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Hydrogen Shift in the Complex Formation between Deuterium Tetracarbonylcobaltate (-I) and 1, 4-Pentadiene

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Deuteration studies seem to indicate that the formation of 1-ethyl-π-allyl tricarbonylcobaltate(-I) involves a 1—2 hydrogen shift in a terminally protonated 1,4-pentadiene to produce the more stable allyl carbonium ion intermediate.

Reactions between hydrogen tetracarbonylcobaltate(-I) or iron dodecacarbonyl and 1,4-pentadiene yield complexes involving rearrangements of the olefin.[1,2] Recent work on preparation of π-allyl complexes from hydrogen tetracarbonylcobaltate(-I) and the olefins, 1,3-pentadiene and 1,4-pentadiene, have shown that two different complexes are formed.

The 1,3-pentadiene gave the *syn* and *anti* isomers of 1,3-dimethyl-π-allyl tricarbonylcobaltate whereas the 1,4-pentadiene gave the *syn* and *anti* isomers of the 1-ethyl-π-allyl tricarbonylcobaltate; however a small amount (10—15 %) of the dimethyl complex was also observed.

In order to elucidate a mechanism for the formation of an allylic system from 1,4-pentadiene, the complex was prepared using deuterium tetracarbonylcobaltate(-I) and 1,4-pentadiene. The resulting complex distilled at 32°C (0.5 mm).

Infrared spectra gave the usual terminal carbonyl absorptions near 2000 cm^{-1}.

The nuclear magnetic resonance data showed approximately 60—70 % deuteration of the 1-ethyl-π-allyl complex. About 30 % of the product was present as the 1,3-dimethyl-π-allyl tricarbonylcobaltate complex, and both complexes were present as mixed *syn-anti* isomers. Heating for 1—1½ h at

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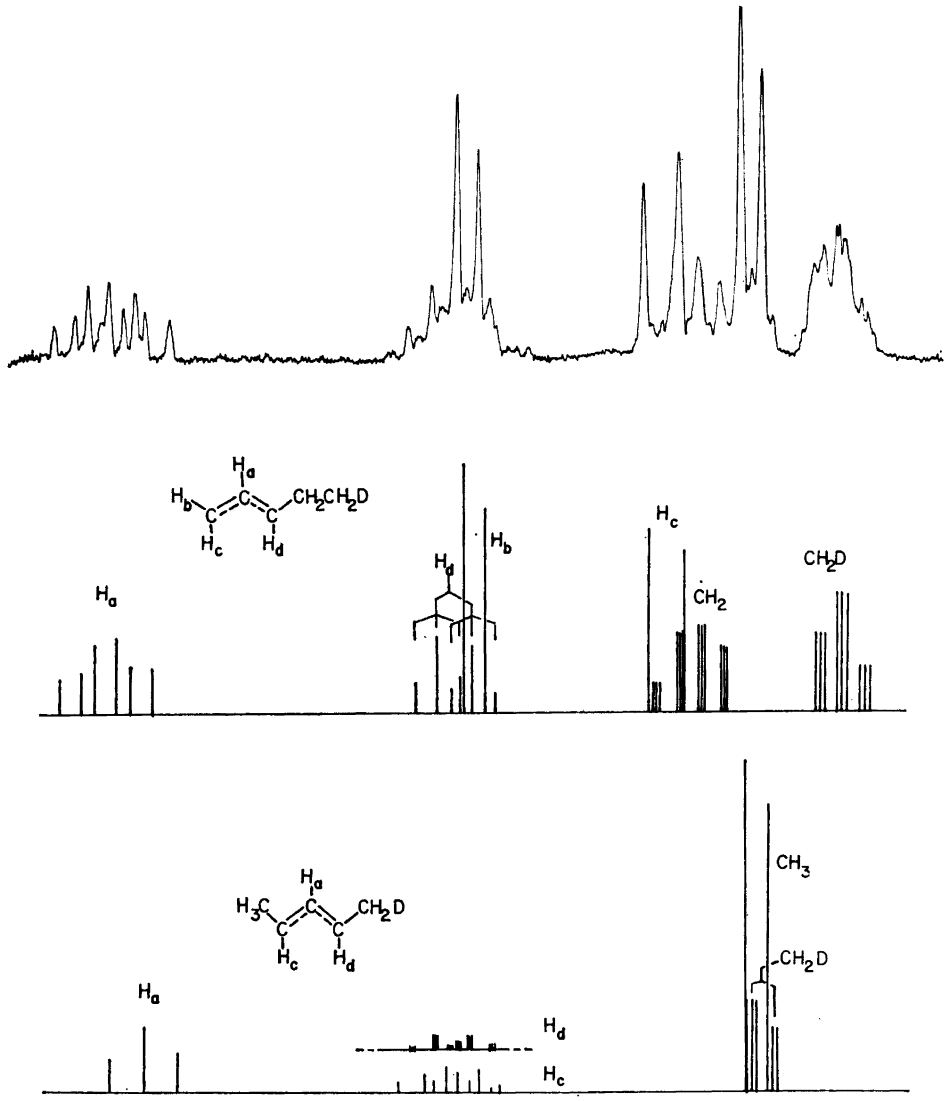


Fig. 1. Nuclear magnetic resonance spectrum (60 Mc) of 1,4-pentadiene adduct with deuterium tetracarbonyl cobaltate. Schematic spectra show principle deuterated π-allylic species.

95°C converted the complexes to nearly pure *syn* forms. The proton magnetic resonance spectrum of this mixture is shown in Fig. 1. A double-resonance experiment at 40.0 Mc using a saturating frequency of 6.1404 Mc to decouple deuterium nuclei, resulted in collapse of the H-D multiplets with considerable simplification of corresponding spectra.

From the spectrum, the deuterium is found to be present in the 1-ethyl-π-allyl complex as $-CH_2D$. The evidence for deuteration of the terminal ethylene is summarized in the following comparison between the ethyl group spectra of the deuterated and normal complexes:

	Normal ethyl		Deutero-ethyl
CH_3	3 lines, J = 6.5 c.p.s., area = 3	CH_2D	9 lines, 1:2:1 triplet of 1:1:1 triplets, area = 2
CH_2	5 lines, J = 6.5 c.p.s., area = 2	CH_2	4 lines, roughly 1:3:3:1, area = 2; possible weak splitting due to D.

This strongly suggest that a 1—2 hydrogen shift has occurred according to the following scheme:

(1) Deuteration of the diolefin.

$H_2C=CH\text{-}CH_2\text{-}CH=CH_2 + DCo(CO)_4 \rightarrow$

$H_2C=CH\text{-}CH_2\text{-}\overset{+}{C}H\text{-}CH_2D + Co(CO)_4^-$

(2) Rearrangement of the carbonium ion by 1—2 hydrogen shift.

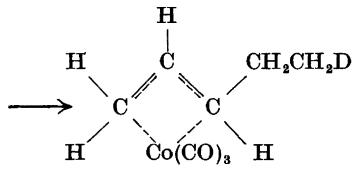
$\rightarrow H_2C=CH\text{-}\overset{+}{C}H\text{-}CH_2\text{-}CH_2D$

(3) Electron delocalization to form a π-allyl carbonium ion.

$\rightarrow H_2C{=}\overset{+}{C}H{=}CH_3\text{-}CH_2D$

(4) Formation of stable tricarbonyl complex by loss of carbon monoxide.

$H_2C{=}\overset{+}{C}H{=}CH\text{-}CH_2D + Co(CO)_4^-$



The presence of the symmetrical 1,3-dimethyl-π-allyl group, as indicated by the NMR spectrum, suggests that the above reaction is accompanied by isomerization of the diolefin to the conjugated 1,3-pentadiene, followed by normal hydrocarbonylation.

In order to see if a similar deuteration on the terminal C atom occurred with a conjugated system, butadiene was allowed to react with deuterium tetracarbonylcobaltate(-I). NMR spectra of this complex indicated deuteration of the terminal methylene group in line with the findings in the 1,4-pentadiene reaction.

EXPERIMENTAL

A) Preparation of potassium tetracarbonylcobaltate(-I)

An aqueous solution of potassium tetracarbonylcobaltate(-I) was made according to a modification of Gilmont and Blanchard's method.[1,3]

About 250 ml of this solution was evaporated to dryness under vacuum, and a white to yellow solid remained. This was then extracted with portions of freshly distilled acetone until the extracts were no longer yellow colored. The potassium tetracarbonylcobaltate was thus separated from most of the other products.

The combined acetone extracts (*ca.* 300 ml) were dried over anhydrous sodium sulphate, then again evaporated to dryness under vacuum. A yellow precipitate of potassium tetracarbonylcobaltate(-I) weighing 15—20 g was obtained. The above procedure was repeated until 50 g of the salt was obtained.

Although all handling and distillation were made under nitrogen, some decomposition occurred as indicated by a change of color towards brown.

B) Preparation of deuterophosphoric acid

Reagent grade phosphorus pentoxide (35 g) and 27 g deuterium oxide were rapidly transferred to a vacuum desiccator in separate containers. The system was then evacuated until the deuterium oxide started boiling. The system was then allowed to stand under vacuum for 24 h. At that time, all the phosphorus pentoxide was dissolved. The remaining deuterium oxide was then added to the solution.

C) Preparation of the complexes

I. Deuterated 1-ethyl-π-allyl tricarbonylcobaltate. 1) *In presence of excess D_2O.* The solid potassium tetracarbonylcobaltate(-I) (0.24 mole) was dissolved in 173 g of deuterium oxide in a 1 liter stainless steel autoclave. The acid (0.50 mole) and a slight excess of 1,4-pentadiene (0.28 mole) were placed in the autoclave in separate test tubes without mixing. The autoclave was then closed maintaining a nitrogen atmosphere inside. It was then rocked with mixing for 48 h. The organic portion was then extracted with pentane, dried and distilled. The complex mixture distilled at 32°C (0.5 mm). The yield was 2.52 g (5.0 %). (Found: C 45.1; H + D 4.7. Calc. for $C_8DH_8O_3Co$: C 46.0; H + D 4.5.).

2) *In absence of D_2O.* A small sample (0.05 mole) of potassium tetracarbonylcobaltate(-I) was allowed to react with a slight excess of deuterophosphoric acid in a 50 ml vessel. This was attached to a vacuum rack which also contained 0.06 mole of pentadiene, a 25 ml vessel, and a liquid nitrogen trap. The $DCo(CO)_4$ was distilled over into the 1,4-pentadiene. The reaction mixture was allowed to stand for 48 h at room temperature. The reaction product was then distilled (32°C, 0.5 mm), yield about 10 % (0.4 g). Infrared and NMR spectra of the product prepared in 1) and 2) were identical.

II. The deuterated methyl-π-allyl tricarbonylcobaltate was prepared in similar fashion using 1,3-butadiene instead of 1,4-pentadiene. (Found: C 42.2; H + D 4.0. Calc. for $C_7DH_6O_3Co$: C 42.4; H + D 3.8.).

III. a. Infrared spectra of the complexes in carbon tetrachloride were obtained on a Beckman IR 5 instrument.

b. Nuclear magnetic resonance spectra. Proton magnetic resonance spectra of the adducts of deuterium tetracarbonylcobaltate(-I) with the olefins have been obtained at 60 and 40 Mc.

Immediately prior to each NMR the samples were vacuum-distilled at room temperature into 10 mm pyrex tubes which were sealed off.

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