Table II. Optical Purities of Recovered **7**, **8**, and **9** from Pyrolysis of (+)-**7** (optical purity ± standard deviation)[13]

Time (min)	(+)-(1*S*,2*S*)-**7**	(−)-(3*S*,4*R*)-**8**	(−)-(3*S*,4*S*)-**9**
60	0.600 ± 0.017	0.632 ± 0.018	0.512 ± 0.057
120	0.344 ± 0.012	0.544 ± 0.020	0.447 ± 0.040

Table III. The Stereochemistry of the Vinylcyclopropane Rearrangement of *trans*,*trans*-2-Methyl-1-propenylcyclopropane (**7**)[13]

Time (min)	si (%)	ar (%)	sr (%)	ai (%)
60	65.0 ± 2.8	7.6 ± 0.9	21.6 ± 2.6	4.8 ± 1.0
120	65.0 ± 2.9	7.6 ± 1.1	21.8 ± 2.6	4.6 ± 0.9
Av	65 ± 2	8 ± 1	22 ± 2.6	5 ± 1

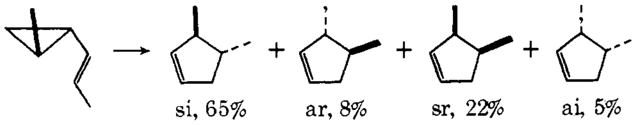
literature values for **3** are 48.6, 45.7 and 14.7, 13.7.[4,5] The isomeric compositions of the C_7H_{12} hydrocarbons recovered (95%) from the two pyrolyses are recorded in Table I. Unreacted starting material and the cyclopentene products were separated and purified by preparative GLC; the optical purities of these materials are shown in Table II.

The expression for the effective optical purity of a substrate undergoing racemization and competitive first-order formation of several products, where P_i is the initial optical purity of the starting material, k is the disappearance rate constant of starting material, and k_α is the one-way racemization rate constant of starting material, is[14] $\bar{P} = P_i k/(k + 2k_\alpha)(1 - \exp(-(k + 2k_\alpha)t))/(1 - \exp(-kt))$.

The data in Tables I and II yield $k = (1.773 \pm 0.008) \times 10^{-4}\ \mathrm{s}^{-1}$ and $k_\alpha = (7.25 \pm 0.16) \times 10^{-5}\ \mathrm{s}^{-1}$. These values, combined with P_i = 100%, give $\bar{P}$(60 min) = 80.1 ± 0.4% and $\bar{P}$(120 min) = 68.8 ± 0.5%. Combinations of the $\bar{P}$ values with the optical purities in Table II and the (2.65 ± 0.12):1 ratio of **8** to **9** lead to the values for the percent contribution of each of the four possible stereochemical outcomes for the vinylcyclopropane rearrangement of (+)-**7** (Table III).

Interestingly, the two migration-with-inversion stereochemical paths account for 70% of the reaction, in remarkable agreement with the 69% value for **1** reported by Doering and Sachdev.[3]

A detailed discussion of extensions of this investigation and the mechanistic implications will be given in the full paper. The high degree of maintenance of optical purity in both the allowed products **8** and the forbidden products **9** rule out the possibility of freely rotating diradical intermediates in the cyclopentene-forming reaction of **7**. The kinetic scheme interrelating hypothetical, slowly interconverting diradicals is much too complex to be solved with the product distributions observed here. For these reasons we presently favor competition among four concerted processes, two allowed, and two forbidden, with the possible intervention of a planar π-vinylcyclopropane intermediate, having an orbital structure appropriate for disrotatory ring closure to racemic **9** accounting for the formation of the ai product and part of the sr product. An analogous intermediate has been postulated in the rearrangements of some vinyl epoxides.[15]



(+)-**7** si, 65% (−)-**8** ar, 8% (+)-**8** sr, 22% (−)-**9** ai, 5% (+)-**9**

Acknowledgment. This work was supported by the National Science Foundation and by Hoffmann-La Roche, Inc.

References and Notes

(1) N. P. Neureiter, *J. Org. Chem.*, **24**, 2044 (1959); E. Vogel, R. Palm, and K. H. Ott, unpublished results quoted in ref 162 of E. Vogel, *Angew. Chem.*, **72**, 4 (1960); C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4896 (1960).
(2) M. R. Willcott, III, and V. H. Cargle, *J. Am. Chem. Soc.*, **91**, 4310 (1969); *ibid.*, **89**, 723 (1967); P. H. Mazzochi and H. J. Tamburin, *ibid.*, **92**, 7220 (1970); **97**, 555 (1975).
(3) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **97**, 5512 (1975).
(4) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 5578 (1964).
(5) W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).
(6) Schmidt and Roth have pyrolyzed racemic **7** and obtained results similar to ours; T. Schmidt, Ph.D. Dissertation (W. R. Roth, sponsor), University of the Ruhr, Bochum, 1972.
(7) T. Sugita and Y. Inouye, *Bull. Chem. Soc. Jpn.*, **39**, 1075 (1966).
(8) J. E. Baldwin, J. Löliger, W. Rastetter, N. Neuss, L. L. Huckstep, and N. De La Higuera, *J. Am. Chem. Soc.*, **95**, 3796 (1973); we thank Professor Baldwin for sending details on his procedure for the preparation of optically pure 2-methylcyclopropanecarboxylic acid.
(9) R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
(10) M. Schlosser and K. F. Christmann, *Angew. Chem., Int. Ed. Engl.*, **5**, 126 (1966); *Justus Liebigs Ann. Chem.*, **708**, 1 (1967); E. J. Corey and H. Yamamoto, *J. Am. Chem. Soc.*, **92**, 226 (1970).
(11) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).
(12) W. C. Kokke and F. A. Varkevisser, *J. Org. Chem.*, **39**, 1535 (1974); we thank Professor Kokke for a generous gift of (−)-(1*R*,2*R*)-*trans*-1,2-dimethylcyclopentane.
(13) Error limits for these numbers and all of the rest used here were estimated by the standard formula for propagation of error in a function $U = f(x_i)$, $S_U = [\Sigma(S_{x_i}\partial U/\partial x_i)^2]^{1/2}$; see for example, L. G. Parrat, "Probability and Experimental Errors in Science", Wiley, New York, N.Y., 1966, pp 109–118.
(14) Compare the analogous expression for a slightly simpler case derived by S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952); see also J. A. Berson and P. B. Dervan, *Ibid.*, **95**, 267, 269 (1973).
(15) J.-C. Paladini and J. Chuche, *Bull. Soc. Chim. Fr.*, 197 (1974).

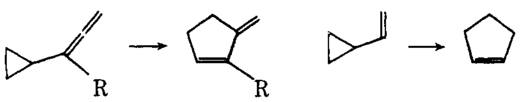
Gerald D. Andrews, John E. Baldwin*
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received January 5, 1976

Stereochemical Specificity in the Vinylcyclopropane Rearrangement vs. MINDO/3 Calculations

Sir:

A recent paper reports experimentally determined activation parameters for the isomerization of 3-cyclopropyl-1,2-butadiene to 2-methyl-3-methylenecyclopentene (**1** → **2**, R = CH_3), MINDO/3 calculations modeling the cyclopropylallene rearrangement to 3-methylenecyclopentene (**1** → **2**, R = H) and the vinylcyclopropane to cyclopentene conversion (**3** → **4**), and assertions regarding the stereochemistry and mechanism of these reactions.[1]



1 **2** **3** **4**

	E_a(calcd)[1]	E_a(obsd)
1 ⟶ **2**, R = H	44.6	50.2[3]
1 ⟶ **2**, R = CH_3		41.5[1]
3 ⟶ **4**	48.4	49.7[2]

The Arrhenius parameters for conversion of 3-cyclopropyl-1,2-butadiene to 2-methyl-3-methylenecyclopentene were measured over a 20° temperature range to give log A = 12.8 and E_a = 41.5 kcal/mol.[1] Application of Benson's expression for propagation of error in calculation of Arrhenius parameters[4] using the stated ±1° limits on temperature and 5% probable error in rate constants leads to calculated error limits of ±3.7 kcal/mol for E_a and ±1.44 for log A.

The activation parameters for the conversion of cyclopropylallene to 3-methylenecyclopentene have been found by Roth and Schmidt to be $E_a = 50.2 \pm 0.2$ kcal/mol and log $A = 14.09$, measured over a 50° temperature range.[3] The disparity between the reported activation parameters for cyclopropylallene and its methyl derivative implies either that the methyl group exerts an 8.7 kcal/mol activation energy lowering effect or that one of the sets of activation parameters is in error.

The MINDO/3 calculations are of especial importance as the first application of this procedure to a sigmatropic process,[1] and therefore an instructive test case for the validity of this method as a technique for probing mechanism. The calculations[1] predict that the reaction is a "forbidden" process "in which a biradical intermediate is the transition state"; the "allowed" *si* process should be truly forbidden; the favored path should involve retention of configuration of the migrating group; and the calculated results explain why rearrangements of vinylcyclopropanes take place with almost complete loss of configuration.

For the one vinylcyclopropane rearrangement of fully known stereochemistry,[5] the conversion proceeds 73% by allowed stereochemical paths; the "allowed" *si* process amounts to 65% of the four stereochemically distinct routes; the two paths with inversion of configuration at the migrating carbon account for 70% of the four; the rearrangement certainly does not take place with almost complete loss of configuration. Similarly, the vinylcyclopropane rearrangement of *trans*-2-isopropenyl-1-cyanocyclopropane proceeds with 69% inversion of configuration at the migrating carbon.[6] Thus, the MINDO/3 model calculations for the vinylcyclopropane rearrangement are directly contrary to experimental fact.

The authors of the work[7] cited to support the generalization that vinylcyclopropanes rearrange "with almost complete loss of configuration"[1] recognized the great experimental difficulty associated with separating the geometrical isomerizations of vinylcyclopropyl substrates from the structural isomerizations leading to cyclopentenes. They made no careless claims regarding the manner in which overall loss of configuration occurs.[7]

While the MINDO/3 model may have merit in some applications,[8] the inaccurate description it gives of the vinylcyclopropane rearrangement reemphasizes the need for skepticism when confronted with its predictions on the stereochemical course and mechanism of reactions. A considerable amount of difficult experimental work has been expended in efforts to determine the stereochemical courses of [1,3] sigmatropic shifts and other thermal hydrocarbon rearrangements. It seems inappropriate to supersede cautious mechanistic speculation based on recognition of experimentally determined facts with mechanistic generalization based on calculations which do not even account for the gross stereochemical preferences observed in these reactions.

References and Notes

(1) M. J. S. Dewar, G. J. Fonken, S. Kirschner, and D. E. Minter, *J. Am. Chem. Soc.*, **97,** 6750 (1975).
(2) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); C. A. Wellington, *J. Phys. Chem.*, **70**, 546 (1966).
(3) T. Schmidt, Ph.D. Dissertation, University of the Ruhr, Bochum, 1972; W. R. Roth, T. Schmidt, and H. Humbert, *Chem. Ber.*, **108,** 2171 (1975).
(4) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", U.S. Government Printing Office, Washington, D.C., 1970, pp 8–9.
(5) G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, preceding paper in this issue.
(6) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **97,** 5512 (1975).
(7) P. H. Mazzochi and H. J. Tamburin, *J. Am. Chem. Soc.*, **92,** 7220 (1970); **97,** 555 (1975).
(8) J. A. Pople, *J. Am. Chem. Soc.*, **97,** 5306 (1975); W. J. Hehre, *ibid.*, **97**, 5308 (1975); M. J. S. Dewar, *ibid.*, **97**, 6591 (1975).

Gerald D. Andrews, John E. Baldwin*
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received January 5, 1976

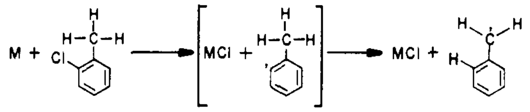
Rearrangement of the *o*-Tolyl Radical to the Benzyl Radical at Zero Pressure

Sir:

The high reactivity of free radical intermediates places stringent requirements on methods for their direct detection, but allows indirect observation by chemical trapping. Thus rearrangement of the *o*-tolyl radical to the benzyl radical was first detected by CIDNP measurements[1] in benzyl chloride, produced by the thermal decomposition of *o,o′*-dimethylbenzoyl peroxide in the presence of hexachloroacetone. Recently, the development of laser-induced fluorescence[2] has provided an experimental probe for measuring the vibrational energy distribution in products of gas-phase chemical reactions under conditions of very low concentration (10^{-15} M). Because of this extreme sensitivity, we are able to obtain the excitation spectrum of the benzyl radical resulting from the following reactions:

(1)

and



(2)

where M is a barium or sodium atom, providing direct evidence for the rearrangement of the *o*-tolyl radical.

Preliminary experiments showed that reactions of barium with various aryl chlorides under single collisions could be monitored by detecting BaCl fluorescence, excited by a tunable dye laser. The impetus for these studies was to determine substitutent effects on the BaCl spectrum, and hence to learn about the dynamics of the reactions.

Figure 1 shows the BaCl excitation spectra for the reactions of barium with benzyl chloride and with *o*-, *m*-, and *p*-chlorotoluene. The relative vibrational populations are calculated from the peak intensities using Franck–Condon factors tabulated elsewhere.[3] Relative rotational populations (assuming a Boltzmann distribution) are calculated by fitting computer-simulated spectra, using the known spectroscopic constants, to the observed spectra. Within experimental error, the BaCl product from each of the four reactions has the same average vibrational energy (~1.5 kcal/mol) and rotational energy (~1.5 kcal/mol). Since the exoergicity of these reactions[4] varies from ~40 kcal/mol for reaction 1 to ~25 kcal/mol for reaction 2, a substantial amount of energy must be released into translation and/or internal excitation of the resulting organic radical.[5]

Benzylic-type radicals are well-known reaction intermediates and have been detected in the condensed phase by ESR,[6] and in absorption following flash photolysis.[7] The latter technique also permitted Porter and co-workers[8] to observe the benzyl radical in the gas phase. Since then, extensive spectroscopic studies have been carried out by observing emission resulting from photon excitation in the solid phase[9a-c] and electron impact excitation in the gas phase.[9d,e] We report here the first gas-phase excitation spectrum of the benzyl radical (Figure 2a) obtained using a pulsed dye laser. The benzyl radical is produced from reaction 1 at a pressure of 2×10^{-4} Torr of benzyl chloride (barium oven temperature is approximately 1150 K). Under these conditions, no vibrational relaxation of the radical occurs, since the relative intensities in the corresponding BaCl spectrum are the same as at a pressure of 5×10^{-5} Torr.

The excitation spectrum of the benzyl radical also is ob-