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reaction scheme: transformations of chloromethylcyclopentadienylmanganese tricarbonyl (I) into phthalimidomethyl derivative (II), aminomethyl derivative (III), acetoxymethyl derivative (IV), formyl derivative (V), and related acylated, reduced, and condensation products; reagents shown include $(NH_2) \cdot H_2O$, HCl (gas), $(CH_3CO)_2O$, C_6H_5COCl, $C_6H_4(CO)_2NK$, $(CH_2)_6N_4$, CH_3COONa, CH_3OH (CH_3ONa), $LiAlH_4$, NH_4OH, CH_3ONa, and $(CO)_3MnC_5H_4CH_2NH_2$

Figure 1: reaction scheme: transformations of chloromethylcyclopentadienylmanganese tricarbonyl (I) into phthalimidomethyl derivative (II), aminomethyl derivative (III), acetoxymethyl derivative (IV), formyl derivative (V), and related acylated, reduced, and condensation products; reagents shown include $(NH_2) \cdot H_2O$, HCl (gas), $(CH_3CO)_2O$, C_6H_5COCl, $C_6H_4(CO)_2NK$, $(CH_2)_6N_4$, CH_3COONa, CH_3OH (CH_3ONa), $LiAlH_4$, NH_4OH, CH_3ONa, and $(CO)_3MnC_5H_4CH_2NH_2$

Abstract

Full Text

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REACTIONS OF CHLOROMETHYLCYCLOPENTADIENYLMANGANESE TRICARBONYL WITH CERTAIN NUCLEOPHILIC REAGENTS

In a previous communication ([1]) it was shown that chloromethylcyclopentadienylmanganese tricarbonyl (I) reacts smoothly with sodium alcoholates to form simple ethers. In the present article we describe the reactions of I with sodium acetate, potassium phthalimide, and urotropine.

From N-methylcyclopentadienylmanganese tricarbonyl phthalimide (II), treatment with hydrazine hydrate gave aminomethylcyclopentadienylmanganese tricarbonyl (III), which on acylation was converted into N-acetyl- and N-benzoylaminomethylcyclopentadienylmanganese tricarbonyl. The hydrochloride of the amine was obtained. The acetoxymethylcyclopentadienylmanganese tricarbonyl (IV) isolated by the action of sodium acetate on I was saponified to oxymethylcyclopentadienylmanganese tricarbonyl. Formylcyclopentadienylmanganese tricarbonyl had previously been obtained ([2–4]) from

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chloroformylcyclopentadienylmanganese tricarbonyl and $Li(C_4H_9\text{-tert.O})_3AlH$, and was characterized as a red oil ([2]) and as a low-melting substance ([4]), without analysis of the compound obtained. The aldehyde (V) obtained by us has m.p. 74–75° and in reactions exhibits the typical properties of aromatic aldehydes. The aldehyde, in the presence of catalytic additives of sodium methylate, is converted into the alcohol and the acid; with ammonia it forms an analog of hyd-

rhodanamide, reacts with aminomethylcyclopentadienylmanganese tricarbonyl with formation of a Schiff base, and can be reduced by $LiAlH_4$ to the alcohol.

IR spectra* were recorded for the compounds listed below. For these compounds we give the frequencies characterizing the functional groups (ν, cm^{-1}): $(CO)_3MnC_5H_4CH_2NH_2$ 1604 (medium), 3314 (medium), $(CO)_3MnC_5H_4CH_2OCOCH_3$ 1729 (strong), $(CO)_3MnC_5H_4CH_2OH$ 1004 (strong), 3609 (medium), $(CO)_3MnC_5H_4CHO$ 1670 (strong), 1691 (strong), $(CO)_3MnC_5H_4COOH$ 927 (strong), 934 (strong), 1669–1692 (strong).

Experimental Part

N-Methylcyclopentadienylmanganese tricarbonyl phthalimide. A mixture of 20.4 g (0.08 mole) of I and 13.3 g (0.072 mole) of potassium phthalimide in 25 ml of dimethylformamide was heated with stirring and maintained at 120° for 6 h. The cooled mixture was poured into 250 ml of water and filtered. The material on the filter was washed with 10 ml of acetic acid and recrystallized from 50 ml of acetic acid. This gave 10.58 g (40.4%) of light-yellow crystals, mp 169–171°, soluble in ether, ethyl alcohol, acetic acid, and chloroform.

Found, %: C 56.46; 56.38; H 2.98; 3.08; N 3.99; 4.02
$C_{17}H_{10}O_5NMn$. Calculated, %: C 56.21; H 2.78; N 3.86;

Aminomethylcyclopentadienylmanganese tricarbonyl. To a suspension of 16.45 g (0.045 mole) of II in 50 ml of ethyl alcohol, 11.5 g (0.23 mole) of hydrazine hydrate was added with stirring, and the mixture was heated to 80°; a solution formed, and then after 5 min a colorless precipitate separated. After 15 min, 25 ml of conc. hydrochloric acid was added and the mixture was heated for another 10 min. The cooled mixture was filtered, the precipitate was washed with water; the filtrate was poured into 200 ml of water, neutralized with 10% alkali solution to alkaline reaction, and extracted with 200 ml of ether; the ethereal solution was washed with water, dried over $MgSO_4$, the ether was distilled off, and the residue was distilled in vacuo. This gave 5.62 g (53.2%) of a yellow-green liquid, bp 37–38°/$2 \cdot 10^{-2}$ mm Hg, n_D^{20} 1.6085, d_4^{20} 1.4358. The amine dissolves in organic solvents.

Found, %: C 46.09; 45.97; H 3.43; 3.49; N 6.37; 6.55; Mn 23.24; 23.37
$C_9H_8O_3NMn$. Calculated, %: C 46.37; H 3.47; N 6.01; Mn 23.56

Aminomethylcyclopentadienylmanganese tricarbonyl hydrochloride was obtained by saturating an ethereal solution of III with dry gaseous

hydrogen chloride. The light-cream-colored crystals are insoluble in petroleum ether, benzene, and ether, and soluble in ethyl alcohol; mp 190–195° (darkening without change of crystalline state up to 230°).

Found, %: Cl 13.63; 13.24
$C_9H_9O_3NClMn$. Calculated, %: Cl 13.17

N-Acetylaminomethylcyclopentadienylmanganese tricarbonyl. In a test tube, to 0.6 g (0.00258 mole) of III were added 1 ml of pyridine and 0.27 g (0.0026 mole) of acetic anhydride. The mixture was left at room temperature for 24 h. The mixture was then diluted with water and extracted with ether; the ethereal solution was washed with water, 10% sulfuric acid, and again with water, dried over $MgSO_4$, and evaporated. This gave 0.58 g (81.6%) of light-yellow crystals, mp 88–89°.

Found, %: C 48.23; 48.35; H 3.84; 3.85; N 5.02; 5.15; Mn 19.44; 19.36
$C_{11}H_{10}O_4NMn$. Calculated, %: C 48.01; H 3.67; N 5.10; Mn 19.96

* The IR spectral measurements were carried out by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.

N-Benzoylaminomethylcyclopentadienylmanganese tricarbonyl. To a solution, cooled with ice water, of 1.5 g (0.0065 mole) of III in 10 ml of benzene and 4 ml of pyridine, with stirring, 1 g (0.007 mole) of benzoyl chloride was added. The mixture was heated at 80° for one hour, diluted with water, and extracted with ether. The organic layer was washed with water, with 10% sulfuric acid, and once more with water, dried over $MgSO_4$, and evaporated; the residue consisted of light-cream crystals, m.p. 99–104°; after recrystallization from ether, m.p. 112–113°; yield quantitative.

Found, %: C 56.96; 57.11; H 3.71; 3.71; N 4.25; 4.14
Mn 15.89; 15.85
$C_{16}H_{12}O_4NMn$. Calculated, %: C 56.99; H 3.59; N 4.15;
Mn 16.29

Acetoxymethylcyclopentadienylmanganese tricarbonyl. To a hot solution of 6.9 g (0.084 mole) of anhydrous sodium acetate in 10 ml of acetic acid, with stirring, a solution of 15.2 g (0.06 mole) of I in 5 ml of acetic acid was added, and the mixture was heated at 130–135° (bath temperature) for 3 h. The cooled mixture was poured into 100 ml of ice water, neutralized with a 20% solution of sodium carbonate to a weakly alkaline reaction, and extracted with 100 ml of ether. The ethereal solution was washed with water, dried over $MgSO_4$, filtered, the ether was distilled off, and the residue was distilled twice in vacuum. After the second distillation the substance crystallized. Obtained: 13.92 g (84%) of a yellow crystalline substance, m.p. 35–35.5°, b.p. 48–49°/$1.5 \cdot 10^{-2}$ mm Hg.

Found, %: C 47.90; 47.81; H 3.31; 3.44; Mn 19.67; 19.81
$C_{11}H_9O_5Mn$. Calculated, %: C 47.84; H 3.30; Mn 19.89

Oxymethylcyclopentadienylmanganese tricarbonyl. To a solution of

sodium methylate (0.15 g of sodium in 45 ml of anhydrous methyl alcohol) a solution of 10.6 g (0.0384 mole) of IV in 10 ml of alcohol was added. The solution was left at room temperature for 48 h. The volatile components (methyl alcohol and methyl acetate*) were distilled off at 20 mm Hg while heating to 50°; to the cooled residue, with stirring, were added 0.4 g of ammonium chloride and 10 ml of methyl alcohol. The mixture was filtered, methyl alcohol was distilled off from the solution, and the residue was distilled in vacuum. After the second distillation the substance crystallized. Obtained: 7.30 g (81.3%) of a light-yellow crystalline substance, m.p. 41.5-42.5°, b.p. 59-62°/$2.5 \cdot 10^{-2}$ mm Hg; insoluble in petroleum ether, soluble in benzene, ethyl ether, methyl and ethyl alcohol.

Found, %: C 46.25; 46.21; H 3.17; 3.09
$C_9H_7O_4Mn$. Calculated, %: C 46.17; H 3.02

Formylcyclopentadienylmanganese tricarbonyl. A mixture of 12.6 g (0.05 mole) of I and a solution of 21.05 g of urotropine in 60 ml of 50% acetic acid was heated at 135-140° (bath temperature) for one hour, cooled, and neutralized with sodium carbonate; the aqueous layer was decanted, and the viscous orange mass was washed with water. Through the bisulfite compound, 6.57 g (57%) of dark-yellow crystals, m.p. 74-75° (from petroleum ether), was isolated. The aldehyde is sparingly soluble in petroleum ether and readily soluble in ethyl ether and ethyl alcohol.

Found, %: C 46.62; 46.83; H 2.23; 2.40; Mn 23.61; 23.24
$C_9H_5O_4Mn$. Calculated, %: C 46.58; H 2.17; Mn 23.67

The aldehyde gives with 2,4-dinitrophenylhydrazine the 2,4-dinitrophenylhydrazone, m.p. 251° (decomposition) (lit. ([2]) m.p. 258° (decomposition)).

Found, %: C 43.86; 44.04; H 2.14; 2.30; N 13.60; 13.32
$C_{15}H_9O_7N_4Mn$. Calculated, %: C 43.71; H 2.20; N 13.59

Cannizzaro reaction. To a solution of sodium methylate (0.07 g of sodium in 20 ml of methyl alcohol) was added a solution of 4.64 g (0.02 mole) of V in 30 ml

* Not isolated separately.

methanol, and the mixture was left at room temperature for 72 h. Then methanol was distilled off from the mixture, 50 ml of water and 50 ml of ether were added, and the mixture was shaken. The ethereal solution was washed with water, dried over $MgSO_4$, evaporated, and the residue was sublimed at $2 \cdot 10^{-2}$ mm Hg. This gave 1.6 g of a yellow crystalline substance, mp 38-39°; after two washings with petroleum ether, 1.3 g (27.7%) of oxymethylcyclopentadienylmanganesetricarbonyl was obtained, mp (and mixed-sample mp) 41.5-42.5°. The compound gives no precipitate with 2,4-dinitrophenylhydrazine.

Found, %: C 45.73; 45.97; H 2.87; 3.02
$C_9H_7O_4Mn$. Calculated, %: C 46.17; H 3.02

The aqueous solution was acidified with hydrochloric acid; the precipitated carboxylcyclopentadienylmanganesetricarbonyl was filtered off, washed with water; weight 1.85 g, mp 193-195°.

One third of the mixture—the solid substance—was dissolved in 5% alkali solution, filtered, acidified with hydrochloric acid; a further 0.22 g of acid was obtained, mp 193-194°.

The total yield of carboxylcyclopentadienylmanganesetricarbonyl was 2.07 g (41.7%), mp 195-196° from ether (lit. [5] mp 189-197°).

Found, %: C 43.79; 43.80; H 2.12; 2.13; Mn 22.06; 22.03
$C_9H_5O_5Mn$. Calculated, %: C 43.57; H 2.04; Mn 22.14

Reaction of the aldehyde with lithium aluminum hydride. To a solution of 4.64 g (0.02 mole) of V in 50 ml of dry ether, a suspension of 0.4 g (0.01 mole) of $LiAlH_4$ in 100 ml of ether was added over 30 min. The mixture was kept at reflux for 3 h, cooled, and saturated ammonium chloride solution was added to it; the ethereal solution was separated, washed with water, dried over $MgSO_4$, evaporated, and the residue was sublimed at $2 \cdot 10^{-2}$ mm Hg. This gave 3.15 g (67.3%) of oxymethylcyclopentadienylmanganesetricarbonyl containing traces of aldehyde, from which the alcohol can be purified by washing with petroleum ether, mp (and mixed-sample mp) 41-42°.

Reaction of the aldehyde with aminomethylcyclopentadienylmanganesetricarbonyl. A mixture of 0.29 g (0.00125 mole) of V and 0.291 g (0.00125 mole) of III was heated in a test tube for 15 min on a boiling water bath. The cooled solid substance was pressed on filter paper and dried over $CaCl_2$; weight 0.54 g (96.6%), mp 93.5-94.5° (from a mixture of petroleum ether and ethyl ether). The dark-yellow crystals are insoluble in petroleum ether and soluble in benzene and ether.

Found, %: C 48.30; 48.19; H 2.55; 2.56; N 3.23; 3.22
$C_{18}H_{11}O_6NMn_2$. Calculated, %: C 48.32; H 2.48; N 3.13

Reaction of the aldehyde with ammonia. To a mixture of 4.6 g (0.02 mole) of V and 10 ml of cold water, 4 ml of ammonia was added. The mixture was heated at 40° for 5 h, filtered, and the green-yellow solid substance was washed with water, pressed on filter paper, and dried over $CaCl_2$; weight 4.39 g (97.5%), mp 110.5-111° (from a mixture of petroleum ether and ethyl ether). The dark-yellow crystals are insoluble in petroleum ether and soluble in benzene and ethyl ether.

Found, %: C 48.04; 48.11; H 2.32; 2.35; N 4.26; 4.18; Mn 23.81; 23.89
$C_{27}H_{15}O_9N_2Mn_3$. Calculated, %: C 47.95; H 2.24; N 4.15; Mn 24.37

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CITED LITERATURE

1. A. N. Nesmeyanov, K. N. Anisimov, Z. P. Valueva, DAN, **157**, 622 (1964).

2. M. Gais, A. Modiano, *Chem. and Ind.*, 1960, 202.

3. T. H. Coffield, K. G. Ihrmann, W. Burns, *J. Am. Chem. Soc.*, **82**, 1251 (1960).

4. T. H. Coffield, K. G. Ihrmann, W. Burns, *J. Am. Chem. Soc.*, **82**, 4209 (1960).

5. R. Riemschneider, K. Petzoldt, *Zs. Naturforsch.*, **15b**, 627 (1960).

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