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Abstract

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REACTION OF KETONES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL WITH NORMANT' S REAGENT

In the present work, which is a continuation of our investigations ([1], [2]) in the field of studying the chemical properties of derivatives of cyclopentadienylmanganese tricarbonyl, we have described the reaction of ketones of cyclopentadienylmanganese tricarbonyl with Normant' s reagent.

Under the action of vinylmagnesium bromide on acetyl-, benzoyl-, and *p*-toluylcyclopentadienylmanganese tricarbonyl in tetrahydrofuran, the corresponding tertiary alcohols were isolated in yields of 46–95%: 2-hydroxybuten-3-yl-2-cyclopentadienylmanganese tricarbonyl, 1-hydroxy-1-phenylpropen-2-yl-1-cyclopentadienylmanganese tricarbonyl, and 1-hydroxy-1-tolylpropen-2-yl-1-cyclopentadienylmanganese tricarbonyl. The compounds obtained are readily soluble in benzene, ethyl ether, and methyl and ethyl alcohols, and less readily soluble in petroleum ether.

For the dehydration of 2-hydroxybuten-3-yl-2-cyclopentadienylmanganese tricarbonyl, Al_2O_3, P_2O_5, and $KHSO_4$ were used. However, it proved impossible to isolate the monomer—divinylcyclopentadienylmanganese tricarbonyl—because of its rapid polymerization. Therefore we attempted to demonstrate indirectly the presence of the divinyl derivative of cyclopentadienylmanganese tricarbonyl by carrying out a diene-synthesis reaction. For this purpose we used maleic anhydride, which at the same time served as a dehydrating agent and a dienophile ([3]). As a result of the reaction carried out between 2-hydroxybuten-3-yl-2-cyclopentadienylmanganese tricarbonyl and maleic anhydride, an adduct was isolated with m.p. 194–195°, readily soluble in tetrahydrofuran and dioxane, and poorly soluble in ethyl alcohol and water.

In the i.r. spectrum of this adduct, the following characteristic vibration frequencies were found*:

$$\text{CH (in cyclopentadiene)—3110 cm}^{-1}; \quad (\text{CO})_3\text{Mn—2020, 1960, and 1930 cm}^{-1};$$

$$> C{=}CH\text{—1662 cm}^{-1}; \quad -\text{CO}_2\text{H—1720, 1440, and 1320 cm}^{-1}.$$

Fig. 1

Figure 1: Fig. 1

Upon potentiometric titration of the adduct in dioxane–methyl alcohol medium (1 : 1) with a methanolic solution of tetraethylammonium hydroxide (^{4}), results were obtained confirming the formation of a dibasic acid.

Analysis, the i.r. spectrum, and potentiometric titration of the adduct allow us to suppose that the reaction between maleic anhydride and 2-hydroxybuten-3-yl-2-cyclopentadienylmanganese tricarbonyl proceeded normally, with formation of a compound of the following structure:

cyclopentadienyl–Mn$(CO)_3$ substituted by a cyclohexene dicarboxylic acid fragment:

$$CpMn(CO)_3{-}C(=CH{-}){-}CH_2{-}CH(COOH){-}CH(COOH){-}CH_2$$

* The i.r. spectra were measured by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.

Experimental Part

1. 2-Oxobut-3-yl-2-cyclopentadienylmanganesetricarbonyl. In a four-necked flask equipped with a stirrer with a mercury seal, a condenser, a dropping funnel, and a nitrogen inlet, to 1.1 g (0.046 mole) of Mg with a crystal of iodine in 10 ml of tetrahydrofuran was added a solution of 4.9 g (0.046 mole) of freshly distilled vinyl bromide in 10 ml of tetrahydrofuran at 30–45°. After the complete disappearance of Mg (1.5 hours), to the organomagnesium compound, with cooling, was added 9 g (0.038 mole) of $CH_3COC_5H_4Mn(CO)_3$ dissolved in a mixture of 15 ml of ether and 20 ml of tetrahydrofuran. After stirring and heating the mixture to 40–45° for 3 hours, 30 ml of ether was added; the complex that precipitated as a gray solid was filtered off, washed with ether, and decomposed under cooling with 10% NH_4Cl. The oil that separated was extracted with ether, dried over Na_2SO_4, and, after removal of the ether, distilled in a high vacuum. 6 g (60%) of a light-yellow oil was obtained, with $n_D^{20} = 1.5872$ and $d_4^{20} = 1.3663$.

Fig. 1

Found, %:	C 52.30, 52.51; H 4.07, 4.05; Mn 19.83, 19.95
$C_{12}H_{11}O_4Mn$. Calculated, %:	C 52.55; H 4.01; Mn 20.07

2. 1-Oxo-1-phenylpropen-2-yl-1-cyclopentadienylmanganesetricarbonyl. In the apparatus described in item 1, to 1.07 g (0.044 mole) of Mg with a crystal of iodine in 20 ml of tetrahydrofuran was added a solution of 4.8 g (0.044 mole) of freshly distilled vinyl bromide in 10 ml of tetrahydrofuran at 30-45°. After dissolution of Mg (1.5 hours), with cooling, a solution of 11.7 g (0.037 mole) of $C_6H_5COC_5H_4Mn(CO)_3$ in a mixture of 25 ml of ether and 25 ml of tetrahydrofuran was added. After heating with stirring for 3 hours, the reaction mixture was decomposed under cooling with 10% NH_4Cl. Distillation in a high vacuum afforded 6.4 g (50%) of a light-yellow viscous oil with $n_D^{20} = 1.6280$, $d_4^{20} = 1.3657$.

Found, %: C 60.67; H 3.84; Mn 15.30
$C_{17}H_{13}O_4Mn$. Calculated, %: C 60.71; H 3.87; Mn 16.35

3. 1-Oxo-1-*p*-tolylpropen-2-yl-1-cyclopentadienylmanganesetricarbonyl. In the apparatus described in item 1, under the conditions indicated above, a reaction was carried out between 0.97 g (0.04 m) of Mg, 4.34 g (0.04 mole) of vinyl bromide, and 11.1 g (0.036 mole) of p-$CH_3C_6H_4COC_5H_4Mn(CO)_3$ in a mixture of 50 ml of tetrahydrofuran and 25 ml of ether. After decomposition of the reaction mixture with 10% NH_4Cl, 11.7 g (92%) of crystalline product was isolated, m.p. 85-86° (from petroleum ether).

Found, %: C 61.35, 61.10; H 4.28, 4.30; Mn 15.63, 15.70
$C_{18}H_{15}O_4Mn$. Calculated, %: C 61.71; H 4.28; Mn 15.71

4. Interaction of 2-oxobut-3-yl-2-cyclopentadienylmanganesetricarbonyl with maleic anhydride. 4.5 g (0.016 mole) of 2-oxobut-3-yl-2-cyclopentadienylmanganesetricarbonyl, 1.61 g (0.016 mole) of maleic anhydride, and 0.01 g of hydroquinone in 5 ml of benzene were heated in a sealed ampoule

at 110-140° for 4 hours. After the ampoule was opened, the light-yellow crystalline precipitate was filtered off and washed with benzene and ether. Yield of crystalline product: 2.7 g (46%); m.p. 194-195°.

Found, %: C 51.40, 51.62; H 3.41, 3.40; Mn 14.25, 14.46
$C_{16}H_{13}O_6Mn$. Calculated, %: C 51.61; H 3.49; Mn 14.78
IR spectrum (ν, cm^{-1}) (paste in Vaseline oil): 538 (m), 554 (m), 607 (w), 635 (s), 655 (m), 672 (s), 725 (s), 778 (m), 790 (m), 843 (m), 860 (m), 923 (m), 965 (m), 990 (m), 1043 (m), 1145 (w), 1180 (m), 1233 (s), 1260 (s), 1290 (m), 1320 (m), 1355 (m), 1380 (m), 1425 (m), 1440 (m), 1470 (m), 1662 (m), 1720 (s), 1930 (s), 1960 (s), 2020 (s), 2600-2700 (m), 2860 (s), 2930 (s), 3110 (m).

Potentiometric titration of the adduct was carried out on an LP-58 potentiometer in a dioxane-methanol (1:1) medium with a methanolic solution of tetraethylammonium hydroxide. The titration curve is shown in Fig. 1.

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