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A Mechanistic Study of the Rhodium-Catalyzed Cyclization of 4-Hexenals. Reactions of Deuterio-4-hexenals[1,2]

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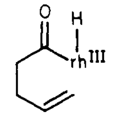
Abstract: In independent experiments, four carbons in the 4-pentenal skeleton have been labeled with deuterium or methyl and the fate of each label has been determined as the pentenal was transformed into a cyclopentanone derivative by $RhCl(PPh_3)_3$ (**1**) at 24–26 °C. The catalyst converted 4-hexenal to 2-methylcyclopentanone (**2**) in $CHCl_3$ and C_6H_6. Approximately equivalent amounts of hydrocarbon decarbonylation products and $RhCl(CO)(PPh_3)_2$ were also formed. 3-Methyl-4-pentenal was isomerized to 3-methylcyclopentanone by **1**. 4-Hexenal possessing deuterium at C-2 was isomerized to **2** which contained deuterium at C-5. *trans*-4-Hexenal-*1-d* was cyclized to **2**-*3-d* and **2**-*2-d* in 9:1 ratio when the reaction was carried to a low conversion. The deuterium in the **2**-*3-d* product was found to be cis to the C-2 CH_3 group. *cis*-4-Hexenal-*1-d* was isomerized by **1** to afford **2**-*3-d* possessing deuterium trans to the C-2 CH_3 group. NMR analyses of these products were assisted by the synthesis and characterization of **2**-*cis-2,3-d_2* by treatment of 2-methylcyclopent-2-en-1-one with D_2 and **1**. The **2**-*cis-2,3-d_2* could be converted to a 1:1 mixture of **2**-*3-d* diastereomers on treatment with HCl in $MeOH/H_2O$. The results demonstrated that the cyclization of 4-hexenal-*1-d* occurred by a syn addition of the C–D bond to the olefinic bond to generate **2**-*3-d*. The presence of C_2H_4 in reaction mixtures of **1** and 4-hexenal-*1-d* resulted in the formation of substantial **2**-d_0 and C_2H_3D. The deuterium locations in the 1-pentene, 2-pentene, and ethylcyclopropane decarbonylation products derived from reaction of 4-hexenal-*1-d* with **1** were determined. The results were interpreted in terms of a hydroacylation mechanism involving an acylrhodium(III) hydride complex and organometallic intermediates derived therefrom. The hydroacylation and decarbonylation products appear to be generated via common intermediates.

Acylmetal hydride species have been proposed as possible participants in a group of very important transformations which are promoted by transition metal complexes in solution. These include hydroformylation,[3] model Fischer–Tropsch type syntheses,[4] aldehyde decarbonylation,[5] and aldehyde hydroacylations of alkenes.[1,6,7] The generation of such an intermediate has also been proposed in the reaction of $Rh_2(CO)_4Cl_2$ with bicyclo[2.2.0]hexane[8] and in the reductive elimination of CH_4 from $Os(CO)_4(H)CH_3$.[9]

To our knowledge, only a few reports of syntheses of acyl transition metal hydride complexes exist and their chemistry has not been systematically studied. Wilkinson and co-workers reported the isolation of an incompletely characterized compound thought to be $Ir(COEt)HCl(CO)(PPh_3)_2$ as an unstable solid in a mixture with $IrCl(CO)(PPh_3)_2$,[3a] and postulated the formation of a formylruthenium hydride complex on treatment of $RuHCl(PPh_3)_3$ with $NaOCH_3$.[10] Suggs has synthesized an acylrhodium hydride complex by reaction of 8-quinolinecarboxaldehyde with $RhCl(PPh_3)_3$,[6] and a similar type of reaction of o-$PPh_2C_6H_4CHO$ with iridium(I) has been observed.[11] Oxidative addition of formaldehyde to an osmium(0) complex has afforded a formylosmium hydride complex,[12] and a relatively stable acyliron hydride complex has been prepared by treatment of benzaldehyde with $HFeNp(dmpe)_2$ (Np = naphthyl; dmpe = bis(dimethylphosphino)ethane).[13]

We wish to report results of a mechanistic study of intramolecular hydroacylation reactions of 4-pentenals which are believed to involve reactions of acylrhodium hydride intermediates. The stoichiometric conversion of highly substituted 4-pentenals to cyclopentanones and cyclopropane derivatives was discovered by Sakai and co-workers,[14] and the synthetic scope of the reaction as applied to a variety of 4-pentenals has recently been examined.[7] Our studies in this area were induced by our attempt to find chemical evidence for the participation of acylrhodium hydride intermediates in the Rh(I)-promoted decarbonylation of aldehydes.[5] 4-Pentenal was treated with Rh(I) complexes with the intention of generating species such as i. It was reasoned that the alkene functional group could occupy a coordination site that would be required by CO in the decarbonylation, and could serve as a potential reactant with the Rh–C and/or Rh–H bond. We found that rhodium(I) complexes *catalyzed* the addition of the aldehyde functional group to carbon–carbon double bonds to generate ketones. Both intermolecular[1a,15] and intramolecular addition reactions[1] were observed, the course of the reaction being dictated by the nature of the rhodium catalyst employed.



i

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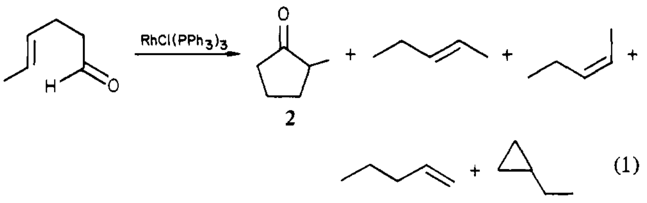
The recent demonstrations that aldehydes can oxidatively add to coordinatively unsaturated transition metal compounds to generate acylmetal hydride products[6,11,12,13] have provided direct precedent for acylmetal hydride participation in reactions of aldehydes with transition-metal compounds in solution. In particular, the isolation by Suggs of a chelate-stabilized acylrhodium hydride[6] has allowed us to assume, with a substantial measure of confidence, the formation of an alkenoylrhodium hydride intermediate in the pentenal hydroacylation reactions. This has provided us the opportunity to study the chemistry of this species, including the mechanisms of its reactions.

Results

Cyclizations of 4-Pentenal Derivatives. Solutions of chlorotris(triphenylphosphine)rhodium(I) (**1**) in chloroform isomerized 4-pentenal to cyclopentanone at room temperature. The reaction was found to be marginally catalytic in rhodium, yields in the 40–50% range being achieved at ca. 30% conversions of pentenal to products when a 10:1 aldehyde:Rh molar ratio was employed. Small amounts of 1-butene decarbonylation product could be detected in the product mixtures. The yields and percent conversions could be increased by introduction of ethylene to reaction mixtures. During 16 h at 25 °C in $CHCl_3$ under 1 atm of C_2H_4, 65% of the 4-pentenal was converted to products and cyclopentanone was afforded in 78% yield. At 96% conversion, the cyclopentanone yield was 72%. No dramatic increases in yields or conversions were achieved when the experiments were conducted at higher ethylene pressures. Catalyst turnovers for cyclopentanone formation of 5.1 and 7.5 were observed during 168 and 259 h, respectively, when a 20:1 aldehyde:Rh ratio was employed under 4 atm of C_2H_4. At 9 atm of C_2H_4 (aldehyde:Rh = 20), catalyst turnovers of 4.1 and 7.2 were achieved during 44 and 164 h, respectively. The rates of formation of products were lower at the higher ethylene pressures and the cyclopentanone yields at 9 atm of C_2H_4 were similar to those achieved at 1 atm.

On treatment with **1** in C_2H_4-saturated $CHCl_3$ or C_6H_6, 4-hexenal (*E*:*Z* = 9) was converted to 2-methylcyclopentanone (**2**), *trans*- and *cis*-2-pentene, ethylcyclopropane, and 1-pentene, eq 1. Yields of **2** ranged from 50 to 70% at 30–50% conversions of hexenal to products with ca. 1:1 ratios of $RhCl(CO)(PPh_3)_2$ and hydrocarbon decarbonylation products having been formed at higher conversions. The 2-methylcyclopentanone was obtained in lower yields in experiments conducted in the absence of C_2H_4.



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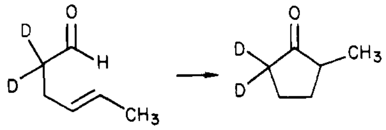
(1)

In an experiment employing 4-hexenal (*E*:*Z* = 9, aldehyde:**1** = 4) in C_6H_6 solution in the absence of C_2H_4, a 56% yield of **2** and a 33% yield of decarbonylation products were afforded at 60% conversion of aldehyde during 60 h. The decarbonylation product mixture consisted of 38% 1-pentene, 20% *trans*-2-pentene, 25% *cis*-2-pentene, and 17% ethylcyclopropane.

4-Hexenal was treated with a free radical trapping agent, duroquinone, in C_6H_6 in the absence of ethylene (aldehyde:duroquinone:Rh = 10:2:1). The yield of **2** and the percent conversion of starting material as a function of time were determined. The yield and conversion vs. time profile was found to be essentially the same as that obtained in an analogous experiment conducted in the absence of duroquinone. The rate of formation of decarbonylation products was also unaffected by the presence of duroquinone.

3-Methyl-4-pentenal was slowly isomerized by **1** to 3-methylcyclopentanone in 98% yield at 32% conversion in C_2H_4-saturated benzene.

Isomerization of 4-Hexenal-*2,2-d*$_2$. 4-Hexenal possessing deuterium at C-2 (15.8% d_0, 23.4% d_1, 60.8% d_2) prepared by the general procedure of Montgomery and Matt[16] was treated with **1** in C_6H_6 and the product mixture at 24% conversion was separated and analyzed. The location of the deuterium at C-2 in the 4-hexenal reactant and in the recovered starting material was established by integration of the 90-MHz ^1H NMR spectra. The isotopic composition of recovered 4-hexenal was found to be 18.2% d_0, 21.2% d_1, 60.6% d_2 and the 2-methylcyclopentanone product was 11.1% d_0, 28.2% d_1, 60.8% d_2. The location of deuterium was determined to be at C-5, eq 2, by ^1H NMR integration of a 90-MHZ spectrum obtained in the presence of $Eu(fod)_3$ shift reagent. The use of the shift reagent to separate the ring proton resonances at C-2 and C-5 from those at C-3 and C-4 was required because the ring proton chemical shifts and coupling constants are of the same order of magnitude and give an extremely complex spectrum of overlapping multiplets at 90 MHz. The $Eu(fod)_3$-altered spectrum consisted of the CH_3 doublet at highest field, overlapping multiplets due to C-3 and C-4 protons at intermediate field, and overlapping resonances of the C-2 and C-5 protons at lowest field, with integrations in the ratio 3.00:4.10:1.49, respectively. The well-resolved CH_3 doublet, $J = 7.5$ Hz, demonstrated the presence of a proton at C-2. The data indicated that the average numbers of deuteriums per molecule of 4-hexenal reactant, recovered starting material, and **2** product were respectively 1.45, 1.49, and 1.42 by mass spectrometry and 1.51, 1.50, and 1.51 by ^1H NMR integration. Other experiments have further established the lack of mobility of the **2** C-2 and C-5 hydrogens in the presence of the catalyst. Neither **1** nor mixtures of **1** and 4-pentenal caused appreciable deuterium scrambling or H–D exchange in **2** possessing deuterium at C-2 and C-5. Descriptions of these experiments, conducted at 24–25 °C in C_6H_6, may be found in the Experimental Section.

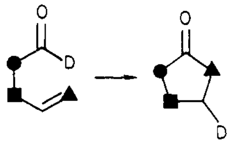


(2)

Isomerization of 4-Hexenal-*1-d*. High-purity 4-hexenal-*1-d* was synthesized via the addition of a slurry of $LiAlD_4$ to ethyl 4-hexenoate in diethyl ether, followed by oxidation of the isolated deuterio alcohol product with CrO_3–pyridine. This procedure afforded deuterio-4-hexenal with >98% d_1 composition as determined by ^1H NMR and mass spectrometry, the location of the deuterium being unambiguously established by the absence of the proton resonance at δ 9.77 ($CDCl_3$).[17]

Treatment of *trans*-4-hexenal-*1-d* with **1** afforded deuterio-**2** which possessed one deuterium per molecule, its location being predominantly at C-3 with a minor amount (ca. 10%) residing at C-2. The isotopic compositions of recovered 4-hexenal and **2** from a number of experiments are given in Table I. The location of the deuterium predominantly at C-3 was suggested by ^1H NMR integration of the spectrum recorded in $CDCl_3$ in the presence of $Eu(fod)_3$ at 90 MHz (CH_3:C-3 + C-4:C-2 + C-5 proton resonances, 3.00:3.02:2.90, consistent with ca. one deuterium residing at C-3 or C-4) and verified by comparison of its 270-MHz ^1H and 41.4-MHz ^2H NMR spectra with those of model deuterio-**2** compounds as described below.

Taken together, the labeling experiments, along with results from experiments employing a variety of alkyl-substituted 4-pentenals,[7,14] define the predominant skeletal change and hydrogen transfer as that depicted in eq 3. They indicate that in the absence



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[16] Montgomery, L. K.; Matt, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 6556.

[17] Attempts to prepare 4-hexenal-*1-d* via oxidation of the deuterio alcohol on a CuO column at 270 °C according to the method of Shiekh and Eadon[18] afforded material with as much as 20% d_2, so this method was not employed.

[18] Sheikh, M. Y.; Eadon, G. *Tetrahedron Lett.* **1972**, 257.

Table I. Isotopic Compositions and Deuterium Locations in Products Derived from Reactions of 4-Hexenal-*1*-*d* with 1[a]

	4-hexenal-*1*-*d*,[b] %	reaction	recovered 4-hexenal			2-methylcyclopentanone					
			%	% composition[c]		% composition[c]			% of total ^{2}H resonance[d]		
run	trans	time, h	trans	d_0	d_1	d_0	d_1	d_2	δ 0.88	δ 1.55	δ 1.59
1	99	24	97	1.4	98.6	1.5	98.5		90	10	
2	97	13.5	95	<1	>99	0.8	98.5	0.7	88	12	
3[e]	97	49	95	3.2	96.8	3.7	94.6	1.7			
4[f]	97	55	95	1.2	98.8	18.2	81.4	0.4			
5	14	19	24	1.3	98.7	7.0	93.0		15		85
6	99	30	95			5.7	90.8	3.5	78	12	10
7	97	49	96	<1	>99	4.2	95.8				

[a] Experiments were conducted at room temperature and a 10:1 aldehyde:Rh ratio was employed in all experiments except run 5, where a 7:1 ratio was used. Benzene was employed as solvent unless noted otherwise. [b] 4-Hexenal was >98% d_1 in all cases. [c] Determined by mass spectrometry. [d] Recorded in C_6H_6 employing a small amount of C_6D_6 (δ 7.15) as internal standard. [e] Conducted in $CHCl_3$ solvent. [f] Conducted in C_6H_6 saturated with C_2H_4 at 1 atm.

Table II. Isotopic Compositions of Cyclic Ketones Derived from D_2 Addition to Cycloalkenones[a]

				time,	conversion,	% composition of cycloalkanone[b]				
run	enone	catalyst	solvent	h	%	d_0	d_1	d_2	d_3	d_4
1	cyclohex-2-en-1-one	10% Pd/C	dioxane	6	90	30.7	26.0	24.8	13.0	5.5
2	cyclohex-2-en-1-one	1	dioxane	7	90	3.2	9.6	86.3	0.9	
3	cyclohex-2-en-1-one	1	benzene	7	98	0.8	6.1	91.9	1.2	
4	2-methylcyclopent-2-en-1-one	1	benzene	27	82	4.3	32.7	46.8	14.7	1.5
5	2-methylcyclopent-2-en-1-one	1	benzene	6	32	0.5	1.8	97.6	0.1	

[a] Experiments were conducted at room temperature under ca. 1 atm of D_2. Cycloalkenone:Rh ratios of 6:1 to 40:1 were employed. [b] Determined by mass spectrometry.

of C_2H_4 essentially all of the deuterium originally at C-2 or C-1 in the 4-hexenal reactant was retained in recovered hexenal and in product **2**. In the presence of C_2H_4, a substantial amount of deuterium loss (run 4, Table I) via transfer to ethylene occurred. Recovered hexenal retained its predominantly d_1 composition with deuterium residing at C-1 as evidenced by the absence of the δ 9.77 proton resonance. A sample of ethylene recovered from reaction of 4-hexenal-*1*-*d* with **1** during 48 h in the presence of C_2H_4 (4-hexenal-*1*-*d*:C_2H_4 = 1) possessed a 82.8% d_0, 16.8% d_1, 0.4% d_2 composition.

Experiments were conducted in which ca. equimolar mixtures of 87% *trans*-4-hexenal and 4-hexenal-*1*-*d* were allowed to compete for the catalyst in C_6H_6 solution at ca. 24 °C. An aldehyde to **1** ratio of 20 was employed in two experiments that were carried to 9 and 11% conversions, and a 10:1 aldehyde:**1** ratio was used in a reaction taken to 21% conversion. Comparisons of the isotopic composition of the product **2** with that of the 4-hexenal reactant, in each case, gave values of k_H/k_D for **2** formation in the 1.3–1.6 range. Although the precision in these preliminary measurements was relatively poor, the results did indicate that the isotope effect is probably substantially less than 2.

Determination of the Steric Course of the 4-Hexenal-*1*-*d* Cyclization. The finding that 4-hexenal-*1*-*d* transformed predominantly into **2**-*3*-*d* provided the opportunity to determine the steric course of the carbon–deuterium addition to the carbon–carbon double bond since syn and anti additions in a given geometric isomer of 4-hexenal must provide different **2**-*3*-*d* diastereomers.

A. Synthesis and Characterization of 2-*cis*-*2,3*-d_2. The synthesis of a deuterio-**2** model possessing deuterium at C-3 with a known steric relationship to the C-2 CH_3 group was accomplished by catalytic addition by **1** of D_2 (1 atm) to 2-methylcyclopent-2-en-1-one in C_6H_6 at room temperature. We conducted a series of experiments to establish the optimum conditions for the generation of d_2 product. These results are given in Table II. The highest d_2 composition was obtained by using **1** in C_6H_6 in an experiment carried to relatively low conversion, run 5.

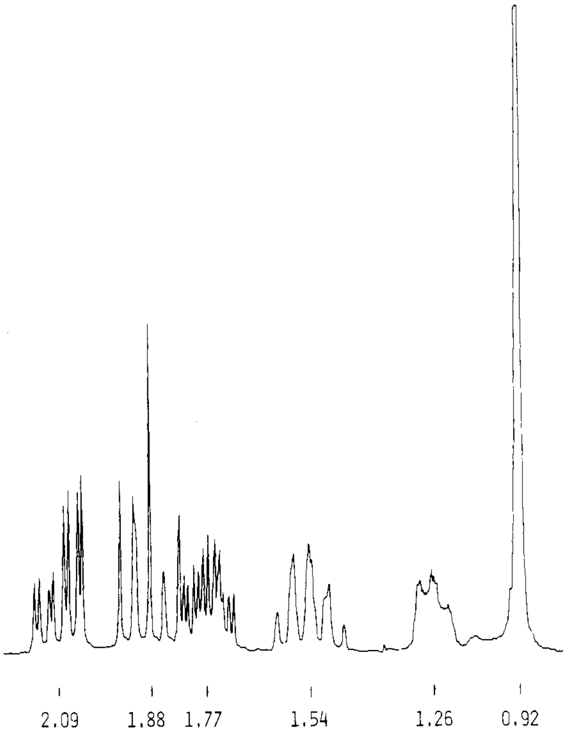

Figure 1. ^{1}H NMR spectrum of **2**-*2,3*-d_2 recorded at 270 MHz in 10% C_6D_6–90% CCl_4 (by volume) solvent at ambient temperature.

Ring proton resonance assignments in the **2**-d_2 (run 5, Table II) could be made by comparison of the 270-MHz ^{1}H NMR spectrum, Figure 1, and the 41.444-MHz ^{2}H spectrum of the sample to those of **2**-*2,5,5*-d_3. The ^{1}H spectrum of the latter consisted of one-proton multiplets at δ 1.26, 1.54, 1.77, and 1.99 and the CH_3 proton resonance at δ 0.92 in a 9:1 CCl_4–C_6D_6 solvent mixture. The comparison revealed that the δ 1.26 resonance in Figure 1 is that of a C-3 proton and δ 1.54 and 1.77 belong to C-4 protons. The remaining C-3 proton must be assigned δ 1.99, and δ 1.88 and 2.09 must be due to C-5 protons. The ^{2}H NMR spectrum of the **2**-*2,3*-d_2 product in C_6H_6[19] consisted of resonances at δ 1.59 and 1.55 in 1:1 ratio, indicating that the D_2 addition had been *completely stereospecific*, the resonance for the alternate C-3 proton at δ 0.88 (C_6H_6) being absent. The precedent for syn

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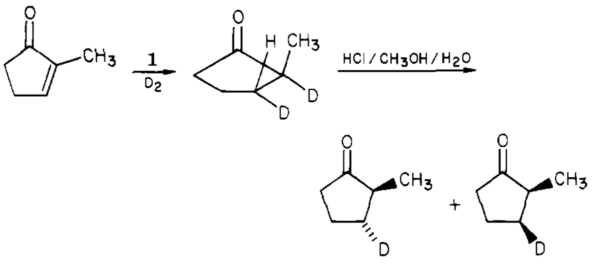
(19) Substantial solvent shifts of ring proton resonances occurred in C_6H_6 relative to chemical shifts in CCl_4. For instance, the resonance for the C-3 proton cis to the CH_3 group shifted to high field (δ 0.88) and overlapped with the CH_3 resonance.

addition in hydrogenations catalyzed by **1**[20] allowed us to assign the δ 1.26 (CCl_4:C_6D_6 = 9) and 0.88 (C_6H_6) resonances to the C-3 proton cis to the C-2 CH_3 group. Treatment of **2**-*2,3-d*$_2$ with 20% hydrochloric acid in methanol afforded a 1:1 mixture of **2**-*3-d* diastereomers as indicated by ^2H resonances at δ 1.59 and 0.88 (C_6H_6) in 1:1 ratio. Therefore, the C-2 proton was assigned δ 1.55 and the C-3 proton trans to the CH_3 group was δ 1.59. The ^2H spectrum of **2**-*2,5,5-d*$_3$ (C_6H_6), with peaks at δ 1.55, 1.59, and 1.80, was consistent with these assignments. These transformations are described in eq 4.

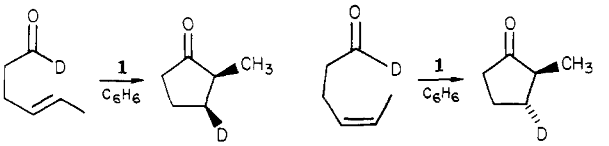


(4)

B. Determination of the Configurations of 2-*d* Derived from *trans*- and *cis*-4-Hexenal-*1-d*. Treatment of *trans*- and *cis*-4-hexenal-*1-d* with **1** in C_6H_6 solution at 25 °C in a series of experiments afforded **2**-*d* products exhibiting the ^2H resonances and percentages of total ^2H peak intensities listed in Table I. At 26–27% conversions (runs 1 and 2), *trans*-4-hexenal-*1-d* was transformed into **2**-*3-d* with essentially all of the deuterium located cis to the CH_3 group (δ 0.88 in C_6H_6) and into **2**-*2-d* (δ 1.55), the product ratio of the former to the latter being 9:1. The presence of the δ 0.88 resonance in the ^2H NMR spectrum of the **2**-*d* product was accompanied by the decrease in intensity of the corresponding peak in the ^1H 270-MHz spectrum at δ 0.88 (C_6H_6) and 1.26 (CCl_4:C_6D_6 = 9). The longer reaction times (run 6) afforded deuterio-**2** with up to 14% of the total ^2H resonance peak area at δ 1.59 (C_6H_6) with substantial residual proton resonance due to the proton at C-3 cis to the CH_3 group being evident.

The results from run 5 indicated that *cis*-4-hexenal-*1-d* was converted to **2**-*3-d* with deuterium located trans to the C-2 CH_3 group.

The data demonstrated that the cyclizations of *trans*- and *cis*-4-hexenal-*1-d* to **2**-*3-d*, at low conversions, were stereospecific and followed the steric course described in eq 5.



(5)

Determination of Deuterium Locations in the Decarbonylation Products. The location of the deuterium label in each decarbonylation product derived from *trans*-4-hexenal-*1-d* was determined in an effort to establish the mechanistic relationship of the decarbonylation to the hydroacylation reaction. Samples of 4-hexenal-*1-d* were treated with **1** (aldehyde:**1** = 4) at 25 °C and the reactions were carried to relatively high conversions in order to isolate enough deuteriopentene and deuterioethylcyclopropane to analyze by NMR spectroscopy.

In a typical experiment carried to 52% conversion of 4-hexenal-*1-d* (*E*:*Z* = 84:16) to products during 60 h, 57 and 35% yields of **2**-*d* and of hydrocarbon decarbonylation products, respectively, were achieved. The decarbonylation product mixture consisted of 37% 1-pentene, 17% *trans*-2-pentene, 29% *cis*-2-pentene, and 17% ethylcyclopropane. The isotopic compositions of the 1-pentene and *trans*-2-pentene afforded in these experiments are given in Table III. The locations of deuterium in the pentenes could be established by examination of their ^2H and ^1H NMR spectra. The label in the 1-pentene resided at C-4 as evidenced by the ^2H resonance at δ 1.35 in CCl_4 containing 1% each of C_6H_6 and C_6D_6 (the only ^2H resonance detected) and by the absence of the corresponding resonance in the ^1H spectrum. Further support for the assignment came from the conversion of the CH_3 triplet proton resonance at δ 0.92 in authentic 1-pentene to a doublet in the deuterio product. Also, an apparent quartet at δ 2.0 in 1-pentene became a triplet in the deuterio sample. The *trans*-deuterio-2-pentene product exhibited a ^2H resonance at δ 0.90 as the only ^2H resonance detected. A triplet ^1H resonance at δ 0.90 in authentic *trans*-2-pentene converted to a finely split triplet of decreased relative intensity in the deuterio product. These observations established the location of the deuterium at C-5.

Table III. Isotopic Compositions of Decarbonylation Products Derived from 4-Hexenal-*1-d*[a]

4-hexenal-*1-d*, % trans	product	%[b]		
		d_0	d_1	d_2
97	1-pentene	0.6	98.2	1.2
97	*trans*-2-pentene	21.8	78.0	0.2
87	1-pentene		95.2	4.8
87	*trans*-2-pentene	15.6	82.7	1.7

[a] Experiments were conducted in C_6H_6 at room temperature employing 4-hexenal-*1-d* of >98% d_1 composition and an aldehyde:Rh ratio of 4. Reaction times of ca. 84 h were used. [b] Determined by mass spectrometry.

The *cis*-deuterio-2-pentene and deuterioethylcyclopropane were isolated in an experiment employing 4-hexenal-*1-d* with 87% trans geometry and >98% d_1 composition. These two products could not be completely separated from each other via preparative GLC. They were therefore collected as a mixture and, for this reason, an accurate determination of the isotopic composition of each component by mass spectrometry was not feasible. It could be established by integration of the 270-MHz ^1H NMR spectrum that the ethylcyclopropane and *cis*-2-pentene were present in ca. 3:1 ratio in the isolated mixture.[21] An authentic sample of ethylcyclopropane exhibited ring proton resonances at δ 0.14, 0.25, and 0.50 ppm and ethyl proton resonances at δ 0.85 (triplet, CH_3) and 1.09 ppm (sharply defined quintet, CH_2) relative to C_6H_6 taken as δ 7.15 ppm. The ^1H spectrum of the deuterioethylcyclopropane component of the product mixture showed a doublet resonance at δ 0.85 and the δ 1.09 resonance became a poorly resolved multiplet with one-half the peak intensity of the corresponding resonance in the authentic nondeuterio sample. The ^2H spectrum of the mixture exhibited the δ 1.09 resonance as the most intense absorption. These results indicated that the deuterium resided at the methylene carbon in the ethyl group and suggested that the ethylcyclopropane was essentially all d_1. The ^2H spectrum of the *cis*-deuterio-2-pentene component exhibited peaks at δ 0.90, 1.97, and ca. 5.3 ppm in 1:2:0.7 ratio, consistent with the presence of deuterium at C-5, C-4, and the carbon–carbon double bond, respectively. As will become apparent in the Discussion section, the most probable source of the δ 0.90 resonance would appear to be a C-5 deuterium in *cis*-2-pentene derived from decarbonylation of the minor *cis*-4-hexenal-*1-d* component of the starting material employed in this experiment. If one accepts this interpretation, the results from decarbonylation of *trans*-4-hexenal-*1-d* may be summarized as in eq 6.

Discussion

The results define the nature of the skeletal change and hydrogen transfer associated with the 4-hexenal to 2-methylcyclopentanone transformation. They are consistent with an intra-

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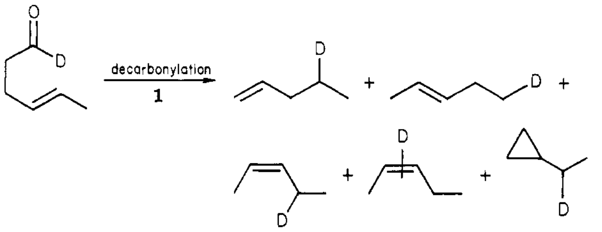
[20] (a) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711. (b) Birch, A. J.; Walker, K. A. M. *Tetrahedron Lett.* **1966**, 4939. (c) Djerassi, C.; Gutzwiller, J. *J. Am. Chem. Soc.* **1966**, *88*, 4537. (d) Senda, Y.; Mitsui, S.; Sugiyama, H.; Seto, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3498.

[21] The 3:1 ethylcyclopropane:*cis*-2-pentene ratio derived from incomplete collection of the entire binary mixture. The percent yields of *cis*-2-pentene and ethylcyclopropane given in the text were determined by integration of the GLC peak areas of the partially resolved binary mixture and by ^1H NMR integration of the carefully collected entire mixture. Both methods gave essentially the same values for the product ratio.



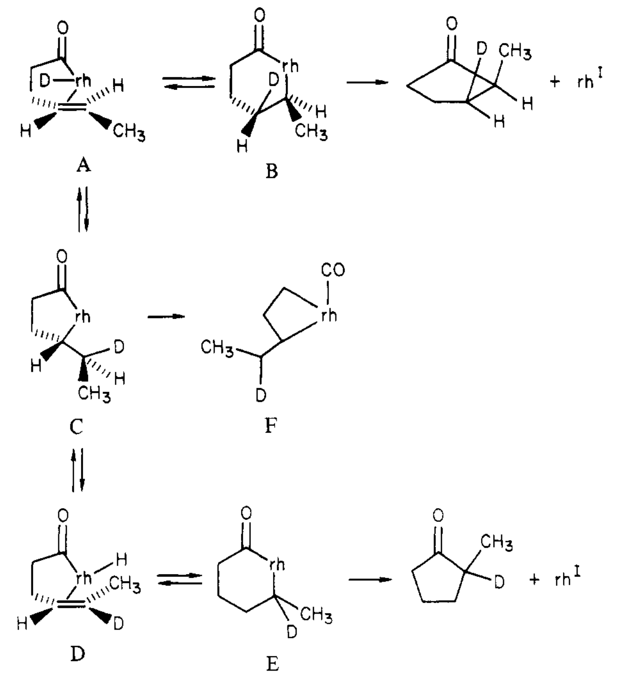
(6)

molecular transfer of hydrogen from the aldehyde functional group to carbons which become C-2 and C-3 in the **2** product. They are inconsistent with a radical chain process. Acceptable mechanisms must account for these facts and must explain the stereospecific formation of **2**-*3-d*. Furthermore, a satisfactory hydroacylation mechanism must account for the fates of the 4-hexenal-*1-d* label in the competing decarbonylation reactions if the two processes are to be considered mechanistically related. We feel that the reaction sequence described in Scheme I meets these criteria. It entails oxidative addition of the aldehyde carbon–deuterium bond to a coordinatively unsaturated rhodium(I) complex to afford acylrhodium deuteride intermediate A, a reaction for which direct evidence exists.[6] The syn addition of the Rh–D bond to the coordinated double bond in A by the two possible modes would afford B and C. Reductive elimination in B via carbon–carbon coupling[22] with retention of configuration at the incipient C-2 would generate **2**-*3-d* with the observed stereochemistry.[23] Intermediate C can participate in an intramolecular route to **2**-*2-d* via D and E.

The structures of the observed decarbonylation products and the locations of the deuterium labels therein provide support for the participation of intermediates A, D, and F, and, by inference, C, in Scheme I. The *trans*-2-pentene-*5-d* and *cis*-2-pentene possessing deuterium at a carbon in the double bond can be envisioned as being derived from A and D, respectively. Ethylcyclopropane possessing deuterium at the ethyl group methylene carbon, 1-pentene-*4-d*, and *cis*-2-pentene-*4-d* could derive from rhodiacyclobutane intermediate F. Evidence for alkene formation via a hydrogen transfer across the face of a rhodiacyclobutane ring system was first presented by Katz and Cerefice.[24] Examination of molecular models reveals that formation of *cis*-2-pentene should be much preferred over *trans*-2-pentene via this process due to steric considerations. The formation of 1-pentene-*4-d* demonstrates that intermediate B is not the source of the 1-pentene decarbonylation product. Rhodium hydride β-elimination in B to generate a 5-hexenoylrhodium intermediate would afford 1-pentene-*3-d* as would rhodium hydride β-elimination from a methyl-substituted rhodiacyclopentane derived from B.[26] The absence of deuterium at C-2 in the 1-pentene product also eliminates E as its source for the same reason. One can conclude that carbon–carbon coupling to give **2** must be rapid relative to Rh–H β-elimination involving hydrogen transfer from the CH_3 groups in B and E.

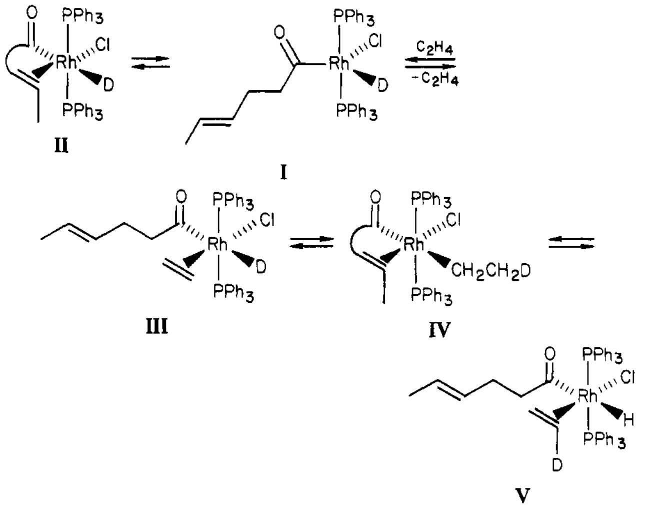
The steric results of the 4-hexenal-*1-d* cyclizations could also be achieved by a syn addition of the carbon–rhodium bond to the olefinic bond in A, Scheme I. Carbon–deuterium reductive elimination with retention of configuration at C-3 in the resulting intermediate would generate the same **2**-*3-d* diastereomer as afforded in Scheme I. Intramolecular carbon–metal additions in alkenoyl transition metal complexes are known and provide precedent for this route.[27] However, this mode of reaction of A does not provide a route to the **2**-*2-d* product nor does it account for the observed structures of and deuterium locations in the decarbonylation products. The structure of such an alkylrhodium deuteride intermediate would be directly analogous to that of a presumed[20] participant in the addition of D_2 to 2-methylcyclopent-2-en-1-one, catalyzed by **1**. A major difference would be the requirement that the bulky rhodium atom and auxiliary ligands be cis to the C-2 CH_3 group in the species that leads to the observed **2**-*3-d* product derived from *trans*-4-hexenal-*1-d*. This very unfavorable steric situation is probably the most compelling reason to consider an alternative reaction path.[28]

Scheme I[a]



[a] rh = $RhCl(PPh_3)_2$.

Scheme II



We wish to emphasize that direct support for the nature of individual reaction steps in Scheme I is still unavailable. Only very recently, for instance, has direct evidence for the participation

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[22] A direct precedent for this step: (a) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515. For other reactions in which this type of carbon–carbon coupling has been postulated: (b) Hegedus, L. S.; Lo, S. M.; Bloss, D. E. *Ibid.* **1973**, *95*, 3040. (c) Schwartz, J.; Cannon, J. B. *Ibid.* **1974**, *96*, 4721. (d) Hegedus, L. S.; Kendall, P. M.; Lo, S. M.; Sheats, J. R. *Ibid.* **1975**, *97*, 5448.

[23] Cyclization of *trans*-4-hexenal-*1-d* via this route would afford the **2**-*3-d* stereoisomer shown in Scheme I along with its enantiomer.

[24] Katz, T. J.; Cerefice, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 1049. For other examples of alkene formation from metallocyclobutanes see ref 25.

[25] (a) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3519.

[26] Whitesides, G. M.; Young, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 5808.

[27] (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3116. (b) Cooke, M. P., Jr.; Parlman, R. M. *Ibid.* **1977**, *99*, 5222.

[28] Results from a study of the addition of 4-hexenal-*1-d* to C_2H_4 to give 6-octen-3-one-*d*, catalyzed by $Rh(AA)(C_2H_4)_2$, have demonstrated that a mechanism involving carbon–rhodium addition to ethylene followed by carbon–deuterium coupling with reductive elimination cannot be the major reaction path in this case. Deuterium was found to be distributed at the two ethyl group carbons in the octenone in ca. 1:1 ratio.[15]

of an alkylrhodium hydride intermediate in homogeneous olefin hydrogenation been reported,[29] although this type of species has been invoked by various workers for more than 14 years.[20a,30] Proposed mechanisms which are in accord with the observed steric courses in alkene hydrogenation,[20a,29] aldehyde decarbonylation,[5] and hydrocarbon rearrangements[31] have inferred that carbon–hydrogen coupling via reductive elimination in a rhodium(III) system can occur with retention of configuration at carbon. We are unaware of any study in which a characterized alkylrhodium hydride complex has been demonstrated to undergo reductive elimination and the steric course of the reaction was determined. To our knowledge, the steric course of reductive elimination via carbon–carbon coupling in a characterized organorhodium system has not been determined nor has it been inferred through the determination of the overall stereochemistry of a multistep process as has been the case in carbon–hydrogen coupling reactions.[5,20,31] If, however, one accepts the arguments that hydridorhodium complexes undergo syn additions to olefinic bonds,[3a,20a,32,33] a carbon–carbon coupling reaction in B, Scheme I, to give **2**-*3-d* must proceed with retention of configuration at carbon to be consistent with the product structure.

If oxidative addition of the alkenal to Rh(I) to form I, Scheme II, occurs, coordination of the olefinic bond to generate II must be rapid relative to the rate of alkenyl group migration to the metal (decarbonylation). In II, the Rh–D bond is cis to the coordinated olefinic bond and can assume the orientation required for a syn Rh–D addition. Little reorganization of ligand positions is required in the interconversion of II and I. Evidence for the participation of a stereochemically rigid chloro analogue of I in the decarbonylation of saturated acyl chlorides has been provided by Stille and co-workers.[33] From a stereochemical viewpoint, conversion of I to II should be favored over the analogous reaction of an isomer of I possessing equatorial phosphine ligands, since the former transformation places the bulky PPh_3 ligands trans to one another in II.

Why does **1**, in the presence of C_2H_4, promote cyclization of 4-pentenals to the exclusion of intermolecular pentenal–C_2H_4 addition? We propose that (1) intermolecular reaction of C_2H_4 with I to form III and isomers thereof does not compete favorably with intramolecular chelate formation to form II; (2) when III and its isomers are formed, their reactions to generate IV are accompanied by alkenoyl chelate formation which places the acyl and ethyl ligands trans to one another; (3) carbon–carbon coupling with reductive elimination only occurs when the carbon–rhodium bonds are cis to one another in an *octahedral* complex. The role of C_2H_4 in increasing the efficiency of the catalysis may involve the creation of coordinatively saturated acyl complexes such as III, therefore obstructing decarbonylation. Also C_2H_4 may promote carbon–carbon coupling in species such as B, Scheme I, through octahedral complex formation via C_2H_4 coordination to the metal. This picture explains how deuterium could be incorporated into C_2H_4 (IV $\rightleftarrows$ V) without C_2H_4 reacting to give ketone product.

Experimental Section

All experiments employing organometallic compounds were conducted under argon or nitrogen. Solvents were purified by conventional means and deoxygenated before use. Chlorotris(triphenylphosphine)rhodium(I) was purchased from Ventron Corp. and stored under argon. 4-Penten-1-ol and ethylcyclopropane standard were purchased from Pfaltz and Bauer. 3-Methyl-4-penten-1-ol was obtained from Chemical Samples Co. 4-Pentenal and 3-methyl-4-pentenal were prepared by oxidation of the corresponding alcohols according to the procedure of Shiekh and Eadon,[18] using a 6 ft × $^1/_4$ in. 40/80 CuO GLC column at 250 °C with a flow rate of ca. 10 mL/min. 4-Hexenal and 4-hexenal-*1-d* were prepared by addition of slurrys of $LiAlH_4$ and $LiAlD_4$, respectively, to ethyl 4-hexenoate in diethyl ether, followed by oxidation of the isolated alcohols with CrO_3–pyridine as described elsewhere.[15,34] 4-Hexenal-*2,2-d*$_2$ was prepared by the general procedure of Montgomery and Matt[16] by treatment of 4-hexenal twice in THF with D_2O in the presence of triethylamine. 2-Methylcyclopentanone and 3-methylcyclopentanone samples for standard use were obtained from Aldrich. Lithium aluminum deuteride was purchased from Stohler Isotope Chemicals and also from Ventron. The 2-methylcyclopentanone-*2,5,5-d*$_3$ was prepared by treatment of 2-methylcyclopentanone with PCl_5 in D_2O.[35] Ethylene, CP grade, was purchased from Matheson Gas Products.

The ^1H NMR spectra were recorded on either a Varian EM 390 or a Bruker HX 270 instrument. The ^2H NMR spectra were recorded on a Bruker HX 270 instrument at 41.44 MHz in C_6H_6 solution employing a small amount of C_6D_6 (δ 7.15 ppm) as internal standard. The 270-MHz ^1H spectra were generally obtained in 10% C_6D_6–90% CCl_4 (by volume), employing a deuterium lock. Mass spectra were obtained on a Du Pont 21-491 instrument. The precision in the determination of each percent composition value in Tables I–III is estimated to be better than ±1 percentage point. Infrared spectra were recorded on a Beckman IR 12 spectrometer.

Yield and conversion data for 4-pentenal and 4-hexenal reactions were determined by GLC, using a Varian 1420 dual column instrument employing two 5-ft 15% XE-60 columns temperature programmed from 65 °C, flow rate 35 mL/min. Ketone and aldehyde product samples were collected by using a Varian 90 P3 instrument employing 6 ft × $^1/_4$ in. 15–30% Silicone GE XE-60 on Chromosorb P columns or a 10-ft 20% Carbowax column. Standard mixtures of reactants and products were analyzed in order to determine the relationships between signal responses and molar ratios. Dodecane was employed as internal standard in 4-pentenal reactions and toluene was used in 4-hexenal experiments. The hydrocarbon decarbonylation products were separated and isolated via GLC on two 20 ft × $^3/_8$ in. 20% β,β'-oxydipropionitrile on firebrick columns operated in series at 0 °C, using a flow rate of 35 mL/min. Percent conversions were based upon consumed aldehyde starting material and percent yields were defined as the percent of reacted aldehyde transformed into a given product.

Reactions of 4-Hexenal with 1. In a typical experiment, 1.7 mL of a deoxygenated solution of 4-hexenal (0.11 mL, 0.962 mmol) and 0.25 mL of toluene standard in benzene was added to 0.096 mmol of **1** under argon. The resulting amber solution in the closed flask was stirred at 24–25 °C. During the course of the reaction, the yellow $RhCl(CO)(PPh_3)_2$ precipitated from solution. In analogous experiments conducted in $CHCl_3$, the reaction mixtures remained homogeneous, turning yellow in color. Reactions were monitored by GLC. Experiments were terminated by removal of all volatile products from the catalyst in vacuo and condensation in a −78 °C cold trap.

In experiments employing ethylene, the solution of 4-hexenal was saturated with C_2H_4 for 5 min at 1 atm at ca. 5 °C prior to its addition to the flask containing **1**. The resulting solution was stirred under 1 atm of C_2H_4.

Experiments employing other 4-pentenal derivatives were conducted in an analogous manner. To conserve deuterio starting material, experiments employing 4-hexenal-*1-d* were conducted on a smaller scale than those using 4-hexenal. The cyclization was found to be stereospecific when the following conditions were satisfied: (1) short reaction times were employed; (2) to avoid enolization of the ketone products, caution was observed in the collection and handling of samples so that no foreign material could come in contact with the samples; (3) all ^1H and ^2H spectra were obtained within ~2 weeks of the time of the experiment.

Isolation of $RhCl(CO)(PPh_3)_2$. The yellow rhodium product was isolated in an experiment employing 4-hexenal and **1** in benzene as described above. When the reaction was terminated, the volatile products and solvent were removed in vacuo, and the yellow solid residue was washed several times with C_6H_6 and then dried in vacuo. The infrared spectrum of the material (KBr) was found to be identical with that of an authentic sample of $RhCl(CO)(PPh_3)_2$.[36]

Isolation of Deuteriopentenes and Deuterioethylcyclopropane. A deoxygenated solution of 0.260 mL (2.20 mmol) of *trans*-4-hexenal-*1-d* in 11.5 mL of benzene was added to 0.513 g (0.555 mmol) of **1** at room temperature under argon. The reaction flask was attached to a series of three cold traps. The volatile products were periodically removed from the reaction flask during an 84-h period by trap-to-trap distillation and cumulatively collected in the third trap which was cooled with liquid

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Table IV. Treatment of Deuterio-**2** with the Catalyst. Isotopic Compositions of Reactant and Recovered Deuterio-**2**

	% composition[a]							
	reactant **2**				recovered **2**			
run	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3
1	0.9	4.9	26.0	67.9	0.9	5.6	27.5	66
2	0.1	4.0	26.8	69.0	0.1	3.8	25.4	70.7
3	0.1	4.0	26.8	69.0	1.0	3.9	21.9	73.2

[a] Determined by mass spectrometry.

nitrogen. The third trap was then connected to a GLC loop, cooled with liquid nitrogen, which was in turn connected to two 20-ft β,β'-oxydipropionitrile on firebrick GLC columns and the products were separated at 0 °C. The decarbonylation products were then analyzed by ^{1}H and ^{2}H NMR and mass spectrometry.

Isolation of Ethylene and Ethylene-*d*. A deoxygenated solution of 0.10 mL (0.90 mmol) of 4-hexenal-*1*-*d* (87% trans) and 0.060 mL of toluene standard in 1.4 mL of benzene was added to 0.084 g (0.090 mmol) of **1**. The mixture was stirred under argon at room temperature for several minutes, cooled to −198 °C, and evacuated. One millimole of C_2H_4 (25 mL at 1 atm) was then transfered to the reaction flask, which was then sealed. The resulting mixture was warmed to room temperature and stirred for 48 h, after which the volatiles were removed in vacuo, the ethylene was collected in a liquid nitrogen cooled trap, and the other volatiles were collected at −78 °C in a trap that preceded it. The ethylene was analyzed by mass spectrometry.

Treatment of 2-*2,5,5*-d_3[35] with the Catalyst. Following the usual procedure, a sample composed primarily of **2**-*2,5,5*-d_3 was treated with **1** (ketone:**1** = 10) in C_6H_6 at 25 °C for 24 h. The isotopic compositions of the ketone reactant and of recovered deuterio-**2** are given in Table IV (run 1).

The data for runs 2 and 3 in Table IV derive from experiments in which 4-pentenal was treated with **1** in C_6H_6 in the presence of deuterio-**2** (4-pentenal:ketone:**1** = 10:1.5:1.0). During 6 h at 25 °C, 46% of the 4-pentenal was converted to cyclopentanone in 41% yield. Recovered 4-pentenal and the cyclopentanone possessed >99% d_0 compositions. No 4-hexenal was detected in the product mixtures. The 90-MHz ^{1}H NMR spectra of the ketone reactant and product in run 3, recorded in the presence of Eu(fod)$_3$ shift reagent, were integrated. They showed an average of 0.31 and 0.34 H, respectively, at C-2 + C-5 in the deuterio-**2** starting material and in the recovered deuterio-**2**. The isotopic compositions for run 3, Table IV, showed values of 0.35 and 0.34 H for reactant **2** and recovered **2**, respectively.

Synthesis of 2-Methylcyclopentanone-*2,3*-d_2. In a typical experiment, a solution of 0.10 mL (0.98 mmol) of 2-methylcyclopent-2-en-1-one[37] in 5 mL of deoxygenated benzene was added to 0.109 g (0.118 mmol) of **1** under argon. The flask was cooled to −78 °C and then attached to a hydrogenation apparatus. An atmosphere of D_2 was introduced; then the reaction mixture was allowed to warm to room temperature. The reaction was monitored by following the rate of consumption of D_2 and by GLC analysis of 5-μL aliquots which were removed periodically. The reaction was terminated after the desired time by removal of all volatiles from the catalyst in vacuo. The deuterio-**2** was then collected via GLC after removal of solvent.

Synthesis of 2-Methylcyclopentanone-*3*-*d* Diastereomers. To a flask containing 0.7 mL of 20% hydrochloric acid and 0.8 mL of methanol was added *cis*-2,3-dideuterio-2-methylcyclopentanone (0.15 mL 1.4 mmol). The mixture was stirred for ca. 16 h, after which the solution was saturated with NaCl and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the mixture of **2**-*3*-*d* isomers, 63% yield, was collected via GLC.

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Role of a Peroxide Intermediate in the Chemiluminescence of Luminol. A Mechanistic Study

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Abstract: By simultaneous generation of the luminol radical and the superoxide radical anion $O_2^{-}\cdot$ in an alkaline aqueous solution containing H_2O_2 but no oxygen, it was possible to measure at different pH values the rate constant for the formation of the peroxide adduct. The rate constant for the decomposition of the adduct was also determined. The latter reaction is shown to be a rate-determining kinetic step in the production of the excited state. Its rate constant is strongly pH dependent. At pH 7.7, where essentially no light is produced, its value is $(2 \pm 0.5) \times 10^3$ s^{-1}, while at pH 11.0 the value $(1.8 \pm 0.3) \times 10^5$ s^{-1} is obtained. It is suggested that the acid (hydroperoxide) and the base (peroxide) react along different chemical pathways yielding different end products. Only the decomposition of the base results in light generation. An overall reaction scheme is proposed. In an indirect measurement the chemiluminescence quantum yield ϕ_{cl} is determined to be $\simeq 0.1$.

Introduction

Ever since the discovery of the chemiluminescence of luminol by Albrecht,[1] many chemists have been intrigued by the elusive nature of the light-producing step. A common feature endemic to all systems where luminol chemiluminescence is observed is the presence of oxygen or hydrogen peroxide and a basic environment. Thanks to the pioneering works of White et al.,[2,3] the stoichiometry of the overall reaction as well as the identity of the emitting species has been firmly established in aprotic solvents. By implication it appears reasonably safe to assume that the same species (3-aminophthalate) is the light emitter even in protic solvents, such as water.

A generally made observation is that the addition of hydrogen peroxide to an otherwise aerated solution enhances the chemiluminescent intensity. The mechanism of luminol chemiluminescence in aqueous solutions in the presence of oxygen (O_2) has been studied by Shevlin et al.[4] and by Baxendale.[5] These workers conclude that the chemiluminescent process is initiated by a

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