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Abstract

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ISOMERIZATION OF 2-HYDROXYPENT-4-YN-2-YL-2-CYCLOPENTADIENYLMANGANESE TRICARBONYL AND 2-HYDROXY-2-PHENYL-(METHYL)-PENT-4-YNE INTO THE CORRESPONDING ENONES

In a preceding communication (^{1}) we described tertiary acetylenic alcohols with a cyclopentadienylmanganese tricarbonyl radical at the hydroxyl-bearing carbon, of the general formula:

$$(\mathrm{CO})_3\mathrm{Mn}\text{—cyclopentadienyl—}\mathrm{C}(\mathrm{OH})(\mathrm{CH}_3)\mathrm{R}$$

where

$$\mathrm{R—C\equiv CH};\quad \mathrm{—CH_2—C\equiv CH};\quad \mathrm{—C\equiv C—C_6H_5};\quad \mathrm{C\equiv C—CH=CH_2}.$$

On heating 2-hydroxypent-4-yn-2-yl-2-cyclopentadienylmanganese tricarbonyl in the presence of potassium bisulfate and magnesium and sodium sulfates, we isolated a crystalline compound with m.p. 60-61°, whose elemental analysis was identical with that of the starting alcohol. However, in the spectrum of this substance the absorption bands of the hydrogen vibrations of the hydroxyl group (3580, 3480 cm^{-1}) and of acetylenic hydrogen (3305 cm^{-1}) were absent, while two strong bands at 1590 and 1680 cm^{-1} were present, characteristic of deformation vibrations of conjugated bonds $\mathrm{—C=C—C=O}$. On treatment of this product with 2,4-dinitrophenylhydrazine, a hydrazone is formed, m.p. 210-212°. Consequently, alcohol I, upon heating in the presence of potassium bisulfate, isomerizes into 2-penten-4-yl-2-cyclopentadienylmanganese tricarbonyl II:

$$\text{(I)}\quad (\mathrm{CO})_3\mathrm{Mn}\text{-cyclopentadienyl-}\mathrm{C(OH)(CH_3)(CH_2C\equiv CH)}\ \xrightarrow{\mathrm{KHSO_4}}\ \text{(II)}\quad (\mathrm{CO})_3\mathrm{Mn}\text{-cyclopentadienyl-}\mathrm{C(C}$$

On heating alcohol I in tetrahydrofuran or benzene solution in the presence of P_2O_5, we isolated a yellow liquid product which rapidly darkens in air (b.p. 60-62°/2-10^{-3} mm, n_D^{20} 1.6070). In the IR spectrum of this product there are absorption bands of conjugated double bonds —C = C— and —C = O (1605 cm^{-1}, 1690 cm^{-1}), and the vibration frequencies of hydrogen in the groups —OH, —C ≡ CH are absent. On treatment with a solution of 2,4-dinitrophenylhydrazine, a raspberry-colored precipitate of the hydrazone was obtained (m.p. 189-195°). On heating in the presence of potassium bisulfate, the liquid product is converted into crystalline isomer II. The same occurs on storage of the liquid isomer without hydrochloric acid.

On the basis of the results obtained, it may be assumed that 2-hydroxypent-4-yn-2-yl-2-cyclopentadienylmanganese tricarbonyl, in the presence of potassium bisulfate and magnesium, sodium, and mercury sulfates, isomerizes into the crystalline isomer–2-penten-4-yl-2-cyclopentadienylmanganese tricarbonyl II, while in the presence of P_2O_5 it isomerizes into the liquid isomer III. More

the stable isomer II is the trans form, and isomer III is the cis form of 2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl:

$$\text{(CO)}_3\text{Mn–cyclopentadienyl–}C(=C(H)COCH_3)(CH_3) \qquad \text{(II)}$$
$$\text{(CO)}_3\text{Mn–cyclopentadienyl–}C(=C(COCH_3)H)(CH_3) \qquad \text{(III)}$$

There are data in the literature indicating that in unsaturated ketones, in cis isomers the frequency of vibration of the carbonyl group is higher by 10-20 cm^{-1} than the vibration frequency in trans isomers (2). In our case, for isomer II (trans) the value of the carbonyl-group vibration frequency is 1680 cm^{-1}, and for the isomer (cis) 1690 cm^{-1}. Since there are no data in the literature on analogous isomeric transformations of β-acetylenic alcohols, we undertook a study of the following two alcohols as model compounds (3)

$$\text{C}_6\text{H}_5-\text{C(OH)(CH}_3)-\text{CH}_2-\text{C}\equiv\text{CH} \qquad \text{(IV)}$$
$$\text{(CH}_3)_2\text{C(OH)}-\text{CH}_2-\text{C}\equiv\text{CH} \qquad \text{(V)}$$

On heating 2-hydroxy-2-phenylpentyne-4 (IV) for 10 hours in the presence of potassium bisulfate, we isolated an isomer of 2-phenyl-2-penten-4-one (b.p. 140°/18 mm; n_D^{20} 1.5660; 2,4-dinitrophenylhydrazone, m.p. 172-174°). This isomer had previously been obtained by M. Julia (4) by isomerization of 4-chloro-2-phenyl-2-penten-3-ol in the presence of sulfuric acid (b.p. 124°/14 mm; n_D^{19} 1.5665; 2,4-dinitrophenylhydrazone, m.p. 172-173°). On prolonged heating of the alcohol with P_2O_5, another isomer of 2-phenyl-2-penten-4-one was isolated (b.p. 128-130°/12 mm; n_D^{20} 1.5468; 2,4-dinitrophenylhydrazone, m.p. 158-160°). Norman and Martin (5) synthesized this isomer by the reaction of 2-phenyl-2-propen-3-magnesium bromide reagent with acetic anhydride (b.p. 130°/12 mm, n_D^{20} 1.5475; 2,4-dinitrophenylhydrazone, m.p. 174°).

Thus, we isolated two forms of 2-phenyl-2-penten-4-one, as in the case of alcohol I. The above-mentioned authors isolated only one form, without determining the configurations of the isomers.

The isomerization of 2-hydroxy-2-methylpentyne-4 was carried out in the presence of $KHSO_4$ for 20 hours. As a result, 2-methyl-2-penten-4-one (mesityl oxide) was isolated, with b.p. 130-132°, n_D^{20} 1.4450; 2,4-dinitrophenylhydrazone, m.p. 200-202°. Literature data: b.p. 129-130°, n_D^{20} 1.444; n_D^{19} 1.447; 2,4-dinitrophenylhydrazone, m.p. 200° and 204°. Isomerization of alcohols I, IV, V also occurs under the action of an acidified solution of 2,4-dinitrophenylhydrazine in ethyl alcohol, the vinyl ketones formed immediately reacting with 2,4-dinitrophenylhydrazine. The indicated phenomenon was previously observed by Henbest et al. (6) using alcohol IV as an example. The authors explained hydrazone formation by a hydration and dehydration reaction of the alcohol, without isolating the corresponding enone.

The isomerization of these alcohols proceeds at different rates: fastest of all isomerizes 2-hydroxypentyne-4-yl-2-cyclopentadienylmanganesetricarbonyl, more slowly 2-hydroxy-2-phenylpentyne-4, and very slowly 2-hydroxy-2-methylpentyne-4.

Experimental Section

For the study we used carefully redistilled 2-hydroxypentyne-4-yl-2-cyclopentadienylmanganesetricarbonyl (n_D^{20} 1.5850; d_4^{20} 1.3635, b.p. 40°/10^{-4} mm (1)).

IR spectrum* (ν in cm^{-1})**: 3580 (medium), 3480 (medium), 3305 (strong), 3110 (medium), 2990 (medium), 2920 (weak), 2015 (strong), 1925 (strong), 1460 (weak), 1415 (weak), 1385 (medium), 1345 (weak), 1285 (weak), 1235 (weak), 1115 (medium), 1095 (medium), 955 (weak), 845 (medium), 730 (strong), 675 (strong), 635 (strong), 540 (strong).

Isomerization of 2-oxypentyn-4-yl-2-cyclopentadienylmanganesetricarbonyl to trans-2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl

5 g of the carbinol were heated in vacuo ($4—5 \cdot 10^{-3}$ mm) with

[structural formula of the trans-enone complex: $(CO)_3$Mn-cyclopentadienyl-$C(CH_3) = C(H)COCH_3$]

0.5 g of $KHSO_4$ for 1 hour. The reaction mixture was washed twice with ether, neutralized with soda solution, dried over $MgSO_4$, and then the solvent was removed in vacuo. The residue was recrystallized from petroleum ether. 4 g of yellow crystals were obtained (80%), m.p. 60—62°.

Found, %: C 54.52, 54.29; H 3.98, 3.75; Mn 18.73, 19.01
$C_{13}H_{11}O_4Mn$. Calculated, %: C 54.54; H 3.85; Mn 19.24

IR spectrum (ν in cm^{-1}): 3120 (weak), 3090 (weak), 2930 (medium), 2860 (medium), 2015 (strong), 1930 (strong), 1675 (strong), 1595 (strong), 1475 (medium), 1425 (medium), 1370 (medium), 1230 (weak), 1190 (strong), 1120 (weak), 1070 (weak), 1055 (medium), 1020 (weak), 970 (medium), 945 (weak), 920 (weak), 910 (medium), 870 (medium), 840 (strong), 720 (weak), 750 (strong), 700 (strong), 640 (strong), 560 (weak), 535 (strong).

2,4-Dinitrophenylhydrazone, m.p. 210–212°.

Found, %: C 48.62, 48.82; H 3.27, 3.45; Mn 11.59, 11.63; N 12.34, 12.26
$C_{19}H_{15}O_8MnN_4$. Calculated, %: C 48.92; H 3.32; Mn 11.80; N 12.06

Isomerization of 2-oxypentyn-4-yl-2-cyclopentadienylmanganesetricarbonyl to cis-2-pentenon-4-yl-2-cyclopentadienylmanganesetricarbonyl

[structural formula of the cis-enone complex: $(CO)_3Mn$-cyclopentadienyl-$C(CH_3) = C(COCH_3)(H)$]

10 g of the carbinol were dissolved in 50 ml of tetrahydrofuran, and 2 g of phosphorus anhydride were added. The reaction mixture was heated at reflux for 5 h, then filtered from the phosphorus anhydride and passed through a column with Al_2O_3, eluting with petroleum ether : acetone solution (4 : 1). After distillation in vacuo (61—62°/2—4 $\cdot 10^{-3}$ mm), 4 g of a yellow, rapidly darkening liquid were obtained (yield 40%). n_D^{20} 1.6070.

Found, %: C 54.57, 54.71; H 3.61, 3.85; Mn 19.50, 19.35
$C_{13}H_{11}O_4Mn$. Calculated, %: C 54.54; H 3.85; Mn 19.24

IR spectrum (ν in cm^{-1}): 3120 (medium), 2035 (strong), 1945 (strong), 1690 (strong), 1650 (medium), 1520 (weak), 1470 (medium), 1425 (medium), 1385 (medium), 1370 (medium), 1290 (strong), 1190 (weak), 1125 (medium), 1050 (weak), 1030 (weak), 970 (weak), 855 (medium), 780 (medium), 720 (medium), 660 (strong), 640 (strong), 540 (strong).

2,4-Dinitrophenylhydrazone, m.p. 189–195°.

Found, %: N 12.25, 12.26
$C_{19}H_{15}O_8MnN_4$. Calculated, %: N 12.01

Isomerization of 2-oxy-2-phenylpentyn-4 to 2-phenyl-2-pentenon-4 in the presence of $KHSO_4$

10 g of the alcohol heated with 5 g of $KHSO_4$ for 10 h. The reaction mixture was then washed with soda solution and extracted with ether. All ether extracts were dried over $MgSO_4$. After removal of the solvent, the residue was distilled in vacuo

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* The IR spectra were taken by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.
** Abbreviations: strong –strong, medium –medium, weak –weak.

(2–$4 \cdot 10^{-3}$ mm), giving 8 g of a light-colored liquid (yield 80%). The product was redistilled at b.p. 140°/18 mm; n_D^{20} 1.5660 (lit.: b.p. 124°/11 mm; n_D^{20} 1.5655 (^{4})).

Found, %:	C 82.69, 82.79;	H 7.40, 7.39
$C_{11}H_{12}O$. Calculated, %:	C 82.50;	H 7.50

2,4-Dinitrophenylhydrazone, m.p. 172° (lit.: m.p. 174° (^{4})).

Found, %:	N 16.42, 16.47
$C_{17}H_{16}O_5N_4$. Calculated, %:	N 16.47

Isomerization of 2-hydroxy-2-phenylpentyn-4 to 2-phenyl-2-penten-4-one in the presence of P_2O_5

10 g of the alcohol were heated with 2 g of P_2O_5 for 10 h in the presence of hydroquinone. The reaction product was extracted with ether and immediately passed through an Al_2O_3 column. After removal of the solvent, the residue was distilled in vacuo at 28–30°/2–$4 \cdot 10^{-3}$ mm. It was redistilled at 128–130°/12 mm. 5.7 g of a light-colored liquid product were obtained (yield 57%). n_D^{20} 1.5468 (lit. n_D^{19} 1.5475; b.p. 130°/12 mm (^{5})).

Found, %:	C 82.54, 82.70;	H 7.47, 7.46
$C_{11}H_{12}O$. Calculated, %:	C 82.50;	H 7.50

2,4-Dinitrophenylhydrazone, m.p. 158–160°.

Found, %:	N 16.26, 16.40
$C_{17}H_{16}O_5N_4$. Calculated, %:	N 16.47

Isomerization of 2-hydroxy-2-methylpentyn-4 to 2-methyl-2-penten-4-one

10 g of the alcohol were heated for 20 h over 5 g of $KHSO_4$. The following fractions were isolated: 1) b.p. 124–126°, n_D^{20} 1.4377—2 g—starting alcohol, 2) b.p. 130–132°, n_D^{20} 1.4450—2 g—mesityl oxide (yield 20%). Lit.: n_D^{20} 1.4440; b.p. 129–130°.

Found, %:	C 73.54, 73.38;	H 10.16, 10.06
$C_6H_{10}O$. Calculated, %:	C 73.46;	H 10.20

2,4-Dinitrophenylhydrazone, m.p. 200–202° (lit.: m.p. 200° and 204°).

Found, %:	N 22.01, 22.67
$C_{11}H_{14}O_5N_4$. Calculated, %:	N 20.15

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Note: Figure translations are in progress. See original paper for figures.