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

William E. Farneth, Michael B. D'Amore, and John I. Brauman*

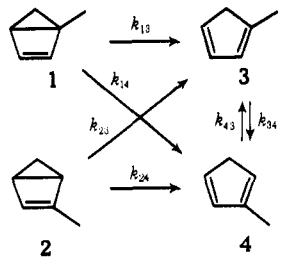
Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received December 22, 1975*

Abstract: The isomerization of 1- and 2-methylbicyclo[2.1.0]pent-2-enes has been studied in the gas phase and in solution. The rates of decomposition, product ratios, and rates of product interconversion have been measured. The results are well explained by a mechanism in which central bond cleavage produces a chemically activated cyclopentadiene, which then undergoes competitive hydrogen shifts and collisional deactivation. This model is supported by RRKM calculations.

The isomerization of bicyclo[2.1.0]pent-2-enes to cyclopentadienes is a mechanistic problem that has been under investigation for several years. The bicyclo[2.1.0]pent-2-enes are the lowest homologues of the fused ring cyclobutene series, but geometric constraints in this system prevent a symmetry-allowed $\sigma_a^2 + \pi_s^2$ electrocyclic ring opening analogous to that observed for cyclobutenes.[1] Therefore, the valence bond isomerization is forced to proceed via an alternative mechanism, and several possible ones have been tested and excluded using deuterium or methyl-substituted bicyclopentenes.[2] Arguments for two of the remaining candidates, a $\sigma_s^2 + \sigma_a^2$ symmetry-allowed concerted process involving the 1,5 and 3,4 or 1,2 and 4,5 bonds in the starting bicyclopentene, or central (1,4) bond cleavage by some nonallowed pathway, have been presented.[3,4] These arguments are based on experiments that determine the relative amounts of 1- and 2-methylcyclopentadienes (**3** and **4**) produced by the decomposition of either 1- or 2-methylbicyclo[2.1.0]pent-2-ene (**1** and **2**); see Scheme I.

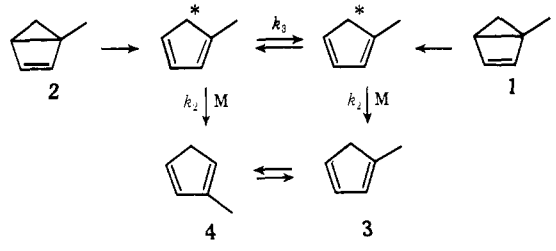
We have investigated the isomerization of the methylbicy-

Scheme I



clopentenes both in solution and in the gas phase. At the time these experiments were undertaken, there appeared to be a direct conflict between the experimental results from two different laboratories on the solution-phase thermolysis of 2-methylbicyclo[2.1.0]pent-2-ene,[2] and one of our motives in undertaking this investigation was to clarify the solution-phase picture. It now appears that a consistent picture has emerged. In the gas phase, interpretation of product ratios in mechanistic terms may be complicated by the possibility of extensive rearrangement due to chemical activation effects, as pointed out by Flowers and Frey.[5] We have directed our gas-phase studies toward the demonstration that chemical activation is indeed occurring in this system. The proposed mechanism is shown in Scheme II.

Scheme II



Results

A. Preparation. 1- and 2-methylbicyclo[2.1.0]pent-2-ene were prepared by photolysis of an equilibrium mixture of the methylcyclopentadienes in a method analogous to that reported for the parent compound by van Tamelen, Brauman, and Ellis.[6] The methylcyclopentadienes used were freshly prepared by cracking of the commercially available dimer. The product bicyclopentenes were separated from cyclopentadienes by treatment with *N*-phenylmaleimide (NPM) in tetrahydrofuran for short periods of time, and from each other by preparative VPC on a 15% β,β-oxydipropionitrile on non-acid-washed Chromosorb P column. Gas chromatographic analysis of the collected samples showed both to be free of the other bicyclopentene isomer and to contain less than 1% methylcyclopentadiene. For storage, the bicyclic compounds were vacuum transferred to gas storage bulbs containing a 10% solution of NPM in tetraglyme. The bulbs were subsequently maintained at −78 °C for the lifetime of the sample. This method of storage was found to be quite convenient, permitting easy access to small amounts of material by vacuum transfer and continuous purification by trapping of the cyclopentadienes with *N*-phenylmaleimide.

B. Solution Results. Since the ratio k_{23}/k_{24} (Scheme I) was not inferred from product ratios, but instead determined by a fitting procedure, products were not trapped as in previous investigations but analyzed directly by VPC. Rate constants for disappearance of 2-methylbicyclopentene ($k_{23} + k_{24}$) (Scheme I) and equilibration of the methylcyclopentadienes, (k_{34}, k_{43}), were measured independently in dry tetrahydrofuran in 5% EDTA-washed sealed tubes. The results are shown in Table I, and for comparison, Baldwin's concurrently published[3] results in hexane are included in parentheses. Both the disappearance and the equilibration data gave good linearity of the appropriate (first-order decay or approach to equilibrium) plots (correlation coefficients >0.99) over at least 3 half-lives. Internal standardization showed that all products (±1%) were accounted for as 1- and 2-methylcyclopentadienes in both cases. Finally, addition of crushed glass to the ampules, increasing the exposed surface area by about a factor of 3, caused no appreciable alteration in the rates. In the case of the equilibration, prewashing the tubes with 10% NaOH or HCl similarly gave rates within experimental error of the normal data. These results indicate that surface catalysis did not contribute significantly to the observed rates. The disparity between the rate constants measured in this work and those of Baldwin (Table I) for the equilibration between the methylcyclopentadienes may be entirely the result of the solvent difference. We have found at 50 °C ($k_{43} + k_{34}$ in pentane)/($k_{34} + k_{43}$ in THF) ≅ 0.66, yielding a value of 3.9×10^{-5} s^{-1} for $k_{34} + k_{43}$ in pentane, in good agreement with Baldwin and co-workers' [3] value of 3.59×10^{-5} s^{-1} in hexane. Furthermore, the ratio ($k_{34} + k_{43}$) 50 °C/($k_{34} + k_{43}$) 30 °C is identical for the two investigations. The other rate constants are seen to be in good agreement with those determined by Baldwin and co-workers.[3] No solvent effect on the rate of decomposition of 2-methylbicyclopentene for the solvents pentane, THF, and methanol was observed. One point rate constants for the disappearance of 1-methylbicyclopentene at 50 °C indicated that it was eight–ten times faster than the 2-methyl compound, and somewhat smaller portions of rearranged methylcyclopentadiene were formed.

Table I. Rate Constants for Isomerization of 2-Methylbicyclopentene and Equilibration of 1- and 2-Methylcyclopentadiene in THF

T, °C	k_d, s^{-1} [a]	k_{eq}, s^{-1} [b]	K [c]
50	1.3×10^{-4}	6.5×10^{-5}	1.32
	(1.01×10^{-4}) [d]	(3.59×10^{-5}) [d]	(1.38) [d]
30	1.1×10^{-5}	5.9×10^{-6}	1.38
	(1.07×10^{-5}) [d]	(3.2×10^{-6}) [d]	(1.44) [d]

[a] $k_{disappearance} = k_{23} + k_{24}$ in Scheme I. [b] $k_{equilibration} = k_{34} + k_{43}$ in Scheme I. [c] K = [2-methylcyclopentadiene]/[1-methylcyclopentadiene]. [d] From ref 3.

C. Gas-Phase Results. The system was investigated in the gas phase in the presence of unreactive bath gases at total pressures ranging from <2 to 900 Torr. The pyrolysis was carried out in a static reaction vessel which consisted of a modified 250 ml pyrex bulb washed with 5% EDTA solution and conditioned with the bicyclopentenes. In all cases, the partial pressure of the bicyclopentene was less than 2 Torr, and the system was pressurized to the appropriate final pressure by addition of nitrogen or pentane. The reactions were studied by analysis of the contents of the flask at various percentage conversions of bicyclopentene to cyclopentadienes, but for the most part at approximately 20% conversion for 2-methylbicyclopentene and 30% conversion for 1-methylbicyclopentene.

Tables II and III list the experimental determinations for the gas-phase isomerizations of 1- and 2-methylbicyclopentene at 50.3 °C. The reported percentage disappearance and rearrangement for each run are the average of about five separate VPC analyses.

Although we have found this reaction to be quite sensitive to surface catalysis, we are confident that these results are free of catalytic problems for several reasons. (1) The amount of reaction is quite reproducible (variations <3%). (2) The rate of disappearance is 30% less than the solution-phase rate constant (8.51×10^{-5} vs. 8.24×10^{-5} s^{-1}).[7] (3) The same rate constant is suitable for the observed disappearance for longer

Table II. Isomerization of 2-Methylbicyclo[2.1.0]pent-2-ene at 50.3 °C in the Gas Phase

Run no.	Pressurizing gas	Time, s	Pressure, Torr	% disappearance[a]	Rearrangement[b]
1	N_2	2700	465	19.7	1.045
2	n-C_5H_{12}	5400	465	35.0	0.739
3	n-C_5H_{12}	2700	465	20.9	0.709
4	N_2	5400	465	37.9	0.927
5	n-C_5H_{12}	0	465	0.80	
6	N_2	0	465	0.85	
7	n-C_5H_{12}	2700	100	20.2	0.883
8	n-C_5H_{12}	2700	900	21.1	0.656
9	n-C_5H_{12}	2700	100	20.1	0.880
10	n-C_5H_{12}	2700	900	19.2	0.639
11	n-C_5H_{12}	2700	465	21.9	0.695
12	N_2	2700	465	22.3	1.004
13	N_2	2700	100	19.8	0.972
14	N_2	2700	100	20.5	0.961
15	N_2	2700	465	20.2	0.996
16	None	2700	<2	19.1	0.894
17	None	2700	<2	18.5	0.908
18	n-C_5H_{12}	2700	100	20.7	0.945
19[c]	None	2700	<2	16.2	0.812
20[c]	None	2700	<2	16.1	0.818

[a] ([Cyclopentadienes]/[cyclopentadienes] + [bicyclopentene]) × 100. [b] [1-Methylcyclopentadiene]/[2-methylcyclopentadiene]. [c] Surface to volume increased six times.

Table III. Isomerization of 1-Methylbicyclo[2.1.0]pent-2-ene at 50.3 °C in the Gas Phase

Run no.	Pressurizing gas	Time, s	Pressure, Torr	% disappearance[a]	Rearrangement[b]
21	N_2	1400	100	31.0	0.838
22	N_2	1310	100	30.0	0.852
23	N_2	1400	465	33.0	0.675
24	N_2	1310	465	29.8	0.855
25	n-C_5H_{12}	1400	100	33.4	0.786
26	n-C_5H_{12}	1310	100	31.6	0.764
27	n-C_5H_{12}	1310	465	32.0	0.543
28	None	1310	<2	28.6	0.855
29[c]	None	1310	<2	18.6	0.757

[a] ([Cyclopentadienes]/[cyclopentadienes] + [bicyclopentene]) × 100. [b] [2-Methylcyclopentadiene]/[1-methylcyclopentadiene]. [c] Surface to volume increased six times.

reaction times. (4) All zero points for 2-methylbicyclopentene showed less than 1% methylcyclopentadiene impurity. In addition to the zero point data shown explicitly in Table II (runs 5, 6), all other runs except 1–4 and 18 had an associated zero point. Because larger amounts of methylcyclopentadienes (usually 2–4% of the total sample, and greater than 90% 1-methyl) were present in the zero points for the less stable 1-methylbicyclopentene, all data reported have been corrected for methylcyclopentadiene concentrations at zero time. These concentrations were determined either by filling and immediately evacuating the bulb at room temperature (1400-s runs) or by filling, immersing in the 50 °C bath for 90 s, and evacuating (1310-s runs). It is apparent from the Tables that the two methods are in reasonably good accord. (5) Runs where the surface to volume ratio was increased by approximately a factor of 6 (runs 19, 20, 29) showed slightly less total reaction, rather than more as would be predicted if surface-catalyzed routes to products were important. This is undoubtedly due to a slower temperature equilibration in these vessels. Initially, many of our experiments did not conform to criteria 1 to 4, indicating substantial surface effects either in the reaction vessel or gas chromatograph. However, careful washing and injections ultimately enabled us to obtain reproducible results.

Discussion

The gas-phase from Tables II and III are averaged and reorganized in Table IV. These product ratios represent an accurate description of the ratio of rate constants for direct production of rearranged and nonrearranged cyclopentadienes from the starting methylbicyclopentene without intervention of "thermal" cyclopentadienes. That "normal" thermal hydrogen shift did not contribute was shown by the small changes in ratios at longer sampling times as displayed in Table II. Runs 1–4 show both the expected effect of longer sampling times—a more nearly equilibrium ratio of methylcyclopentadienes and the small magnitude of the change. Furthermore, computer modeling by numerical integration using approximate interconversion rate constants and variable direct production ratios showed that the observed fraction of hydrogen shift at 2700 s could, as a result of normal thermal equilibration of the methylcyclopentadienes, differ by no more than 2% from that produced directly.

Qualitatively, the results in Table IV are well accounted for by a model in which central-bond cleavage of 1- or 2-methylbicyclopentene leads to a chemically activated methylcyclopentadiene which can then undergo 1,5-hydrogen migration to the other methylcyclopentadiene in competition with

Table IV. Ratios of Rearranged to Nonrearranged Cyclopentadienes at 50 °C

Bath gas	Reactant[a]	Pressure, Torr <2	100	465	900	Solution
Pentane	2		0.90 ± 0.04	0.71 ± 0.03	0.65 ± 0.03	0.09 ± 0.04
	1		0.78 ± 0.10	0.54 ± 0.10		
Nitrogen	2		0.97 ± 0.03	0.99 ± 0.05		
	1		0.85 ± 0.10	0.77 ± 0.13		
None	2	0.90 ± 0.03				
	1	0.86 ± 0.10				

[a] 2 = 2-methylbicyclo[2.1.0]pent-2-ene, 1 = 1-methylbicyclo[2.1.0]pent-2-ene .

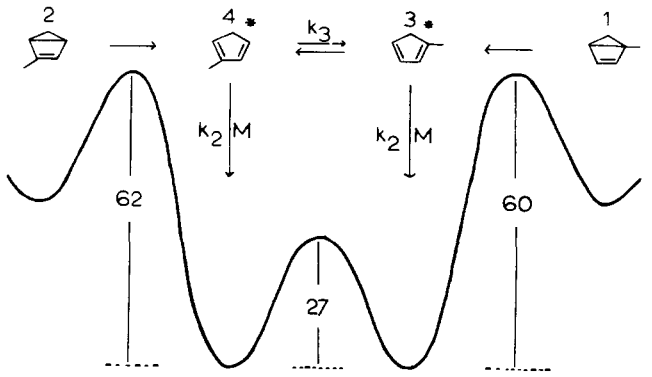


Figure 1. Potential surface for methylbicyclopentenes and methylcyclopentadienes.

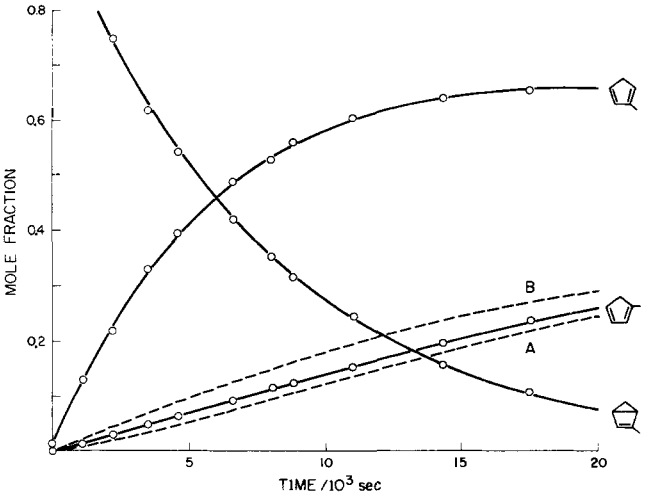


Figure 2. Experimental and calculated concentrations for solution decomposition. See text for explanation and quantities.

deactivation to its ground state. The energetics for the model are shown in Figure 1. As a consequence of the model, changes in reaction conditions that increase k_2M should decrease the amount of rearranged cyclopentadiene observed, and, similarly, increases in k_3 should lead to increases in the amount of rearranged cyclopentadiene. These trends are clearly apparent in Table IV. Thus, when the rate constant for deactivation, k_2, is increased by changing from what one expects to be an inefficient deactivator, N_2, to a more efficacious one, pentane,[8] less of the secondary, rearranged product is obtained. This is true starting from either 1- or 2-methylbicyclopentene, and independent of the pressure over the range investigated. Similarly, with pentane as bath gas, increasing the rate of deactivation by increasing the pressure is correlated with larger amounts of the methylcyclopentadiene formed by breaking the central bond. Finally, both 1- and 2-methylbicyclopentene show the same trends, but in all cases the more reactive 1-methylbicyclopentene, which as a result should produce a somewhat less activated cyclopentadiene (decreased k_3), gives less rearranged product. These results, as a whole, indicate not only that chemical activation is occurring, but also that the predominant pathway for decomposition of methylbicyclopentenes involves cleavage of the central bond.

The same model is in accord with the solution-phase results as well. In order to determine the relative amounts of 1- and 2-methylcyclopentadienes being produced directly from 2-methylbicyclopentene, the rate constants for disappearance and equilibration (Table I) in conjunction with a variable value of k_{24}/k_{23} (Scheme I) were used to fit the experimental concentration vs. time data via a numerical integration procedure. The best value of k_{24}/k_{23} was evaluated by the least-squares fit of the calculated to experimental points for all three components of the system. Within the reproducibility of our rate constants, this ratio was 10 ± 1 at 50 °C. The fit is shown in Figure 2 where the dashed lines represent calculated concentrations for ratios of infinity (A) and 5 (B) (see Figure 2). If we permit ±20% variation in the interconversion rate constants ($k_{34} + k_{43}$), the ratio varies from approximately 5 to 18. Thus, the ratio is fairly sensitive to changes in these rate constants, and these larger limits are probably more representative of the accuracy of the kinetic data. However, all combinations of reasonable values of the rate constants require some formation of **3** directly from **2**. The same data were fit using a nonlinear least-squares fitting program[9] in which the disappearance and equilibration rate constants were allowed to vary over ±20%, and no constraints were placed on the ratio k_{24}/k_{23}, and a value of 11/1 was obtained.

For the 30 °C data, a value of approximately 40 ± 10 is obtained by the first method described above. Again, however, ±20% variation in the equilibration rate constants gives a possible range of about 15 to ∞. These results must be compared with the solution-phase temperature-dependence studies of Baldwin, Andrews, and Davalt,[3] in which the ratio of rate constants k_{24}/k_{23} is invariant over a range of 60 °C. A value of 12.2 ± 3.5 fits their data at five temperatures between 30 and 90 °C in hexane solution. Within the error limits of our experimental data there may, in fact, be no significant temperature dependence, in agreement with Baldwin.

All of these data are consistent with the mechanism we have proposed and which has already been shown to predict qualitatively the gas-phase results at 50 °C very well. In solution, deactivation should be much faster than in the gas phase at one atmosphere, resulting in increased quantities of the first-formed central bond cleavage isomer—precisely as observed starting from either methylbicyclopentene. Furthermore, one would expect a change of 20 °C in the temperature to have a relatively small effect on the rate of a reaction already activated by 35 kcal, but that any change should be in the direction of decreasing rearranged cyclopentadiene with decreasing temperature as we have observed.

Table V. Pressure Dependence of Product Ratios[a]

	Pressure (collision rate in s^{-1})				
	<2	100 (1.22×10^9)	465 (5.67×10^9)	900 (1.10×10^{10})	Solution (1×10^{12})
Exptl	0.91	0.88	0.70	0.65	0.09
Calcd[b]	1.00	0.64	0.28	0.17	0.0022
Calcd[c]	1.00	0.90	0.66	0.50	0.011

[a] Pressure in Torr. Ratio of 1-methylcyclopentadiene to 2-methylcyclopentadiene from 2-methylbicyclopentene. [b] Assuming $A = 13.0$, $E_a = 27$ kcal/mol, collision efficiency = 1.0, for the 1,5-hydrogen shift. The minimum total energy is taken as 61 kcal/mol ($\Delta H° = 34$, $E_a = 27$ kcal/mol) for the ring opening. [c] Collision efficiency = 0.2, other parameters as in *b*.

One can make a somewhat more quantitative analysis of the data by comparison of experimental product ratios with those predicted by RRKM calculations on this system.[10] In an attempt to determine the amount of rearranged isomer expected from the central-bond cleavage mechanism in solution, we have undertaken some simplified RRKM calculations for the rearrangement of activated methylcyclopentadiene.

Provision for back reaction (k_{-3} in Scheme II) has been made by assuming $k_3 = k_{-3}$; no account of the possibility of complications due to rearrangement to 5-methylcyclopentadiene has been made; deactivation has been treated as collisional efficiency rather than the more realistic exponential or stepladder models. The input for the calculation consists of the critical energy for the reaction, vibrational frequencies for the ground state (estimated from cyclopentadiene plus a methyl group), and vibrational frequencies for the activated complex (estimated from cyclopentadienide plus a methyl group). The remaining frequencies in the activated complex associated with the reaction coordinate were adjusted to give the correct high-pressure Arrhenius parameters, $k = 10^{13} \exp[-27\,000/RT]$. The input energy distribution was determined through a thermal RRKM analysis of the methylbicyclopentene to methylcyclopentadiene reaction. Use of this input gives a calculated rate constant of 2.2×10^9 s^{-1} for the isomerization of the activated methylcyclopentadiene. This result is relatively insensitive to the exact choice of high-pressure parameters, provided they give the same thermal rate constant.

This rate constant is sufficiently low that using the strong collision assumption, and an estimate of the rate of collisional deactivation of 10^{12} in solution, we are unable to reproduce either the small magnitude of the gas-phase pressure effect or the amount of rearranged isomer observed in solution (see Table V). However, this result is not unexpected, since such a highly energized molecule will retain substantial excess energy after some collisions. In fact, even after loss of 7 kcal/mol (a fairly typical value for energy loss per collision with large bath gas molecules[11-13]), methylcyclopentadiene is calculated to isomerize at one-half of its initial activated rate. Thus, molecules are gradually (stepwise) de-energized, undergoing isomerization progressively more slowly as they lose energy. We can approximate this picture crudely by assuming a collision efficiency of about 20% (Table V). We do not expect such an approximation to be especially good, since the "efficiency" will depend upon the pressure, and indeed our data do not show a linear pressure dependence. Efficiencies of less than 10% have been observed for small bath gas molecules such as N_2,[13,14] so the requirements that have been proposed for nitrogen are not extraordinary. In solution, the proposal of a deactivation rate constant of 10^{10}–10^{11} s^{-1} is quite compatible with values of vibrational excitation lifetimes of tens of picoseconds for hydrocarbons in solution as measured by laser spectroscopic techniques,[15] particularly since these involve only one quantum of excitation. The possibility of a nonstatistical component in our reaction[16] is unlikely in view of the nature of the initial rearrangement which would be expected to produce a nonlocalized energy distribution in the cyclopentadienes. Although our analysis has been done in a rather crude way, the gross features are probably correct, and a reasonably slow deactivation rate in this system appears to be implicated.

Flowers and Frey in previous calculations on 1-methylbicyclopentene employed a stepladder model for deactivation with a 3–5 kcal step size.[5,17] Their results are also in good agreement with our experiment and might even be improved with a larger step size.

The calculations also explain other aspects of the experimental data. For instance, the percentage reaction and rearrangement in the low-pressure run is, surprisingly, less than that with 100 Torr of N_2, but RRKM treatment of the thermal decomposition of the bicyclopentene at this pressure indicates that the reaction should be about 20% into the fall-off region in agreement with the observed decrease in percent reaction. The lower percentage rearrangement is also understandable in these terms since the average energy of reacting molecules in the fall-off regime is somewhat lower, leading to less activation in the product. This is the same qualitative argument that predicts lower percentage rearrangement for the less stable isomer. In that case, since the difference in E is known, the magnitude of the difference can be calculated. The strong collision prediction is that at 100 Torr the ratio of rearranged to nonrearranged cyclopentadiene should be 0.56 for 1-methylbicyclopentene and 0.63 for 2-methyl in good agreement with the experimental increase of 0.76 to 0.88.

These results in both a qualitative and semiquantitative sense demonstrate the operation of chemical activation effects in this system, although the data are probably not good enough to test the theory completely. In addition to the previously presented thermochemical analysis which shows a variation in activation energies for homologous bicyclo[2.*n*.0] compounds consistent with predictions based on an identical central bond cleavage mechanism throughout,[18] this leads to the conclusion that the mechanism illustrated in Scheme II is an adequate description of the bicyclo[2.1.0]pent-2-ene rearrangement. Dewar and Kirschner,[19] on the basis of MINDO/3 calculations, have also concluded that central bond cleavage and subsequent hydrogen shift is the preferred route to methyl-shifted cyclopentadiene in the thermal decomposition of methylbicyclopentenes. While these arguments strongly imply this mechanistic conclusion, it is impossible, on the basis of available experimental evidence, to rule out unequivocally the possibility that some part of the products arises from concerted bond-switching processes. Double-labeling experiments[20] should shed further light on this question. The interesting question of whether the central bond cleavage is a concerted disrotatory process or involves a biradical intermediate is beyond the scope of these data.

Experimental Section

General. NMR spectra, Varian A-60 or T-60; ir spectra, Perkin-Elmer 421; uv spectra, Cary 14.

Materials. Decane and *cis*- and *trans*-decahydronaphthalene, used

as solvents for the photolysis of the methylcyclopentadienes, were both purified by stirring over two portions of concentrated sulfuric acid for a period of 2 days, followed by successive washings with water, saturated $NaHCO_3$, and water. After drying over magnesium or sodium sulfate, the liquids were distilled; decane (174–175 °C), decalin [83–85 °C (10–15 mm)]. Purity was checked by gas chromatographic or uv spectroscopic analysis.

Pentane and isopentane used as diluent gases in the gas-phase pyrolytic studies were purified in much the same manner, extraction with several portions of concentrated sulfuric acid, washings with water and sodium bicarbonate solution, drying and distillation, pentane (35–36 °C), isopentane (28–29 °C). Both were degassed with several freeze–thaw cycles prior to their use in the kinetic experiments.

Nitrogen, employed as a diluent gas, was Matheson Prepurified and was passed through a drying tube prior to use.

Vapor-Phase Chromatography. Quantitative VPC measurements were carried out on a Hewlett-Packard F and M Model 700 Chromatograph fitted with a dual flame ionization detector. The only column used analytically in this work was an 8 ft × ¼ in., 15% β,β-oxydipropionitrile on non-acid-washed Chromosorb P, 60/80 mesh. Early results indicated that isomerization of the bicyclopentenes in the injection port was a serious problem. Consequently, all analyses were performed by direct on-column injection. Even so, it was determined that with aging and repeated heating and cooling, the column packing in the injection port section became active as a catalyst for the decomposition. Therefore, the injection port was frequently repacked with newly prepared material. For analysis, the injector block temperature was 25–50 °C, oven temperature 40 °C, flow rate 30–50 ml/min, and detector temperature 75 °C. Calibration of the attenuator on the Model 700 showed it to be accurate to 1% over the range employed.

Preparative VPC was done on a Varian Aerograph Model 90-F using a column and conditions similar to those described above.

Preparation of 1- and 2-Methylbicyclo[2.1.0]pent-2-ene. To 225 ml of purified *cis*- and *trans*-decahydronaphthalene was added 5 ml of the equilibrium mixture of methylcyclopentadienes, prepared by cracking of the commercially available dimer (Aldrich). The mixture was placed in a photolysis flask containing a magnetic spin bar. The photolysis well was lowered into the flask and the entire assembly immersed in ice water. The lamp (450 W, medium pressure, Hanovia) was turned on and progress of the reaction followed by VPC. A maximum concentration of product was reached after 1.5 h, at which point the lamp was extinguished. The photolysate was twice vacuum distilled at 0 °C 0.02 mm into a trap at −196 °C. The combined distillate (6 ml) was added to a solution of approximately 2 g of *N*-phenylmaleimide in hexamethylphosphoramide. After stirring for 10 min at 0 °C, the mixture was subjected to vacuum transfer at 25 °C from which resulted ~1.0 ml of reasonably pure (90% by VPC) 1- and 2-methylbicyclopentenes. They were separated by VPC and transferred for storage to tubes sealed in vacuo and maintained at −78 °C. 1-Methylbicyclo[2.1.0]pent-2-ene: NMR ($CDCl_3$) δ 3.88–3.90 (m, 2), 7.70–7.82 (m, 1), 8.1–8.3 (m, 1), 8.52 (s) + 8.4–8.6 (m, 4). 2-Methylbicyclo[2.1.0]pent-2-ene: NMR ($CDCl_3$) 4.0–4.2 (m, 1), 8.0–8.2 (m, 3), 8.30 (d, J = 1.5 Hz) + 8.2–8.5 (m, 4).

Storage and Subsequent Use of Bicyclopentenes. For storage and ease of handling in the gas-phase experiments, it was found that gas sample tubes fitted with vacuum stopcocks were ideal. To each sample tube was added approximately 2 ml of a saturated solution of *N*-phenylmaleimide in tetraglyme. The pure sample of 1- or 2-methylbicyclo[2.1.0]pent-2-ene was then vacuum distilled into the sample tube, the stopcock closed, and the solution stored under vacuum at −78 °C. To extract the bicyclopentene for use, it was simply warmed and vacuum transferred into a receiver flask. This method allowed for continuous purification of the bicyclic compound from isomerized material and simple access to very small amounts of compound.

Solution-Phase Kinetics of the Decomposition of the Methylbicyclopentenes. A stock solution of the 2-methyl isomer was prepared by addition of approximately 30 μl to 0.70 ml of THF. As internal standard, 20 μl of methylcyclohexane was added. (In other cases pentane or methanol were employed as solvent.) Nine 6-cm sections of 4-mm i.d. pyrex tubing had been previously prepared by washing in 5% sodium ethylenediaminetetraacetic acid solution and distilled water, drying, sealing one end, and drawing out the glass to form a constriction near the other end. About 70 μl of the stock solution was added to each of the tubes which were then immersed half way in dry ice while being sealed at the constriction with a gas flame. The sealed ampules were placed in a beaker which was capsized in a water bath previously equilibrated at the appropriate temperature. At 1–5 min a zero point ampule was removed from the bath. Subsequently, tubes were removed at appropriate intervals. Between removal and analysis they were stored, still sealed, at −78 °C.

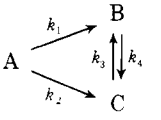
Solution-Phase Kinetics of the Equilibration of Methylcyclopentadienes. A method identical with that described for bicyclopentene disappearance was employed. The methylcyclopentadienes were purified by VPC. Kinetic runs starting with either isomer in excess were performed.

Gas-Phase Pyrolysis of 1- and 2-Methylbicyclo[2.1.0]pent-2-ene. The pyrolysis flask was immersed in liquid nitrogen and bicyclopentene was vacuum transferred from the storage bulb. The total amount transferred was on the order of 1 Torr. When transfer was complete, the bulb was closed to the line while the N_2 inlet was pumped out and N_2 admitted to a suitable pressure monitored by manometer. When pentane was used as bath gas the procedure was reversed; pentane added first, bicyclopentene second. The bulb was closed, removed from the line, and warmed to room temperature. It was then immersed in the previously equilibrated water bath. The water bath was shown to maintain a constant temperature ±0.2 °C. At the conclusion of a run, the flask was immersed in liquid N_2 for 15 min while all the volatiles condensed. Still at liquid N_2 temperatures, the bulb was pumped out. After rewarming to room temperature, all the volatiles were recondensed into one of the tubes at the base of the bulb. The tube was sealed with a torch. For analysis solvent was added if required. For zero points an identical procedure was followed except that the bulb was never or only for 90 s immersed in the water bath.

Surface Effects. Initial runs in the gas-phase reactor produced a decomposition rate for the methylbicyclopentenes that was far larger than expected. However, as a result of several EDTA washings and repeated exposure to 2-methylbicyclopentene, the walls became desensitized, and the disappearance rates decreased to a constant limiting value. Subsequently, the presence of surface effects was probed by the following procedure. A 1-m length of 5-mm o.d. pyrex tubing and two 1-m lengths of 6-mm o.d. pyrex tubing, both with an inside diameter of 4 mm, were cut into 2.5-cm segments. Each segment was fire-polished to insure uniform surface features and soaked overnight in a 5% solution of EDTA. Upon removal from the EDTA, the tubes were washed with copious amounts of distilled water and dried in the oven. Finally, they were added to the pyrolysis flask, a small amount of 2-methylbicyclopentene leaked in, and the flask was closed for overnight storage. For use, the bulb was pumped out and the usual pyrolysis procedure followed. The increase in surface-to-volume ratio achieved by this method was calculated to be about a factor of 6.

Analysis of Products from Pyrolysis Runs. The analysis of reaction mixtures was carried out by VPC using the Hewlett-Packard F and M Model 700 Chromatograph under the conditions given in the VPC section. Retention times under these conditions were methylcyclohexane 6.5 min, 2-methylbicyclopentene 8.5 min, 1-methylbicyclopentene 10.5 min, 2-methylcyclopentadiene 15.0 min, 1-methylcyclopentadiene 17.0 min. Product ratios were obtained by cutting out and weighing the appropriate peaks. The recorder was run at the highest chart speed (2 in/min) to maximize the peak areas. Xeroxing or tracing the curves onto higher quality paper made insignificant, within the reproducibility of the method, changes in the observed ratios. For successive injections of the same mixture, reproducibility errors in the ratios of peak weights of less than ±2.5% were ordinarily observed. Each gas-phase run is the average of three to seven separate injections. Each zero point is the average of two–five separate injections.

Computer Analysis. In order to determine the relative rates of production of 1- and 2-methylcyclopentadiene from either 1- or 2-methylbicyclopentene, a computer program was written that would calculate concentrations as a function of time of all the components of a given system of first-order reactions by a trapezoid-type numerical integration procedure. For this work, the kinetic system modeled was that shown below where the input parameters were initial concentrations of A, B, C and A_0, B_0, C_0, k_3, k_4, k_1, and k_2 all measured



independently, and k_1/k_2 which was varied to fit the data. The fit was

evaluated by sum of the squares of the deviations of the calculated from the observed concentrations at each data point.

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Electronic Effects in Transition Metal Porphyrins. The Reactions of Imidazoles and Pyridines with a Series of Para-Substituted Tetraphenylporphyrin Complexes of Chloroiron(III)

F. Ann Walker,* Man-Wai Lo, and Molly Tutran Ree

Contribution from the Department of Chemistry, San Francisco State University, San Francisco, California 94132. *Received November 19, 1975*

Abstract: Equilibrium constants for addition of Lewis bases to TPPFeCl in chloroform and several other solvents have been measured by visible spectral techniques. The equilibria observed are: $TPPFeCl + 2B \rightleftharpoons [TPPFeB_2]^+Cl^-$ (β_2), where the product is an ion pair, and in some cases: $TPPFeCl + B \rightleftharpoons TPPFeClB$ (K_1), where the product may either be the six-coordinate or the five-coordinate $[TPPFeB]^+Cl^-$ ion pair. Increased solvent polarity causes β_2 to increase for B = *N*-methylimidazole more than for B = imidazole. The hydrogen bonding capabilities of N–H as compared with N–R imidazoles appear to stabilize the product of reaction 1 by about 3 log units in β_2. This suggests that $Fe-N_{Im}$ bond strength in heme proteins may be significantly strengthened by weakening of the N–H bond of the histidine and further increased if this N–H proton can be transferred to some adjacent basic protein residue. The steric effect of addition of a methyl group to the 2 carbon of imidazole is approximately equal to the effect on β_2 of the loss of $N-H\cdots Cl^-$ hydrogen bonding. The basicity of B also has a dramatic effect upon β_2 within each class of B (imidazoles, pyridines). The addition of two B was also investigated as a function of para substituent, X, on the four phenyl rings of TPPFeCl for B = *N*-methylimidazole. A Hammett relationship between log β_2 and σ_X is observed, with ρ −0.39. The sign of ρ is opposite those observed for the reactions of (*p*-X)TPPM complexes (M = Ni^{2+}, VO^{2+}, Co^{2+}). This is because the product of the reaction contains a positively charged center (Fe), which is stabilized by electron-donating groups on the porphyrin ring.

Introduction

The physical properties (electronic,[1,2] NMR,[3-8] ESR,[9] Mössbauer[10,11] spectra, magnetic moments[12]) and reactions of ferric porphyrins have been studied by many investigators. The great interest in ferric porphyrins stems in part from the unique and sometimes puzzling variation in physical properties and chemical reactivity with changes in porphyrin substituents and/or axial ligands, and also from the desire to understand the mode of action of the iron porphyrin center in the ubiquitous heme proteins. In all of the heme proteins investigated to date, the heme moiety is bound to the protein by at least one coordinate covalent bond between iron and the "aromatic" nitrogen of a histidine residue of the protein. In some cases there are additional covalent or coordinate covalent linkages as well, as in the cytochromes *b* and *c*, but the iron–imidazole linkage is common to all those where axial ligands have been identified. The cytochromes b_2 and b_5, which are low on the electron-transport chains of yeasts and mammals, respectively, both appear to have two imidazoles coordinated to the heme iron.[13,14]

One is thus led to the question of why imidazole should be the ligand of choice for hemes rather than some other Lewis base, for example, a pyridine. As more data have become available, in recent years, the question of why Fe(III)–porphyrin–imidazole complexes are so much more stable, purer in magnetic state, and generally much more well defined in physical properties than the corresponding pyridine complexes has arisen.[7] The underlying question of the nature of the difference in electronic properties between pyridines and imida-