-Pr[6]	32
EtS(O)SMe[6]	40
n-$C_{12}H_{25}S(O)SC_{12}H_{25}$-*n*[d]	52
t-BuS(O)S-*t*-Bu[e]	148
MeS(O)S-*t*-Bu[6]	~10^3
1-AdS(O)SAd-1[b,7]	>10^5 [c]

[a] Analysis by quantitative ir and/or quantitative gc. [b] 1-Adamantyl 1-adamantanethiolsulfinate.[7] [c] After 1.2 × 10^5 min, >70% remaining thiolsulfinate. [d] P. Allen, Jr., and J. W. Brook, *J. Org. Chem.*, **27**, 1019 (1972). [e] R. W. Murray, R. D. Smetana, and E. Block, *Tetrahedron Lett.*, 299 (1971).

The effect of structure on stability of the dialkyl esters is seen through a comparison of ease of disproportionation (indicated by time for 50% decomposition of *neat* thiolsulfinate at 96°) for the representative esters in Table I. The composition of the thiolsulfonate ester mixtures produced by disproportionation of several *unsymmetrical* thiolsulfinate esters[6] under a variety of conditions is indicated in Table II. Table I shows that thiolsulfinates are stabilized by alkyl substitution adjacent to *either* sulfur. Particular stability results when neither α-sulfenyl nor β-sulfinyl protons are available for β-elimination processes (eq 2[6b] and 3,[1b] respectively) as demonstrated by the remarkable stability of 1-adamantyl 1-adamantanethiolsulfinate.[7] Table II reveals that unsymmetrical thiolsulfonate is favored over symmetrical thiolsulfonate in pyrolysis of neat samples of thiolsulfinates (entries 1–5) by a factor of 4–15 with the singular exception of isopropyl methanethiolsulfinate. In none of the pyrolyses studied were we able to detect thiolsulfonates or thiolsulfinates derived from oxygen crossover (*i.e.*, $EtSO_2SMe$, $EtSO_2SEt$, or EtS(O)SMe from MeS(O)SEt, or $MeSO_2SEt$, $MeSO_2SMe$, or MeS(O)SEt from EtS(O)SMe) although our gc analytical method was capable of detecting as little as 0.1% of a crossover product in the presence of the noncrossover mixture of thiolsulfonates and thiolsulfinates. By way of comparison, Fava and coworkers found approximately 10% oxygen crossover in thiolsulfonates and thiolsulfinates recovered from pyrolysis of aryl thiolsulfinates specifically labelled (^{35}S) on the sulfinyl sulfur.[2a]


(2)


(3)

In order to minimize problems associated with different steric environments at the two thiolsulfinate sulfurs, we have examined the products from pyrolysis of the unsymmetrically deuteriated thiolsulfinates MeS(O)-SCD_3 and EtS(O)SCD_2Me (Table II, entries 6 and 7). Here too we find a predominance of unsymmetrical

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(1) (a) Presented at the Vth Symposium on Organic Sulfur Chemistry, Lund, Sweden, June 5–9, 1972. (b) Paper III: E. Block, *J. Amer. Chem. Soc.*, **94**, 644 (1972).

(2) Thermal disproportionation: (a) P. Koch, E. Ciuffarin, and A. Fava, *ibid.*, **92**, 5971 (1970); (b) C. J. Cavallito, J. H. Bailey, J. S. Buck, and C. M. Suter, *ibid.*, **66**, 1950, 1952 (1944); (c) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 73, 129 (1954); (d) D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(3) Photochemical disproportionation: (a) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (b) P. J. Berner, Ph.D. Thesis, Stevens Institute of Technology, 1964 (γ radiation).

(4) Catalyzed disproportionation: J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **95**, 109 (1973).

(5) E. Block and J. O'Connor, *ibid.*, **95**, 5048 (1973).

(6) (a) Prepared by condensation of the appropriate sulfinyl chloride and mercaptan;[2c] satisfactory spectral and, where product stability permits, analytical data were obtained for all new compounds. (b) E. Block, *J. Amer. Chem. Soc.*, **94**, 642 (1972).

(7) Prepared in 53% overall yield by oxidation of 1-adamantanethiol;[8] ir 9.25 μ (S=O), uv λ_{max} (cyclohexane) 258 nm (ϵ 2300); mass spectrum *m/e* 350 ($C_{20}H_{30}S_2O$, parent). *Anal.* Calcd for $C_{20}H_{30}S_2O$: C, 68.52; H, 8.63; S, 18.29. Found: C, 68.61; H, 8.43; S, 18.52.

(8) H. Stetter, M. Krause, and W.-D. Last, *Chem. Ber.*, **102**, 3357 (1969).