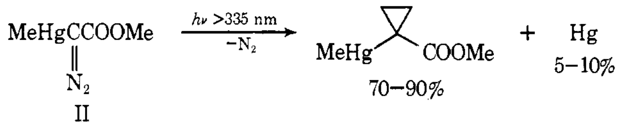
by various means led either to ring opening or to recovery of starting ketone.

The additions of methylmercuriacetylcarbene to *cis*- and *trans*-2-butene were shown by nmr analyses of the primary reaction products and by glc analyses of the residues after bromination to be completely stereospecific. The lack of radical character in the intermediate was also demonstrated by the absence of any preference for addition to 1,3-butadiene in competition experiments with monoolefins. With the heavy mercury atom in close proximity to the carbene site relaxation to the ground state should be rapid.[8] Thus, a singlet ground state is indicated for $CH_3Hg\underset{\cdot\cdot}{C}{-}COCH_3$.

α-Mercuricarboalkoxycarbenes have also been shown to react with olefins yielding cyclopropanes almost exclusively. The non-mercury-containing carbenes have important competitive pathways of rearrangement[9] and insertion. The photolysis of methyl methylmercuridiazoacetate (II) in olefins produces the corresponding



methyl 1-methylmercuricyclopropanecarboxylates in 70–90% yields.[10,11] The ready cleavage of the carbon–mercury bond by electrophilic reagents affords many possibilities for further syntheses.

The introduction of a mercury atom adjacent to the reactive site in carbenes has produced a chemistry different from that observed for the mercury-free carbenes: the elimination of Wolff rearrangement and insertion reactions in the photolyses of diazo ketones and diazo esters.

Acknowledgments. The financial support of the Air Force Office of Scientific Research (Grant No. 1983) is gratefully acknowledged. S. J. Valenty wishes to thank the National Institutes of Health and the Stauffer Chemical Co. for personal financial support during this work.

---

(8) P. S. Skell and S. J. Valenty, *J. Amer. Chem. Soc.*, **95**, 5041 (1973).

(9) J. Shafer, P. Barnowsky, R. Laursen, P. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966); O. P. Strausz, Th. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968); H. Chaimovich, R. J. Vaughan, and F. H. Westheimer, *ibid.*, **90**, 4088 (1968); T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970); D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *ibid.*, **92**, 1768 (1970).

(10) II was prepared from methyl diazoacetate and methylmercuric ethoxide in 80–90% yield as a yellow solid; mp 71–72°. The preparation and characterization are fully detailed in a paper submitted for publication to *J. Org. Chem.*

(11) Also, no Wolff rearrangement product was observed when II was photolyzed in alcohol.

P. S. Skell,* S. J. Valenty
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

Received October 9, 1971

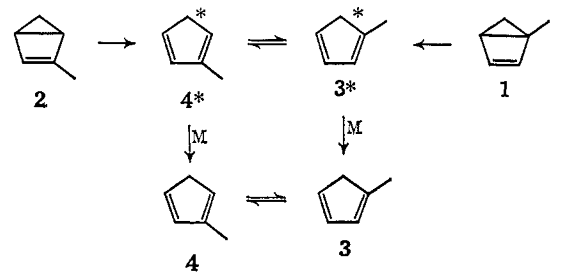
Mechanism of Isomerization of Bicyclo[2.1.0]pent-2-enes

Sir:

The mechanism of isomerization of bicyclo[2.1.0]pent-2-enes to cyclopentadienes is a matter of some controversy.[1–5] We wish to report experimental evidence which makes it clear that cleavage of the central bond in methylbicyclopentenes is the predominant isomerization path and that subsequent hydrogen shifts in the chemically activated product cyclopentadienes can account for rearranged (methyl-shifted) isomers. None of the evidence requires or supports concerted ${}_{\sigma}2_s + {}_{\sigma}2_a$ isomerizations.

Recent RRKM calculations of Flowers and Frey[5] show that the chemically activated cyclopentadienes formed by any pathway would be expected to undergo subsequent rearrangement. Thus, observation of rearranged products could not be used to support parallel concerted reactions. On the other hand, parallel concerted isomerizations are also consistent with extensively rearranged products.

Our studies of product ratios in the gas phase show[6] not only that chemical activation is important but also that central bond cleavage to give the non-methyl-shifted isomer is the primary reaction path. See eq 1 and Table I. First, at a given pressure more of the rearranged (methyl-shifted) product appears when nitrogen is used as ambient gas than when the more efficient deactivator pentane is employed.[7] Second, a decrease in rearrangement accompanies increases in pressure when pentane is the bath gas. Thus rearrangement must be occurring competitively with thermal deactivation. Application of the strong collision assumption to the kinetics of eq 1 predicts a pressure dependence of the ratio of products arising from deactivation to those from chemical activation (corrected for back reaction) in general agreement with that observed. Furthermore, the observed ratio in solution is in accord with the same model, assuming a solution collision frequency of 10^{12}. Third, both 1- and 2-methylbicyclopentene show qualitatively similar trends, but in all cases the more reactive 1-methylbicyclopent-2-ene gives



(1)

---

(1) (a) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968); (b) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(2) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, **92**, 5249 (1970); (b) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(3) S. McLean, D. M. Findlay, and G. I. Dmitrenko, *J. Amer. Chem. Soc.*, **94**, 1380 (1972).

(4) J. E. Baldwin and G. D. Andrews, *ibid.*, **94**, 1775 (1972).

(5) M. C. Flowers and H. M. Fry, *ibid.*, **94**, 8636 (1972).

(6) Gas-phase experiments were carried out in a 250-ml Pyrex bulb washed with 5% EDTA solution and conditioned with the bicyclopentenes. In all runs, bicyclopentene partial pressure was below 2 Torr. Reactions were studied at *ca.* 30% conversion, and "normal" thermal product isomerization was shown not to contribute significantly. Reactant and product mixtures were analyzed by vpc on a 10 ft × 0.25 in. aluminum column packed with 15% β,β-oxydipropionitrile on Chromosorb P regular. The rate of disappearance of the bicyclopentene was in excellent agreement with previously published results.[4] The difference in product ratios from those reported[4] is understandable in terms of our larger vessel size. Much of the deactivation results from wall collisions, consistent with the weak dependence on N_2 pressure. Runs in a packed vessel showed slight decreases in amount of rearrangement, consistent with this explanation, and simultaneously showed surface catalytic routes to the methyl-shifted isomer to be unimportant.

(7) For a thorough study of bath gas collision deactivation efficiencies, see Y. N. Yin and B. S. Rabinovitch, *J. Phys. Chem.*, 74, 3151 (1970).

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.

Acknowledgment. We thank the National Science Foundation (GP-27532) and the Alfred P. Sloan Foundation for support.

---

(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).

John I. Brauman,* William E. Farneth, Michael B. D'Amore
Department of Chemistry, Stanford University
Stanford, California 94305

Received January 30, 1973

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 ${}_\sigma2_s + {}_\sigma2_a$ 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-

---

(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).