Journal of Organometallic Chemistry, 186 (1980) C27—C31

Preliminary communication

A STEREOSPECIFIC RHODIUM CATALYZED HYDROACYLATION. CYCLIZATION OF *trans*-4-HEXENAL-1-*d*

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(Received October 15th, 1979)

Summary

Treatment of *trans*-4-hexenal-1-*d* with $RhCl(PPh_3)_3$ (I) in C_6H_6 afforded 2-methylcyclopentanone-3-*d* and -2-*d* (II-3-*d*, and II-2-*d*) in 9/1 ratio when the reaction was carried to a low conversion. The deuterium in the II-3-*d* product was found to be *cis* to the C(2) methyl group by analysis of the 270 MHz ^1H and 41.4 MHz ^2H NMR spectra. This analysis was assisted by the synthesis of II-*cis*-2,3-d_2 by treatment of 2-methylcyclopent-2-en-1-one with D_2 and I. The 270 MHz ^1H and 41.4 MHz ^2H spectra of II-*cis*-2,3-d_2 and of II-2,5,5-d_3 were instrumental in the assignments of proton resonances in spectra of II-3-*d*. 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 II-3-*d*. The results were interpreted in terms of a mechanism involving intervention of an acylrhodium(III) hydride complex and organorhodium(III) intermediates derived therefrom.

The mechanism by which 4-pentenal undergoes rhodium promoted aldehyde-alkene addition reactions [1—3] is of particular interest because of the potential similarity of reaction steps to those in aldehyde decarbonylation [4—8], hydroformylation [9,10], and model Fischer—Tropsch type processes [11]. We wish to report results which elucidate the steric course of the cyclization of 4-hexenal.

We have achieved the synthesis of high purity 4-hexenal-1-*d* via the addition of a slurry of $LiAlD_4$ to ethyl 4-hexenoate in diethyl ether, followed by oxidation of the isolated deuterioalcohol product with CrO_3-pyridine. This procedure resulted in 4-hexenal with $> 98\%$ d_1 composition as determined by PMR and mass spectrometry, the location of the deuterium being unambiguously established by the absence of the proton resonance at δ 9.77 ppm ($CDCl_3$).

Treatment of 4-hexenal-1-*d* ($E/Z = 9$) with $RhCl(PPh_3)_3$ (I) in $CHCl_3$ or C_6H_6 at room temperature afforded 2-methylcyclopentanone (II) with the

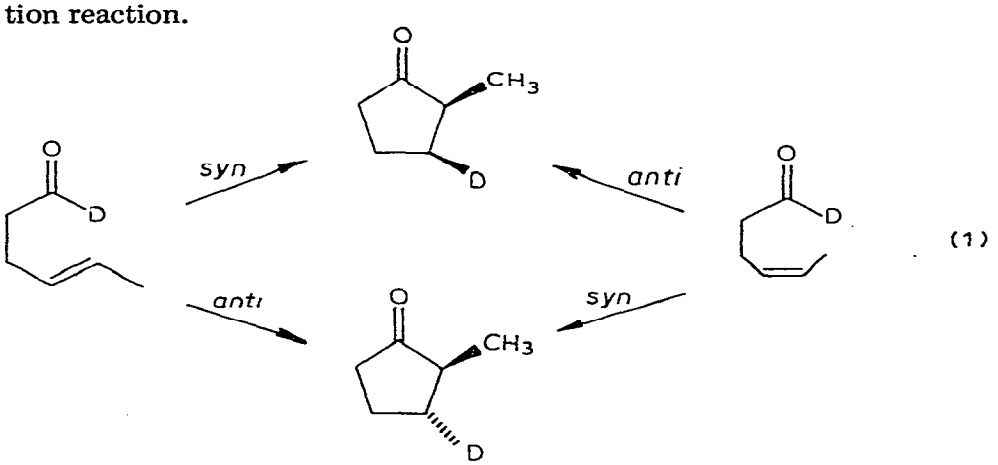
TABLE 1

ISOTOPIC COMPOSITIONS OF 2-METHYLCYCLOPENTANONE PRODUCTS AND RECOVERED 4-HEXENAL [a]

Medium	Product	d_0 (%)	d_1 (%)	d_2 (%)
C_6H_6	4-hexenal	<1	>99	
	2-methylcyclopentanone	4.2	95.8	
$CHCl_3$	4-hexenal	3.2	96.8	
	2-methylcyclopentanone	3.7	94.6	1.7
C_6H_6 satd. with C_2H_4	4-hexenal	1.2	98.8	
	2-methylcyclopentanone	18.2	81.4	0.4

[a] Determined by mass spectrometry, using a duPont 21—491 instrument. Experiments were conducted at room temperature employing a 10/1 4-hexenal (>98% d_1)/Rh molar ratio. The precision in the determination of each % composition value is estimated to be better than ±1. % composition values which were determined for the same sample of deuterio-II using our instrument and that of Morgan Shaffer Corp., Montreal Canada, were within 2 percentage points.

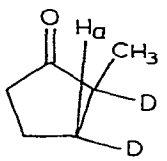
isotopic compositions given in Table 1 at 30—40% conversions [2] of reactant to products. Very little, if any, intermolecular H—D exchange occurred in the absence of added C_2H_4. In the presence of C_2H_4, a substantial amount of deuterium loss was evident, apparently via transfer to ethylene since recovered hexenal retained its predomiantly d_1 composition with the deuterium residing at C(1). The formation of deuterio-II was accompanied by the generation of approx. equivalent amounts of $RhCl(CO)(PPh_3)_2$ and deuteriopentenes at higher conversions, both 1-pentene and 2-pentene being present. We have found that 4-hexenal-1-*d* transforms predominantly into 2-methylcyclopentanone-3-*d*. This result has provided the opportunity to determine the stereochemistry of the aldehyde 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-methylcyclopentanone-3-*d* diastereomers (eq 1). Mechanistic information concerning the addition reaction might be inferred from the results of experiments involving the formation of 2-methylcyclopentanone-3-*d* if one could be assured that (a) loss of configuration at C(2) by enolization or by some rhodium promoted process does not occur subsequent to the addition, and (b) geometric isomerization of the 4-hexenal does not occur prior to the cyclization. Either of these could screen the actual steric course of the addition by a process independent of the cyclization reaction.



(1)

We have therefore conducted a number of control experiments to assess the lability of hydrogen at C(2) in 2-methylcyclopentanone. The reluctance of II-2,5,5-d_3 and II-5-d_2 to undergo H—D exchange or deuterium scrambling under conditions of the catalysis in benzene has been established. Finally, our synthesis and characterization of 2-methylcyclopentanone-*cis*-2,3-d_2 has demonstrated its configurational stability.

Treatment of 2-methylcyclopent-2-en-1-one [12] with I and D_2 (1 atm) in C_6H_6 for 6 h at room temperature afforded a 32% conversion of the cyclopentenone to deuterio-2-methylcyclopentanone (0.5% d_0, 1.8% d_1, 97.6% d_2). Ring proton assignments could be made by comparison of its 270 MHz ^1H NMR spectrum and 41.444 MHz ^2H spectrum with those of II-2,5,5-d_3. These revealed that the D_2 addition had been completely stereospecific (^2H NMR; δ 1.59 and 1.55 ppm in 1/1 ratio). The precedent [5,13—15] for *syn*-addition in hydrogenations catalyzed by I allowed us to assign the II-*cis*-2,3-d_2 structure with H_a assigned δ 0.88 ppm (C_6H_6 solution) relative to C_6D_6 internal standard taken as δ 7.15 ppm. Treatment of II-*cis*-2,3-d_2 with HCl in C_6H_6 afforded a 1/1 mixture of II-3-*d* diastereomers (^2H NMR, δ 1.59 and 0.88 ppm in 1/1 ratio). Therefore, the C(2) proton is assigned δ 1.55 ppm and the C(3) proton *trans* to CH_3 is δ 1.59 ppm.



(II-*cis*-2,3-d_2)

The configurational stability of II-*cis*-2,3-d_2 under the conditions of its synthesis, isolation (GLC on a Silicone XE-60 column at 100°C) and analysis (1500 mile trip to New Haven) is pertinent to our stereochemical study of the 4-hexenal-1-*d* cyclization.

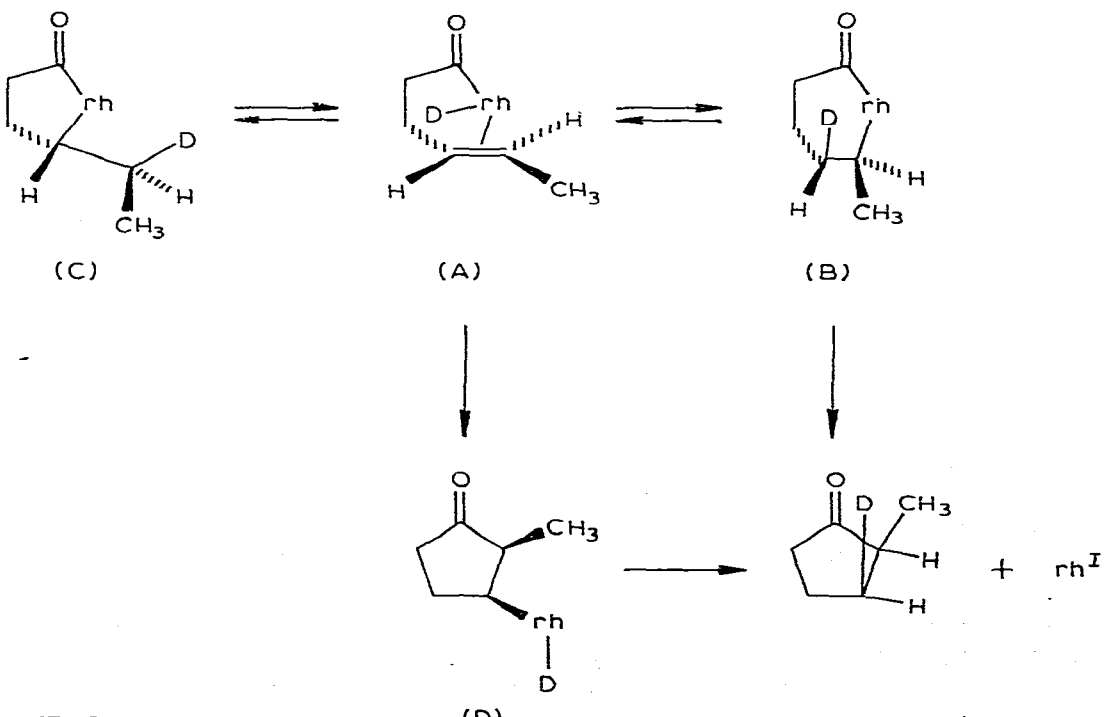
Reaction of 4-hexenal-1-*d* (>99% d_1, 97% *trans*) with I in C_6H_6 at 25°C (aldehyde/Rh 10) led to a 27% conversion of aldehyde to products during a 13.5 h period. The deuterio-II product possessed a 0.9% d_0, 98.4% d_1, 0.7% d_2 composition and recovered 4-hexenal (95.4% *trans*) consisted of >99% d_1 molecules. The presence of deuterium at C(3), *cis* to the C(2) CH_3 group in the deuterio-II product was unambiguously verified by its resonance at δ 0.88 ppm (C_6H_6) in the deuterium NMR spectrum, and by the decrease in intensity of the corresponding proton resonance in the 270 MHz spectrum. The deuterium spectrum exhibited one other peak (at δ 1.55 ppm), the ratio of 0.88/1.55 being 9/1. A similar experiment conducted for 24 h afforded the same results in terms of deuterium compositions of products and the nature of the deuterium NMR spectrum of the deuterio-II product. We found however, that reaction times longer than ca. 20 h generally afforded deuterio-II with up to 14% of the total peak area in the deuterium NMR

spectrum at δ 1.59 ppm with substantial residual proton resonance due to the proton at C(3) *cis* to the CH_3 group, being evident.

The decarbonylation products derived from treatment of *trans*-4-hexenal-1-*d* with I have been isolated and the 1-pentene was found to possess one deuterium at C(4) as unambiguously determined by analysis of its ^2H and ^1H NMR spectra. Determination of the deuterium location in the 2-pentene is in progress.

Our results demonstrate that, at low conversion, *trans*-4-hexenal-1-*d* cyclizes to II-3-*d* via a ca. 100% *syn* addition of the aldehyde C—D bond to the olefinic bond. The findings are consistent with the participation of organorhodium intermediates [2,16,17] described in Scheme 1 where the rh symbol represents the rhodium(III) atom with its auxiliary ligands. The results emphasize mechanistic differences between rhodium(I) and $SnCl_4$ [18] promoted pentenal cyclizations. A *syn* Rh—D addition to the alkene bond in A to generate B, followed by concerted carbon—carbon coupling with retention of configuration at C(2) would provide *cis*-3-deuterio-2-methylcyclopentanone and regenerate the catalyst. The same result would be achieved by a *syn* C—Rh addition to the alkene bond in A followed by carbon—deuterium coupling in D with retention of configuration at C(3). We have no direct evidence that would distinguish between these two routes to II-3-*d*.

A number of possible modes by which the pentene isomers can form exist and a detailed discussion of the mechanistic relationship of the decarbonylation to ketone formation will be deferred to the full paper. For instance, the surprising formation of 1-pentene-4-*d* can be explained by decarbonylation



SCHEME 1

of C to form a rhodiacyclobutane derivative which could generate the 1-pentene [19]. Intermediate C is also a possible participant in the formation of the minor cyclization product, II-2-*d*.

Intramolecular carbon—metal additions in alkenoyl transition metal complexes are known and would provide precedent for the formation of D [20]. Proposed mechanisms which are in accord with the observed steric course in alkene hydrogenation [5], aldehyde decarbonylation [8], and hydrocarbon rearrangement [21] have implied that carbon—hydrogen coupling with reductive elimination from rhodium(III) can occur with retention of configuration at carbon. To our knowledge, the steric course of reductive elimination via carbon—carbon coupling in an organorhodium system has not been established.

Acknowledgement is made to the National Science Foundation (Grant CHE-76-01786) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this Research. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the NIH (RR798).

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