SYNTHESIS AND ISOMERIZATION OF 4-HYDROXY-4-METHYL-2-HEPTEN-6-YN-2-YL-2-CYCLOPENTADIENYLMANGANE TRICARBONYL

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Abstract

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SYNTHESIS AND ISOMERIZATION OF 4-HYDROXY-4-METHYL-2-HEPTEN-6-YN-2-YL-2-CYCLOPENTADIENYLMANGANESE TRICARBONYL

(Presented by Academician A. N. Nesmeyanov, 26 IV 1965)

Previously $^{(1,2)}$ we described the anionotropic rearrangement of tertiary β-acetylenic alcohols into enones in the presence of the catalysts $KHSO_4$, $HgSO_4$, H_2SO_4, and P_2O_5:

$$\begin{matrix}R_1\\R_2\end{matrix} > C(OH) - CH_2 - C \equiv CH \longrightarrow \begin{matrix}R_1\\R_2\end{matrix} > C = CH - C(=O) - CH_3$$

In studying certain tertiary β-acetylenic alcohols with various substituents, it was found that the rate and completeness of isomerization of the alcohols increase with increasing electron-donating ability of the substituent.

It was of interest to study the anionotropic rearrangement of β-acetylenic alcohols with enyl substituents at the hydroxyl-bearing carbon atom. For this purpose we obtained 4-hydroxy-4-methyl-2-hepten-6-yn-2-yl-2-cyclopentadienylmanganese tricarbonyl II by the following reaction:

$$(CO)_3Mn\text{-}C_5H_4\text{-}C(CH_3) = CH - C(=O) - CH_3 \ + \ BrMgCH_2 - C \equiv CH$$

$$\text{(I)} \qquad \xrightarrow[2.\ 10\%\,NH_4Cl]{1.\ (C_2H_5)_2O}$$

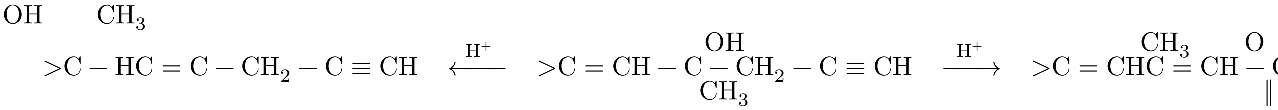
$$(CO)_3Mn\text{-}C_5H_4\text{-}C(CH_3) = CH - C(OH)(CH_3) - CH_2 - C \equiv CH$$

$$\text{(II)}$$

The Grignard reagent, in reactions with enones, usually adds not only in the 1,2-position but also in the 1,4-position. In our case only 1,2-addition is observed. This may be explained by steric hindrance to 1,4-addition arising from the presence of the acetylenic group in the reagent.

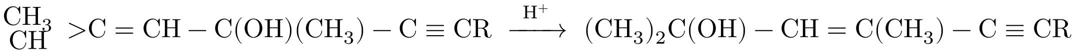
The structure of alcohol (II) was confirmed by its IR spectrum. In the region 3600–3400 cm^{-1} the spectrum contains a doublet of broad bands of medium intensity (3585, 3450 cm^{-1}), characteristic of stretching vibrations of the hydroxyl group with intermolecular hydrogen bonding. The stretching vibrations of $\equiv CH$ give an intense narrow band in the usual spectral region, 3312 cm^{-1}. In addition, the presence of a triple bond is confirmed by a weak band at 2125 cm^{-1}, characteristic of stretching vibrations of the $-C \equiv C-$ group. The frequencies of the stretching vibrations of the terminal carbonyl groups, 2017 and 1930 cm^{-1}, are somewhat lowered relative to unsubstituted cyclopentadienylmanganese tricarbonyl. The presence of a trisubstituted ethylenic group ($R_1R_2C = CHR_3$) is indicated by weak absorption in the region 1680–1650 cm^{-1}.

The anionotropic rearrangement of 4-hydroxy-4-methyl-2-hepten-6-yn-2-cyclopentadienylmanganesetricarbonyl (II) can proceed in two directions: 1) with formation of the isomeric vinylacetylenic alcohol, i.e., by the type of an allylic rearrangement; 2) with formation of a dienone, i.e., by the type of rearrangement of β-acetylenic alcohols into enones that we studied earlier:



$$\begin{array}{l} OH \quad\quad CH_3 \\ \quad >C - HC = C - CH_2 - C \equiv CH \xleftarrow{H^+} >C = CH - \overset{OH}{\underset{CH_3}{C}} - CH_2 - C \equiv CH \xrightarrow{H^+} >C = CH\overset{CH_3}{C} = CH - \overset{O}{} \end{array}$$

It should be noted that in the case of α-acetylenic alcohols with enyne substituents an allylic rearrangement takes place with formation of isomeric vinylacetylenic alcohols (3):



$$\begin{matrix} CH_3 \\ CH \end{matrix} >C = CH - C(OH)(CH_3) - C \equiv CR \xrightarrow{H^+} (CH_3)_2C(OH) - CH = C(CH_3) - C \equiv CR$$

On isomerization of alcohol II under various conditions, 4-methyl-2,4-heptadienon-6-yn-2-cyclopentadienylmanganesetricarbonyl (III) was always obtained:

$$\begin{array}{l} (CO)_3Mn\text{–}(cyclopentadienyl) - C(CH_3) = CH - C(OH)(CH_3) - CH_2 - C \equiv CH \\ \qquad\qquad\qquad (II) \longrightarrow (CO)_3Mn\text{–}(cyclopentadienyl) - C(CH_3) = CH - C(CH_3) = CH - C(= O) - \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (III) \end{array}$$

The isomerization proceeds most readily in alcoholic solution in the presence of mercuric sulfate. When the isomerization is carried out in tetrahydrofuran in the presence of P_2O_5, the yield of the dienone is low as a result of strong resinification. With strong resinification, although less than in the case of P_2O_5, isomerization proceeds when alcohol II is heated in vacuo (10^{-2} mm Hg) in the presence of $KHSO_4$.

Dienone III is a yellow viscous liquid, unstable in air and light. On treatment with an acidic solution of 2,4-dinitrophenylhydrazine, a precipitate of the 2,4-dinitrophenylhydrazone of the dienone is formed. The 2,4-dinitrophenylhydrazone is also formed on treatment of the initial alcohol II with an acidic solution of 2,4-dinitrophenylhydrazine.

The structure of the dienone was also confirmed by IR and UV spectra. In the IR spectrum of the dienone there is no absorption in the region 3640–3400 and 3300 cm^{-1}, characteristic of the stretching vibrations of the $-\mathrm{OH}$ and $\equiv\mathrm{CH}$ groups. The weak absorption at 2125 cm^{-1}, present in the spectrum of alcohol II and characteristic of $-\mathrm{C}\equiv\mathrm{C}-$vibrations, is also absent in the spectrum of the dienone. In the region 1600–1700 cm^{-1} the spectrum contains intense absorption bands—1720–1690, 1600 cm^{-1}—characteristic of the stretching vibrations of conjugated $-\mathrm{C{=}O}-$and $-\mathrm{C{=}C}-$groups.

Figure 1 gives the UV spectra of dienone III and trans-cis-2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl (I). The spectra were recorded in ethyl alcohol in the region 200–500 mμ. As is seen from Fig. 1, in the spectrum of the dienone a bathochromic shift of the λ_{max} $\pi \to \pi^{\#}$ band (300 mμ) by 30 mμ relative to the trans isomer of the enone (270 mμ) (I) is observed. For comparison one may cite the data of Kuhn and Grundmann (4) concerning a bathochromic shift of λ_{max} in carotenoid systems upon addition of one ethylenic bond by 20 mμ. Analogous data on the shift for ferrocene derivatives are given by Schlegel and Eger (5): on going from 1-ferrocenyl-1-propenal to 1-ferrocenyl-1,3-pentadienal, the λ_{max} of the $\pi \to \pi^*$ band shifts by 34 mμ.

In conclusion it should be noted that the hydroxyl group in alcohol II is more mobile than in 2-oxypentin-4-yl-2-cyclopentadienylmanganesetricarbonyl, since the latter, under the given conditions of complete isomerization of alcohol II, is isomerized only by approximately 50–65%.

Experimental Part

4-Oxy-4-methyl-2-hepten-6-yl-2-cyclopentadienylmanganesetricarbonyl. To 2 g (0.08 mole) of magnesium, activated with sublimate, in 25 ml of ethyl ether, 9.6 g (0.081 mole) of propargyl bromide in 15 ml of ethyl ether was added slowly over 30 min. After complete dissolution of the magnesium, over 20 min a solution of 17.20 g (0.06 mole) of 2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl in 40 ml of ethyl ether was added dropwise. The reaction mixture was stirred under reflux for 3 h, after which it was decomposed with a 10% solution of ammonium chloride. The ether extracts were dried over $\mathrm{MgSO_4}$. After removal of the solvent, 18.6 g of a reddish liquid remained, which was distilled twice in vacuum (85–86°—$7 \cdot 10^{-3}$ mm Hg). 16.1 g of a yellow viscous liquid was isolated (81% based on the starting enone); n_d^{20} 1.5945, d_4^{20} 1.2936.

Fig. 1. UV spectra of cis-trans-2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl (1, 2) and 4-methyl-2,4-heptadienon-6-yl-2-cyclopentadienylmanganesetricarbonyl (3). All spectra were recorded in ethyl alcohol.

$C_{16}H_{15}MnO_4$. Found, %: C 58.63, 58.38; H 4.45, 4.52; Mn 16.17, 16.49
Calculated, %: C 58.89; H 4.60; Mn 16.87

The IR spectrum* was recorded on a UR-10 instrument with KBr, NaCl and LiF prisms.
(ν in cm^{-1}): 3585, 3450 s, 3312 s, 3120, 2986 s, 2840, 2125 sl, 2017 s, 1930 s, 1685-1650 sl, 1520 sl, 1480, 1460 s, 1415 s, 1385 s, 1350, 1284 s, 1152, 1120-1070 s, 1045 s, 1000 sl, 960-915, 850 s, 797 sl, 762 sl, 730 s, 660, 534 s, 495 sl.

4-Methyl-2,4-heptadienon-6-yl-2-cyclopentadienylmanganesetricarbonyl. 1) 4 g of alcohol I in the presence of 3 g of $KHSO_4$ was heated in vacuum (10^{-2} mm Hg) for 5 h at 100-120°. The reaction mixture was then distilled in vacuum. After a second distillation (95-96°—$7 \cdot 10^{-3}$ mm Hg), 2.1 g of a thick viscous yellow liquid was isolated (about 50%); n_d^{20} 1.6112, d_4^{20} 1.3030.

2) A mixture of 10 g of alcohol I and 3 g of $HgSO_4$ in 50 ml of absolute ethyl alcohol was stirred with gentle heating for 5 h. The reaction mixture was then filtered from $HgSO_4$, and the filtrate was treated with saturated soda solution. The reaction product was extracted with ethyl ether. The ether extracts were dried over $MgSO_4$. After removal of the solvent, there remained—

9.8 g of a dark-yellow liquid was obtained, which was distilled in vacuo (95-97° —$7 \cdot 10^{-3}$ mm Hg). 8.9 g of a yellow viscous liquid was isolated (89% based on the starting alcohol); n_d^{20} 1.6105; d_4^{20} 1.3030.

Found, %: C 58.87, 59.04; H 4.67, 4.65 Mn 16.42, 16.26
$C_{16}H_{15}MnO_4$. Calculated, %: C 58.89; H 4.60; Mn 16.93

IR spectrum: 3120, 2990 s, 2930 s, 2016 s, 1920 s, 1720-1690 s, 1600 s, 1480 w, 1450-1420, 1385, 1365 s, 1275 w, 1240 w, 1220, 1185 s, 1170, 1115 w, 1070-1020 w, 990 w, 970, 910 w, 890 w, 845 s, 730 s, 710 s, 655 s, 635 s, 540 s, 480 w.

2,4-Dinitrophenylhydrazone—dark-red crystals with m.p. 156°.

Found, %: N 11.43
$C_{22}H_{19}O_7N_4Mn$. Calculated, %: N 11.06

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