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Abstract

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ISOMERIZATION OF TERTIARY β-ACETYLENIC ALCOHOLS, DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL AND FERROCENE

Earlier we (^{1}) carried out the isomerization of tertiary β-acetylenic alcohols

$(CO)_3Mn\text{–}Cp\text{–}\ C(OH)(CH_3)(CH_2C \equiv CH)$ (I) $\quad C_6H_5C(OH)(CH_3)(CH_2C \equiv CH)$ (II) $\quad (CH_3)_2C(OH)(CH_2C \equiv CH$ (III)

to enones on heating in vacuum (10^{-2}—10^{-3} mm Hg) in the presence of $KHSO_4$, and also in tetrahydrofuran solution in the presence of P_2O_5. It is obvious that the isomerization of the indicated tertiary β-acetylenic alcohols to enones in anhydrous solvents, as well as on heating in vacuum (10^{-2}—10^{-3} mm Hg) in the presence of $KHSO_4$, is an intramolecular anionotropic rearrangement.

We have continued the study of the isomerization of tertiary β-acetylenic alcohols with new β-acetylenic alcohols containing ferrocenyl and cyclopentadienylmanganese tricarbonyl as substituents:

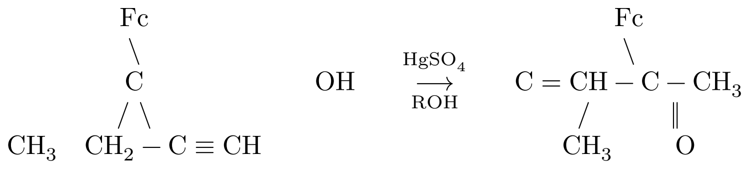
$Fc\,C(OH)(CH_3)(CH_2C \equiv CH)$ (IV) $\quad (CO)_3Mn\text{–}Cp\text{–}\ C(OH)(C_2H_5)(CH_2C \equiv CH)$ (V) $\quad (CO)_3Mn\text{–}Cp\text{–}\ C(OH)(C_6H_5$ (VI)

$$Fc = C_5H_5 - Fe - C_5H_4 -$$

The alcohols were obtained by the Grignard reaction in high yields (see Table 1). The IR spectra of the alcohols contain characteristic vibrational frequencies of the groups:

$-OH$	IV 3560, 3470;	V 3600, 3460;	VI 3565
$-C \equiv CH$	3300;	3316;	3285 cm^{-1}.

Since, in electron-donor capacity, ferrocenyl considerably exceeds the cyclopentadienylmanganese tricarbonyl residue, one should expect greater mobility of the hydroxyl group in 2-ferrocenylpentin-4-ol-2 (IV) than in alcohol (I). Indeed, 2-ferrocenylpentin-4-ol-2 (IV) isomerizes to 2-ferrocenylpentene-2-one-4 (VII) in ethyl alcohol in the presence of mercury sulfate over the course of 5 hours without heating:



(IV) (VII)

Table 1

Compound	b.p., °C (mm Hg)	m.p., °C	n_d^{20}	d_4^{20}	Found, % C	Found, % H	Found, % Mn	Found, % Fe	Found, % N	Calculated, % C	Calculated, % H	Calculated, % Mn	Calculated, % Fe	Calculated, % N	Yield, %	Isomerization conditions
$C_5H_5FeC_5H_4C(OH)(CH_3)CH_2C\equiv CH$	92–95(6·10^{-3})	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20,39, 20,50	—	67,16	5,93	—	20,89	—	82	—
$(CO)_3MnC_5H_4C(OH)(CH_3)CH_2C\equiv CH$	65–67(6·10^{-3})	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible], 18,56	—	—	56,00	4,33	18,13	—	—	85	—
$(CO)_3MnC_5H_4C(OH)(C_6H_5)CH_2C\equiv CH$	—	84–85	[illegible]	[illegible]	[illegible]	[illegible]	[illegible], 15,70	—	—	62,06	3,75	15,80	—	—	66	—
$C_5H_5FeC_5H_4C(CH_3)=CH-CO-CH_3$	—	89–90	—	—	[illegible]	[illegible]	—	20,81, 20,72	—	67,16	5,93	—	20,89	—	95	Ethyl alcohol, $HgSO_4$, 5 h, room temperature

Compound	b.p., °C (mm Hg)	m.p., °C	n_d^{20}	d_4^{20}	Found, % C	Found, % H	Found, % Mn	Found, % Fe	Found, % N	Calculated, % C	Calculated, % H	Calculated, % Mn	Calculated, % Fe	Calculated, % N	Yield, %	Isomerization conditions
2,4-Dinitrophenylhydrazone	—	150	—	—	—	—	—	—	12,85	13,08	—	—	—	12,50	—	—
$(CO)_3MnC_5H_4-C(C_2H_5)=CH-CO-CH_3$		69			[illegible]	[illegible]	[illegible]	—		56,00	4,33	18,33	—	—	96	Ethyl alcohol, boiling, $HgSO_4$, 20 h
2,4-Dinitrophenylhydrazone	—	205	—	—	—	—	—	—	11,72	11,63	—	—	—	11,66	—	—
$(CO)_3MnC_5H_4-C(C_6H_5)=CH-CO-CH_3$		73—74			[illegible]	[illegible]	[illegible]	—		62,06	3,73	15,80	—	—	93	Ethyl alcohol, 40—50°, $HgSO_4$, 7 h
2,4-Dinitrophenylhydrazone	—	201—203	—	—	—	—	—	—	16,42	16,38	—	—	—	16,47	—	—
$(CO)_3MnC_5H_4-C(OH)(C_6H_5)-CH_2-CO-CH_3$		97			[illegible]	[illegible]	[illegible]	—		59,01	4,09	15,02	—	—	92	Aqueous ethyl alcohol, room temperature, $HgSO_4$, 5 h

The isomerization proceeds completely and without resinification: the melting points of the crude and recrystallized products are identical (89-90°). 2-Oxypentyn-4-yl-2-cyclopentadienylmanganesetricarbonyl (I), under analogous conditions, isomerizes only by 25-30%. The IR spectrum of 2-ferrocenylpenten-2-one-4 (VII) contains no bands characteristic of stretching vibrations of the –OH and –C CH groups; however, in the region 1600-1700 cm^{-1} there are two strong bands (1599, 1678 cm^{-1}), characteristic of stretching vibrations of conjugated –C=C–and C=O groups.

$$\text{(V)}\quad (CO)_3Mn\text{—cyclopentadienyl—}C(OH)(C_2H_5)(CH_2\text{—}C{\equiv}CH) \xrightarrow[\text{ROH}]{\text{HgSO}_4} (CO)_3Mn\text{—cyclopentadienyl—}C(C_2H$$

The isomerization of 3-oxyhexyn-5-yl-3-cyclopentadienylmanganesetricarbonyl (V) proceeds under more severe conditions than in the case of alcohol (I). Thus, when alcohol (V) is boiled in vacuo in the presence of $KHSO_4$, isomerization proceeds only by 40-50%. With quantitative yield, isomerization of this alcohol proceeds on boiling it in ethyl alcohol in the presence of $HgSO_4$ for 20 h. The IR spectrum of enone (VIII) contains bands of stretching vibrations of the –C=C–and C=O groups (1590, 1682 cm^{-1}). Absorption in the region 3300-3600 cm^{-1} is absent.

The isomerization of 1-oxy-1-phenylbutyn-3-yl-1-cyclopentadienylmanganesetricarbonyl (VI) occurs on gentle heating in the presence of $HgSO_4$ in absolute ethyl alcohol. When the reaction is carried out in aqueous ethyl alcohol under the same conditions, hydration of the triple bond of alcohol (VI) occurs, with formation of the keto alcohol (X)–1-oxy-1-phenylbutanone-3-yl-1-cyclopentadienylmanganesetricarbonyl.

Thus, 1-butenone-3-yl-1-cyclopentadienylmanganesetricarbonyl (IX) was obtained both by isomerization of alcohol (VI) in anhydrous alcohol and by dehydration of keto alcohol (X) with 50% sulfuric acid:

$$(CO)_3Mn\text{—cyclopentadienyl—}C(OH)(C_6H_5)(CH_2\text{—}C{\equiv}CH)\quad \text{(VI)} \xrightarrow[C_2H_5OH\ (\text{abs}\cdot)]{\text{HgSO}_4} (CO)_3Mn\text{—cyclopentadienyl—}$$

$$(CO)_3Mn\text{—cyclopentadienyl—}C(OH)(C_6H_5)(CH_2\text{—}C{\equiv}CH)\quad \text{(VI)} \xrightarrow[C_2H_5OH{+}H_2O]{\text{HgSO}_4} (CO)_3Mn\text{—cyclopentadienyl—}$$

The IR spectrum of keto alcohol (X) contains bands of stretching vibrations of the C=O and –OH groups (1710, 3420 cm^{-1}). Absorption is absent in the regions 3300 and 1600 cm^{-1}, characteristic of stretching vibrations of the –C CH and –C=C–groups.

The IR spectrum of enone (IX) contains bands of stretching vibrations of conjugated –C=C–and C=O bonds (1596, 1615, 1660 cm^{-1}). Absorption in the region 3300-3600 cm^{-1} is absent.

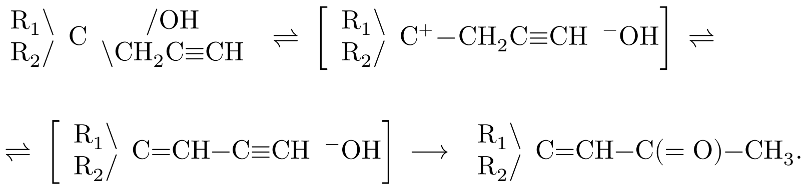
Hydration of the triple bond in aqueous solvents proceeds only for alcohol (VI); the remaining alcohols (I–V), both in aqueous solvents,

both in wet and in dry solvents give, in the presence of $HgSO_4$, only enones. The latter, in addition to their IR spectra, were also identified by formation of 2,4-dinitrophenylhydrazones (see Table 1). The 2,4-dinitrophenylhydrazones of the corresponding enones are also formed upon the action on the alcohols (IV–VI) and the keto alcohol (X) of a sulfuric-acid solution of 2,4-dinitrophenylhydrazine.

The isomerization of the β-acetylenic alcohols examined depends on the solvent in which the reaction is carried out. With an increase in the ionizing power of the solvent, the rate and completeness of the isomerization increase. Thus alcohol (I) isomerizes in tetrahydrofuran in the presence of $HgSO_4$ (on boiling) by only 10%, whereas in ethyl alcohol it isomerizes completely. Moreover, as has already been shown, the rate and completeness of isomerization in one and the same solvent depend on the electron-donor ability of the substituents at the hydroxyl-bearing carbon atom. The mobility of the hydroxyl group decreases in the following series of substituents:

$$C_5H_5FeC_5H_4 \longrightarrow (CO)_3MnC_5H_4 \longrightarrow C_6H_5 \gg -CH_3.$$

On the basis of these facts, it may be assumed that the isomerization of tertiary β-acetylenic alcohols is an anionotropic rearrangement, the first stage of which is heterolysis of the C–OH bond with formation of a carbonium ion. When the isomerization is carried out in dry solvents and upon heating with $KHSO_4$ in vacuo (10^{-2}-10^{-3} mm Hg), an intramolecular rearrangement probably occurs through the intermediate formation of an ion pair:



$$\begin{array}{l}R_1\backslash\\ R_2/\end{array} C \begin{array}{l}/OH\\ \backslash CH_2C\equiv CH\end{array} \rightleftharpoons \left[\begin{array}{l}R_1\backslash\\ R_2/\end{array} C^+{-}CH_2C\equiv CH\ {}^-OH\right] \rightleftharpoons$$

$$\rightleftharpoons \left[\begin{array}{l}R_1\backslash\\ R_2/\end{array} C{=}CH{-}C\equiv CH\ {}^-OH\right] \longrightarrow \begin{array}{l}R_1\backslash\\ R_2/\end{array} C{=}CH{-}C({=}\,O){-}CH_3.$$

The catalysts evidently affect only the first stage, the heterolysis of the –C–OH bond.

The IR spectra were recorded by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude. A detailed discussion of the IR and UV spectra will be given in the following communication.

Experimental Part

1. Preparation of alcohols. To a solution of $BrMgCH_2{-}C\ CH$ in ethyl ether, 10 g of the corresponding ketone in 20 ml of ethyl ether was added slowly. The reaction mixture was stirred for 3 h with gentle heating. After decomposition of the reaction mixture with a 10% solution of NH_4Cl, the reaction products were extracted with ethyl ether. After removal of the solvent, the residue was distilled in vacuo ($6\text{-}7 \cdot 10^{-3}$ mm Hg) in the case of alcohols (IV-V), or recrystallized from heptane (alcohol VI).

2. Isomerization of alcohols. 10 g of alcohol was dissolved in 50 ml of abs. ethyl alcohol and 3 g of $HgSO_4$ was added. The enones—the products of isomerization of the alcohols—were recrystallized from heptane. The keto alcohol (X) was obtained under the same conditions, only using 95% ethyl alcohol. Dehydration of the keto alcohol was carried out by heating with 50% sulfuric acid. The constants and results of elemental analysis are given in Table 1.

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References

[1] A. N. Nesmeyanov, K. N. Anisimov et al., DAN, **158**, 163 (1964).

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

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