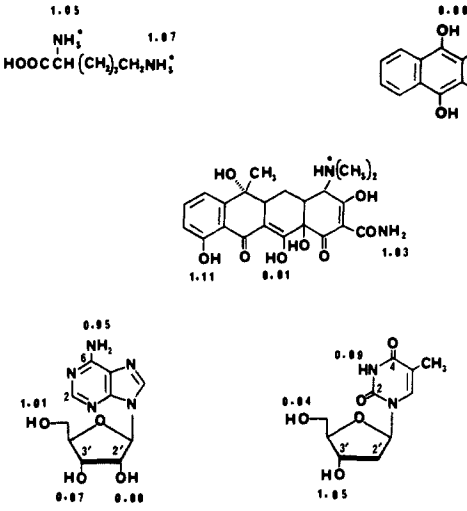
Table I. Deuterium Isotope Effects on Carbon-13 Shifts, Deuterium/Protium Ratios, and Fractionation Factors in Different Solvents

	D_2O/H_2O	$(CD_3)_2SO$	$(CD_3)_2CO$	$CDCl_3$	C_6D_6
methanol					
Δ^a	189[b]	127	141	155	141
R		0.527	2.622	0.677	0.495
N-methylacetamide					
$\Delta(CH_3N)^a$	140	127	142	145	143
$\Delta(C{=}O)^a$	94	88	85	87	74
$\Delta(CH_3CO)^a$	50	46	42	49	42
R		0.603	2.638	0.662	0.585
α^c	1.16[d]	1.18[e]	1.13[e]	1.10[e]	1.32[e]

[a] Upfield isotope shift in ppb ± 3. [b] This is the shift between H_2O and D_2O solutions under conditions of fast exchange, from ref 4. [c] Estimated uncertainty ±0.03. [d] Calculated with eq 2. [e] Calculated with eq 3 using $\alpha_{methanol} = 1.12$.

Chart I. Deuterium/Protium Fractionation Factors



resonances of *N*-methylacetamide in solutions of D_2O/H_2O mixtures appear as doublets. The fractionation factor was determined in a series of such mixtures of known composition. The fractionation factor in organic solvents was determined by using methanol as the reference and CH_3OD as the deuterium source. The results along with the isotope effects on the chemical shifts are summarized in Table I. The variation of the fractionation factor with the solvent is within experimental error, except for the C_6D_6 solution. Extensive solute–solute interactions in the nonpolar solvent may be responsible for the anomaly. The solvent dependence of the isotope shifts, which results from isotope perturbations on bond lengths and bond angles,[13] demonstrates that solute–solvent and solute–solute interactions are important in governing the isotope effects in this system.

The fractionation factors determined for a series of small molecules of biological interest are summarized in Chart I. *N*-Methylacetamide was used as the reference for L-lysine (in Me_2SO-d_6 containing D_2O and concentrated HCl), leucoquinizarin (in Me_2SO-d_6), and tetracycline hydrochloride (in Me_2SO-d_6), while methanol was the reference in a 2:1 adenosine/thymidine mixture in Me_2SO-d_6. Conditions of fast exchange prevailed for functional groups other than those indicated. The results confirm eariler observations[4] that hydroxyl groups engaged in intramolecular hydrogen bonds exhibit a preference for protium over deuterium. However, a direct correlation with the hydrogen bond energy (as measured by the hydroxyl proton chemical shift[14]) was not observed.

Acknowledgment. The excellent technical assistance of David S. Rice is gratefully acknowledged.

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Note Added in Proof. The fractionation factor for the SH group in 2-mercaptoethanol and cysteine derivatives was determined by the present method and found to be in the range 0.44 ± 0.01.[12]

Registry No. L-Lysine, 56-87-1; leucoquinizarin, 17648-03-2; tetracycline monohydrochloride, 64-75-5; adenosine, 58-61-7; thymidine, 50-89-5.

Kinetics of the Thermal Isomerization of 7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene and of 8,8-Dimethylbicyclo[5.1.0]octa-2,4-diene. Evidence for a Nonconcerted 1,5-Carbon Sigmatropic Shift

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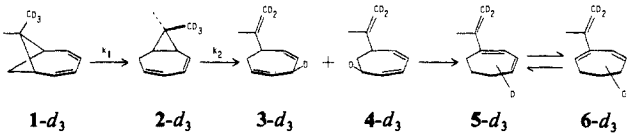
Received November 13, 1985

The previously reported flow system thermolysis of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (**1**) to 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene (**2**) and to the hydrogen shift products from



1-d_3 **2**-d_3 **3**-d_3 **4**-d_3 **5**-d_3 **6**-d_3

2 is remarkable.[1] To the extent that **3** and **4** come exclusively from **2**, the 1,5-sigmatropic shift of **1** occurs primarily (~80%) via Woodward–Hoffmann[2a] orbital symmetry "forbidden" but Berson–Salem[2b] "allowed" suprafacial-inversion pathway; this follows from the deuterium positions shown above. Moreover, **4** is the result of a homo-1,7-deuterium shift process from **2**, which here competes favorably with the generally observed, orbital symmetry allowed, homo-1,5-deuterium shift process that converts **2** to **3**. While previous work indicated that **2** was an intermediate in the thermolysis of **1**, it seemed appropriate to determine the kinetics of reaction of **1** and **2** to measure the relative values of k_1 and k_2. Further, activation parameters for loss of **1** are useful to gauge the extent of concert in this rearrangement.

The kinetics for loss of **1** were determined in a well-conditioned 2-L static reactor from 173.0 to 209.0 °C over one half-life using GC to follow the reaction; this gave $\log k_1(s^{-1}) = (15.1 \pm 0.4) - (41\,900 \pm 900)/2.3RT$ (E_a in cal/mol). Since **2** rearranged rapidly at 125 °C, the rates were determined in degassed benzene-d_6 in sealed NMR tubes from 100 to 139 °C; $\log k_2(s^{-1}) = 11.8 - (29\,400 \pm 800)/2.3RT$ (E_a in cal/mol).[3]

The initial product distribution from both **1** and **2** appeared to be roughly independent of temperature but the homo-1,5-shift product, **3**, is converted slowly to the homo-1,7-shift products **4**–**6** in the pyrolysis of **1**. There may be reversibility in the homo-1,5-shift, giving back **2**, which ultimately affords the more stable trienes. The initial distribution of homo-1,5- to homo-1,7-hydrogen shift products from **1** at 191 °C is 1:1.59 with the ratio of the major 1,7-shift products **5** and **6** being 2.2:1. The ratio 1,5- to

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(3) A copy of the rate and product data was given to the referees and is available upon request.

0002-7863/86/1508-1083$01.50/0

1,7-homo hydrogen shift products from **2** at 100 °C in solution is 0.9:1.0 with **4** being the major 1,7-shift product at low conversions.[4]

A significant difference between the previously reported product distribution from flow system pyrolysis of **1** and these results is the observation of only small amounts of **2** in the gas-phase, static pyrolysis of **1**. The present observations are reasonable given the kinetics for conversion of **2**. For sequential first-order reactions the mole fraction of **2** calculated to be present over the time range investigated at 209.0 °C is 0.002–0.004. The observed values are 0.005 ± 0.002. This agreement lends credibility to the suggestion[1] that **2** is, indeed, along the reaction pathway. We have found that **1** and related hydrocarbons, like α-pinene,[8c] are very sensitive to wall catalysis, and surface catalysis of the rearrangement of **1** may have been responsible for the flow system product distribution.

The *syn*-7-(trideuteriomethyl) derivative of **1**, **1**-d_3,[1] was also pyrolyzed in the static reactor at 209.0 °C. The GC peak corresponding to **2** on two different columns increased by a factor of ~4 at both 15% and 29% conversion. The ratio of 1,5- to 1,7-hydrogen shift products was not affected by the deuterium. In addition, the high-field ^{2}H NMR of the reaction mixture revealed a 2:1 ratio of deuterium on the exo methylenes of **3**–**6** relative to the methyls at both 25% and 45% reaction. Since most of **2** is converted to **3**–**6** under these conditions and since the hydrogen shifts in **2** have been shown to be stereospecific,[1] this corresponds to 75% inversion and 25% retention in the conversion of **1** to **2**. There was no scrambling (syn–anti isomerization) in **1**-d_3. From the kinetics of loss of **1** it was also possible to determine $k_1^H/k_1^{D_3} = 1.26 \pm 0.05$ at 209.0°.

The factor of 4 increase in the amount of **2** observed upon deuterium substitution is consistent with $k_2^H/k_2^{D_3} \simeq 4$. This value is reasonable for a primary isotope effect.[5] On the other hand the small kinetic isotope effect in the loss of **1** excludes formation of **3**–**6** by a process involving C–H bond breaking in the rate-determining step for rearrangement of **1**. However, this small value is consistent with the secondary kinetic isotope effect expected if formation of **2** is the rate-determining step in the loss of **1**.

The activation parameters for disappearance of **1** are consistent with a biradical reaction. The *A* factor is high, and the activation energy is close to the 43 kcal/mol estimated for the dissociation energy of the C-1,C-7 bond using Doering's upwardly revised estimates of C–C bond energies.[6] The major stereochemical path is clearly opposite to the prediction of the Woodward–Hoffmann rules for a concerted suprafacial 1,5-carbon shift, but there is no violation of the Woodward–Hoffmann rules if the reaction is not concerted. We suggest that nonconcerted ring opening occurs in a conrotatory-bevel sense,[7] and this is followed by a least motion closure. These results are similar to those of Klarner,[8a] of Baldwin[8b] on the Berson–Willcott tropilidene circumambulatory 1,5-carbon shift,[9] and of the cleavage of α-pinene.[8c]

The relatively slow rate of rearrangement of **1** would appear to rule out the intermediacy of bicyclo[4.1.1]octa-2,4-diene in the Grimme–Doering butadienylcyclopropane degenerate rearrangement of bicyclo[5.1.0]octa-2,4-diene ($t_{1/2}$ = 0.5 h vs. 140 h for **1** at 150 °C).[10a] Further, Kirmse found only a small rate effect from 8-methoxy substitution on this diene indicating that cleavage of the C-1,C-8 bond does not occur.[10b] This rearrangement is not observed with **2**, despite the fact that the rate constant for carbon rearrangement of the parent bicyclo[5.1.0]-octadiene is comparable to that for the hydrogen shift in **2**. Models suggest that the endocyclic methyl in **2** should sterically destabilize the transition state for the Grimme–Doering rearrangement.

Acknowledgment. We thank the NSF and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this investigation and Professor Staley for directions to prepare **2**.

Registry No. **1**, 62235-10-3; **2**, 57354-42-4; D_2, 7782-39-0.

(4) The low *A* factor and small activation energy for rearrangement of **2** are consistent with both hydrogen shifts being concerted as suggested previously.[1]

(5) *anti*-1,5-Bishomocycloheptatriene exhibits a 1° deuterium KIE for the homo-1,5-hydrogen shift of 6.7 at 173 °C. Detty, M. R.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1978**, 365.

(6) Doering, W. v. E. *Proc. Natl. Acad. Sci. U.S. A.* **1981**, *78*, 5279. BDE(3°–4° C–C) = 80 kcal/mol; Pentadienyl radical RE ≃ 19 kcal/mol; RE of diene = 5 kcal/mol. The strain energy for 7,7-dimethylbicyclo-[4.1.1]octa-2,4-diene = 36 kcal/mol and biradical intermediate = 13 kcal/mol calculated from a modification by N. L. Allinger's MM2 program (QCPE 345) with MMPI π subroutines (QCPE 318), by J. J. Gajewski and K. E. Gilbert, Indiana University.

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Gas-Phase Infrared Spectroscopy and Recombination Kinetics for $Mn(CO)_5$ Generated via XeF Laser Photolysis of $Mn_2(CO)_{10}$

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Received October 11, 1985

There is currently intense interest in the photochemistry of metal carbonyls, in part due to the important role played by coordinatively unsaturated species in a variety of reaction mechanisms. Of particular interest are those species such as $Mn_2(CO)_{10}$ having a metal–metal bond where two distinct types of primary photochemical events can occur; one involving loss of CO without metal–metal bond cleavage and the other involving homolytic cleavage of the Mn–Mn bond. Both processes have been reported in the UV photolysis of solution-phase $Mn_2(CO)_{10}$.[1,2] In addition, the kinetics of the $Mn(CO)_5$ recombination reaction and the reaction of $Mn_2(CO)_9$ with CO have been measured in solution.[3] Both $Mn(CO)_5$ and $Mn_2(CO)_9$ have also been studied in a matrix environment.[3]

Gas-phase studies are considerably more limited. Freedman and Bersohn have measured the effect of polarized light on the angular distribution of fragments produced via photodissociation of $Mn_2(CO)_{10}$ setting an upper limit of several picoseconds on the excited-state lifetimes.[4] Leopold and Vaida's report of the presence of Mn_2 ion signals in the mass spectrum of the photoproducts generated via photolysis of gas-phase $Mn_2(CO)_{10}$ suggests that CO loss is a photochemical pathway in the gas phase.[5]

In this paper we report on the first example of direct detection via transient infrared spectroscopy of the $Mn(CO)_5$ radical produced via XeF (351 nm) laser photolysis of a gas-phase sample of $Mn_2(CO)_{10}$. In addition the recombination kinetics of the $Mn(CO)_5$ radical have been studied, and a rate constant for recombination has been determined. Finally, we are able to make some comments on the nature of the primary photolytic processes

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