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Thermal Isomerization of 5-Methylbicyclo[2.1.0]pent-2-enes and [1,5-$^{13}C_2$]Bicyclo[2.1.0]pent-2-ene

Sir:

The thermal isomerizations of 1- and 2-methylbicyclo[2.1.0]pent-2-enes give mixtures of both 1- and 2-methylcyclopentadienes in the gas phase at atmospheric pressure and in solution. 2-Methylbicyclo[2.1.0]pent-2-ene has been the most carefully investigated: the kinetically controlled 2- to 1-methylcyclopentadiene ratio from this substrate at 50 °C is 13:1 in hexane[1] and 10:1 in tetrahydrofuran;[2] in the gas phase it is reported to be 1.2:1 at 2 mm of substrate,[2] 1.3:1 at 760 mm of nitrogen as the bath gas,[3] and 1.5:1 at 900 mm of pentane.[2]

To explain these results,[1] two possibilities have been recognized. The first views the reaction as occurring with C(1)-C(4) bond cleavage to afford a vibrationally excited methylcyclopentadiene; 1,5-hydrogen shifts then compete with collisional deactivation of the "hot" product molecule, giving both 1- and 2-methylcyclopentadienes as observed initial products.[2,4] The second recognizes the possibility of C(1)-C(2)/C(4)-C(5) and C(3)-C(4)/C(5)-C(1) reaction modes.[1,3]

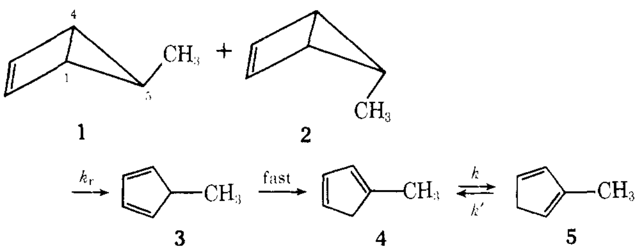
The strongest experimental evidence supporting the first possibility is the apparent pressure sensitivity of the product ratio in the gas phase.[2] Yet, formidable and unavoidable experimental difficulties have limited this line of clarification: the experimental errors associated with these product ratios are such that the ratio could well be constant from 2 mm (no bath gas) to 900 mm (in pentane). We calculate, assuming a 5% uncertainty in a twice-measured ratio of the rate constants compared, 90% confidence limits on these ratios of (1.2 ± 0.3):1 and (1.5 ± 0.4):1.[5]

Theoretical inclination toward the "hot molecule" mechanism comes from RRKM[2,4] and semiempirical molecular orbital[6] calculations. Fits between RRKM calculations and the relatively flat product ratio vs. pressure profile are not absolutely persuasive, since they incorporate a disposable parameter adjusted to obtain the fit, the efficiency of collisional deactivation.

We now report experiments which unambiguously demonstrate extensive "hot molecule" effects at an atmosphere of nitrogen and exclusive operation of the C(1)-C(4) bond cleavage mechanism in the parent hydrocarbon reaction, bicyclo[2.1.0]pent-2-ene to cyclopentadiene.

The *exo*- and *endo*-5-methylbicyclo[2.1.0]pent-2-enes (**1** and **2**) would give, through either C(1)-C(4) cleavage or C(1)-C(2)/C(4)-C(5) cycloreaction, 5-methylcyclopentadiene (**3**). The thermal isomerization of 5- to 1-methylcyclopentadiene (**4**) would be expected to be much faster than the other rearrangements in Scheme I;[7] thus both alternative mechanisms predict 1-methylcyclopentadiene as the observable primary product. Any 2-methylcyclopentadiene (**5**) found as a kinetically controlled product would unequivocally demonstrate a hot molecule effect in the rearrangement.

Scheme I

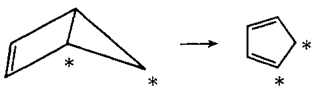


An approximately 1:1 mixture of 1- and 5-methylcyclopentadiene (25 mL) in 1 L of decalin was photolyzed with a 450-W Hanovia lamp at 5 °C for 5 h. The volatile material collected was treated with dimsyl anion in Me_2SO and vacuum transferred to give 0.5 ml of colorless liquid. Preparative GLC on a TCEP column separated this material into two fractions. The early-eluting fraction was shown by NMR to be 1-methylbicyclo[2.1.0]pentene.[3] The other fraction was a 4:1 mixture of *exo*- and *endo*-5-methylbicyclo[2.1.0]pentene contaminated with ~5% 2-methylbicyclo[2.1.0]pentene. The latter component could be removed by treatment of the mixture with dimsyl anion solution followed by GLC purification.[7]

exo-5-Methylbicyclopentene (**1**) had NMR absorptions at δ 6.18 (2 H, m), 2.54 (1 H, q of m, J = 6 Hz), 1.9 (2 H, m), 0.90 (3 H, d, J = 6 Hz). *endo*-5-Methylbicyclopentene (**2**) had NMR absorptions at δ 6.06 (2 H, m), 2.4 (1 H, m), 2.10 (2 H, d of d, J = 5, 2 Hz), and 1.32 (3 H, d, J = 6 Hz). Reduction of the crude photolysis product with diimide in THF gave a mixture (60%) of the four expected methylbicyclopentanes in about the same proportions as the corresponding bicyclopentenes.

Rearrangement of the *exo*- and *endo*-5-methylbicyclopentenes at 50 °C in the gas phase with 1-atm. pressure of nitrogen gave a kinetic 1- to 2-methylcyclopentadiene ratio of (1.20 ± 0.08):1 (k_r = (6.91 ± 0.11) × 10^{-5} s^{-1}), while in hexane the ratio increased to 60:1 (k_r = (1.08 ± 0.04) × 10^{-4} s^{-1}). The 60:1 ratio and its error limits are compatible with no formation of the 2-methyl isomer (**5**) in the kinetically controlled product mixture. The calculated rate for the 5- to 1-methylcyclopentadiene conversion at 50 °C is 2.61 × 10^{-3} s^{-1};[8] the maximum concentration of 5-methylcyclopentadiene attainable is thus 4% in the solution runs. The formation of the large amounts of 2-methylcyclopentadiene, in the gas phase, which must arise from a hot-molecule reaction across two activation barriers, demonstrates the effect, but makes no distinction between the two alternative modes for the first step in the scheme.

Samples of bicyclo[2.1.0]pent-2-ene from the photolysis of vicinal [$^{13}C_2$]cyclopentadiene[9] were isomerized at 50 °C in pentane, and the product [$^{13}C_2$]cyclopentadiene was reexamined by ^{13}C NMR spectroscopy. The bicyclo[2.1.0]pent-2-ene had 20.2 ± 0.5% of the C(5) resonance ascribable to $^{13}C_1$ (9.9%) and $^{13}C_2$-2,5 (10.3%) species, with the balance, 79.8%, due to the $^{13}C_2$-1,5 isomer.[10] One run, in which the bicyclic and 12.5 mol % of [$^{13}C_2$]tricyclo[2.1.0^{2,5}]pentane were isomerized together, gave 22.0 ± 0.7% intensity in the central C(5) resonances of the cyclopentadiene produced. A calculated correction for the cyclopentadiene derived from the [$^{13}C_2$]tricyclo[2.1.0.0^{2,5}]pentene gave 20.7 ± 0.7% as the relative intensity of the central C(5) ^{13}C NMR absorptions of cyclopentadiene derived from bicyclopentene. Another run using tricyclopentane-free bicyclo[2.1.0]pentene gave 19.8 ± 0.5% as the relative intensity of the central C(5) absorptions in the cyclopentadiene formed. The three determinations of the sum of monolabeled and $^{13}C_2$-2,5-labeled hydrocarbons, one of starting bicyclopentene (20.2 ± 0.5%) and two of the cyclopentadiene derived thermally from that bicyclopentene in separate runs (20.7 ± 0.7% and 19.8 ± 0.5%) agree within experimental error. For exclusive operation of the C(1)-C(2)/C(4)-C(5) and C(3)-C(4)/C(5)-C(1) processes, the predicted result would have been 40.4%.[11] Thus the thermal conversion of bicyclopentene to cyclopentadiene occurs through the C(1)-C(4) cleavage mechanism, and nonparticipation of the $[\sigma 2 + \sigma 2]$ alternative is demonstrated.



The controversy over the reaction mode followed in the bicyclo[2.1.0]pent-2-ene to cyclopentadiene isomerization may thus be retired. The experimental distinction which proved so elusive in molecules labeled with substituents has been achieved through double labeling of carbons in bicyclopentene itself. The reality of hot-molecule effects at substantial pressures in the gas phase, and even in solution,[1,2] is confirmed, supporting the postulates of Brauman and coworkers[2] and of Flowers and Frey.[4]

One may anticipate that hot-molecule chemistry in solution will receive fresh attention; the conveniently simplifying generalization that collisional deactivation in solution always preempts thermal reactions of vibrational excited molecules can no longer be credited.

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(10) Determined by the cut-and-weigh method on five copies of spectra obtained on four occasions with various acquisition and pulse-delay times.

(11) This prediction neglects $^{13}C_i$ contributions when $i = 3, 4$, and 5, and uses a simplified model for the processes leading to nonvicinally labeled bicyclopentene: cyclopentadiene → bicyclopentene → bicyclopentene′ through a 1,3-carbon shift. An alternative postulate, cyclopentadiene → bicyclopentene and cyclopentadiene → bicyclopentene′, through a di-π-methane mechanism, gives an identical prediction. The experimental design makes the results insensitive to 1,5-hydrogen shifts. A 10% contribution from the C(1)-C(2)/C(4)-C(5) and C(3)-C(4)/C(5)-C(1) reaction modes would have given 22.2% relative intensity in the central C(5) absorptions; the mean of the two independent experiments was 20.2 ± 0.4 (90% confidence interval, 20.2 ± 1.8).

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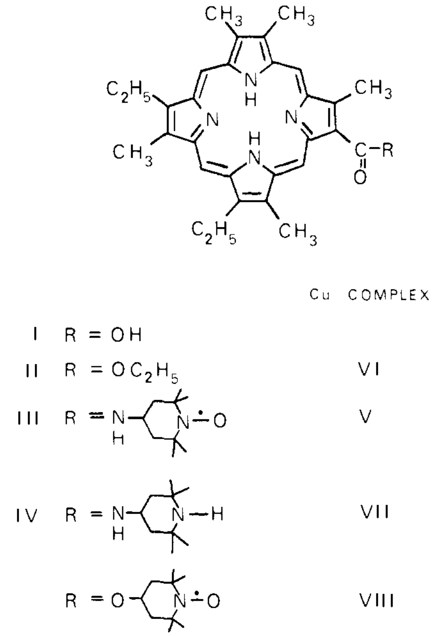
Metal-Nitroxyl Interactions. 4. Electron-Electron Exchange in Spin-Labeled Metalloporphyrins

Sir:

Most spin-label studies of hemoglobin have involved attachment of a nitroxyl radical to the β-93 sulfhydryl group or to reactive sites on the periphery of the porphyrin ring of the heme group. The first published suggestion that there could be observable interaction between a nitroxyl spin label and a paramagnetic transition metal in a spin-labeled molecule was made by Symons in the discussion of a paper by McConnell and Boeyens.[1] At that time no interaction had been detected.[1] Subsequently a large number of papers reported changes in the nitroxyl EPR spectrum upon changing the oxidation state and/or spin state of the iron in hemoglobin. Definite interaction between the heme iron and the nitroxyl spin label was established in a series of papers by Asakura and coworkers.[2] They observed that, when spin labels were attached to the propionic acid side chains of the heme group in hemoproteins, changes in the spin state of the iron caused changes in the amplitude of the nitroxyl EPR spectrum.[2a] Interpretation as dipolar interaction effects in accordance with Leigh's treatment[3] resulted in estimates of the distance between the iron and the nitroxyl in a variety of hemoproteins.[2]

In this paper we report observation of exchange interaction between copper and a nitroxyl radical in a spin-labeled copper porphyrin.



The porphyrin I, reported by Dolphin,[4] was condensed with 4-amino-2,2,6,6-tetramethylpiperidinooxy free radical via the acid chloride of I to yield III. The crude III was purified by chromatography on silica gel, eluting with $CHCl_3$ and keeping the second band. The product was analytically pure and homogeneous by TLC ($CHCl_3$/alumina and $CHCl_3$/silica gel). A similar reaction yielded the amine analogue IV. The copper complex (V) of III was made by refluxing III with copper(II) acetate in pyridine or *N,N*-dimethylformamide. Purification by repeated recrystallization from $CHCl_3$/hexane yielded analytically pure V. The copper complexes VI and VII of the porphyrins II and IV were prepared similarly. Details of the preparation and characterization of these compounds will be reported in a subsequent paper.

The EPR spectra of the spin-labeled and non-spin-labeled copper porphyrins are presented in Figure 1. The EPR spectra of the copper porphyrins VI and VII are essentially identical, indicating that the mere change from H to O on going from VII to V would not be expected to give observable changes in the Cu EPR spectrum in the absence of copper-nitroxyl interaction. The high-field copper hyperfine line in the spectra of VI and VII exhibits superhyperfine splitting from the porphyrin nitrogens (expected intensity ratio 1:4:10:16:19:16:10:4:1).[5] The EPR spectrum of the spin-labeled porphyrin III consisted of the well-known three-line pattern ($a_N \approx 15.9$ G), each line of which was further split by coupling to hydrogens in the piperidine moiety. The high-field multiplet was significantly