Academician A. N. NESMEYANOV, K. N. ANISIMOV, N. E. KOLOBOVA,

I. B. ZLOTINA

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Abstract

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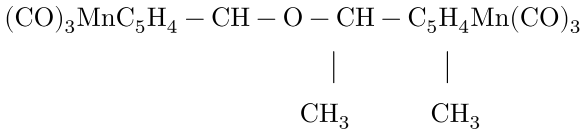
Academician A. N. NESMEYANOV, K. N. ANISIMOV, N. E. KOLOBOVA, I. B. ZLOTINA

REDUCTION OF KETONES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL AND DEHYDRATION OF SECONDARY ALCOHOLS

In a previous communication it was described that acetylcyclopentadienylmanganese tricarbonyl reacts normally with the Grignard reagent and with Iotsich' s "complex," forming tertiary alcohols, and, in the second case, acetylene alcohols ([1]).

In the present work we describe the reduction of ketones of cyclopentadienylmanganese tricarbonyl with lithium aluminum hydride, with and without aluminum trichloride, to the corresponding alcohols and alkyl-(aralkyl)-cyclopentadienylmanganese tricarbonyls ([2],[3]). We also describe the dehydration of the secondary alcohols obtained with potassium bisulfate and sulfuric acid to alkenylcyclopentadienylmanganese tricarbonyls and an ether:



$$(CO)_3MnC_5H_4-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_5H_4Mn(CO)_3$$

The structure of the compounds presented here is confirmed by the IR spectrum*. The spectrum of each of these compounds contains vibration frequencies characteristic of the principal groups of atoms composing the molecules of cyclopentadienylmetal carbonyls and their derivatives ([4–7])

$$\mathrm{CH} — 3120—3105\ \mathrm{cm}^{-1};$$

$$\mathrm{Me(CO)_3} — 2060—2019\ \mathrm{cm}^{-1};\quad 1967—1908\ \mathrm{cm}^{-1};$$

$$\mathrm{Me = V,\ Mn,\ Fe,\ CO.}$$

In addition to these general vibration frequencies, there are characteristic vibration frequencies of the introduced functional groups, which are given in boldface.

Experimental Part

1-Oxyethyl-1-cyclopentadienylmanganese tricarbonyl. In a 5-necked flask of volume 0.5 liter, fitted with a stirrer, reflux condenser, dropping funnel, and nitrogen inlet**, there was dissolved under nitrogen 10 g (0.0407 mole) of acetylcyclopentadienylmanganese tricarbonyl in 100 ml of absolute ether. Then, over the course of 0.5 hour, a suspension of 0.75 g (0.0203 mole) of $LiAlH_4$ in 100 ml of absolute ether was added. After heating for 2 hours, the reaction mixture was cooled and decomposed with 50 ml of absolute ethyl acetate and a concentrated solution of NH_4Cl. After filtration, the ether layer was dried over Na_2SO_4, and then the solvent was removed. Distillation in vacuo at 55—56° ($5 \cdot 10^{-3}$ mm) gave 7.2 g (71%) of a light-yellow viscous oil; n_D^{20} 1.5940; d_4^{20} 1.4347.

Found, %:	C 48.39, 48.55; H 3.66; 3.69; Mn 22.02; 22.26
$C_{10}H_9O_4Mn$. Calculated, %:	C 48.38; H 3.62; Mn 22.09

IR spectrum (ν, cm^{-1})***: 580 (s.), 635 (s.), 670 (s.), 840 (av.), 876 (av.), 930 (av.), 1011 (av.), 1037 (av.), 1050 (av.), 1080 (av.), 1100 (av.), 1246 (w.), 1270 (w.), 1322 (w.), 1380 (av.), 1416 (av.), 1460 (av.), 1935 (s.), 2030 (s.), 2880 (w.) 2940 (w.), 2990 (av.), 3130 (w.), 3400 (s.), **3610 (av.)**.

* Measurement of the IR spectra was carried out by Yu. N. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.
** The apparatus described was used in all subsequent experiments.
*** s.—strong intensity; av.—average intensity; w.—weak intensity.

1-Oxypropyl-1-cyclopentadienylmanganese tricarbonyl. To 15 g (0.0577 mole) of propionylcyclopentadienylmanganese tricarbonyl, dissolved in 125 ml of abs. ether, over the course of 0.5 hr was added a suspension of 1.07 g (0.0282 mole) of $LiAlH_4$ in 125 ml of abs. ether. After heating for 2 hr, the reaction mixture was cooled and worked up as in the preceding experiment. Vacuum distillation at 69-70°/$6 \cdot 10^{-3}$ mm gave 11 g (73%) of a yellow viscous oil; n_D^{20} 1.5823; d_4^{20} 1.3773.

Found, %: C 50.64; 50.73; H 4.40, 4.47; Mn 20.17; 20.08
$C_{11}H_{11}O_4Mn$. Calculated, %: C 50.38; H 4.19; Mn 20.99

IR spectrum (ν, cm^{-1}): 500 (medium), 540 (strong), 635 (strong), 670 (strong), 740 (weak), 792 (weak), 840 (strong), 855 (strong), 882 (medium), 911 (medium), 938 (medium), 976 (strong), 1040 (strong), 1092 (strong), 1240 (medium), 1382 (medium), 1416 (medium), 1465 (medium), 1932 (strong), 2022 (strong), 2890 (medium), 2950 (strong), 2985 (strong), 3125 (medium), 3450 (strong), 3620 (medium).

Phenyl-oxymethylcyclopentadienylmanganese tricarbonyl. To 10 g (0.0325 mole) of benzoylcyclopentadienylmanganese tricarbonyl, dissolved in

100 ml of abs. ether, over the course of 0.5 hr was added a suspension of 0.6 g (0.0160 mole) of $LiAlH_4$ in 100 ml of abs. ether. After heating for 2 hr, the reaction mixture was cooled and worked up as indicated above. 8.55 g (85%) of yellow crystals with m.p. 82–83° (from petroleum ether) were obtained.

Found, %: C 58.42; 58.47; H 3.69; 3.64
$C_{15}H_{11}O_4Mn$. Calculated, %: C 58.06; H 3.54

IR spectrum (ν, cm^{-1}) (crystals in petroleum jelly): 435 (weak), 580 (strong), 636 (strong), 655 (strong), 707 (strong), 740 (strong), 791 (weak), 830 (weak), 845 (strong), 918 (medium), 933 (medium), 1000 (strong), 1031 (medium), 1042 (medium), 1082 (medium), 1197 (weak), 1255 (strong), 1307 (strong), 1335 (medium), 1380 (medium), 1407 (strong), 1430 (strong), 1460 (strong), 1502 (medium), 1920 (strong), 1942 (strong), 2020 (strong), 2865 (strong), 2880 (strong), 2925 (strong), 2960 (strong), 3045 (medium), 3080 (medium), 3130 (strong), 3450 (strong).

Ethylcyclopentadienylmanganese tricarbonyl. Into abs. ether (20 ml), under nitrogen, were introduced 5.44 g (0.0407 mole) of $AlCl_3$, and after cooling, a suspension of 1.54 g (0.0407 mole) of $LiAlH_4$ in 100 ml of abs. ether was added. Then, at room temperature and with vigorous stirring, over the course of 0.5 hr, 10 g (0.0407 mole) of acetylcyclopentadienylmanganese tricarbonyl in 50 ml of abs. ether was added. After 15 min the reaction mixture was decomposed with ice water, and the ether layer was washed with $NaHCO_3$ solution and dried over Na_2SO_4. After removal of the ether, vacuum distillation (34–35°/$2 \cdot 10^{-2}$ mm) gave 6.8 g (72%) of a light-yellow oil; n_D^{20} 1.5784; d_4^{20} 1.3358. Literature data ([8]): n_D^{20} 1.5760, d_4^{20} 1.3298.

Found, %: C 51.67; 51.97; H 3.94; 3.95
$C_{10}H_9MnO_3$. Calculated, %: C 51.72; H 3.88

IR spectrum (ν, cm^{-1}): 540 (strong), 635 (strong), 668 (strong), 790 (weak), 837 (medium), 910 (medium), 1028 (weak), 1050 (weak), 1212 (weak), 1270 (weak), 1323 (medium), 1370 (weak), 1384 (weak), 1412 (weak), 1447 (medium), 1465 (medium), 2489 (medium), 1930 (strong), 2025 (strong), 2880 (medium), 2950 (medium), 2980 (strong), 3125 (weak).

Propylcyclopentadienylmanganese tricarbonyl. To 5.86 g (0.0438 mole) of $AlCl_3$ in 30 ml of abs. ether saturated with nitrogen, with cooling, was added a suspension of 1.67 g (0.0438 mole) of $LiAlH_4$ in 100 ml of abs. ether. Then, at room temperature, over the course of 0.5 hr and with stirring, 11.4 g (0.0438 mole) of propionylcyclopentadienylmanganese tricarbonyl in 50 ml of abs. ether was introduced. After 15 min the reaction mixture was decomposed with ice water. After the usual work-up, vacuum distillation (51–52°/$3 \cdot 10^{-2}$ mm) gave 7.3 g (68%) of a light-yellow oil; n_D^{20} 1.5681; d_4^{20} 1.2974.

Found, %: C 53.53; 53.40; H 4.62, 4.58; Mn 21.96, 22.12
$C_{11}H_{11}MnO_3$. Calculated, %: C 53.65; H 4.47; Mn 22.35

IR spectrum (ν, cm^{-1}): 540 (medium), 635 (strong), 720 (medium), 795 (weak), 838 (weak), 1033 (weak), 1053 (weak), 1093 (weak), 1382 (weak), 1415 (weak), 1468 (weak), 1487 (weak), 1928 (strong), 2022 (strong), 2885 (weak), 2945 (weak), 2975 (weak), 3120 (weak).

Benzylcyclopentadienylmanganese tricarbonyl. Under the conditions described above, benzylcyclopentadienylmanganese tricarbonyl was obtained from 4.34 g (0.0325 mole) of $AlCl_3$ in 20 ml of abs. ether, 1.23 g (0.0325 mole) of $LiAlH_4$ in 100 ml of abs. ether, and 10 g (0.0325 mole) of benzylcyclopentadienylmanganese tricarbonyl in 50 ml of abs. ether. After decomposition of the mixture with ice water, the ethereal layer was washed with a solution of $NaHCO_3$, dried over Na_2SO_4, and the ether was removed. The separated viscous mass was chromatographed on Al_2O_3 in heptane. On elution with a heptane-benzene mixture (1 : 1), 11 g (85%) of a yellow crystalline product was isolated, m.p. 37-38° (from petroleum ether at −70°).

Found, %: C 61.78, 61.47; H 3.82, 3.98; Mn 18.71, 18.33
$C_{15}H_{11}MnO_3$. Calculated, %: C 61.22; H 3.74; Mn 18.70

IR spectrum (ν, cm^{-1}) (crystals in Vaseline oil): 430 (w.), 470 (m.), 492 (w.), 500 (w.), 540 (s.), 565 (m.), 606 (w.), 630-640 (s.), 692 (s.), 713 (s.), 766 (s.), 835 (s.), 860 (m.), 888 (w.), 920 (m.), 936 (m.), 1028 (m.), 1048 (w.), 1066 (m.), 1072 (m.), 1371 (m.), 1383 (m.), 1411 (m.), 1441 (m.), 1457 (s.), 1480 (s.), 2497 (s.), 1586 (m.), 1602 (m.), 1903 (m.), 1940 (m.), 2020 (s.), 2860 (s.), 2925 (s.), 2965 (s.), 3035 (s.), 3080 (s.), 3100 (s.), 3120 (s.), 3135 (s.).

Vinylcyclopentadienylmanganese tricarbonyl. 4.7 g (0.0189 mole) of 1-hydroxyethyl-1-cyclopentadienylmanganese tricarbonyl (n_D^{20} 1.5936), 0.4 g of $KHSO_4$, and a small amount of hydroquinone were heated in a sealed ampoule for 2 h at 200°. After opening the ampoule, 3.25 g (75%) of a light-yellow mobile liquid was isolated by distillation in vacuo at 29-30°/5 $\cdot 10^{-3}$ mm; n_D^{20} 1.6080; d_4^{20} 1.3807.

Found, %: C 52.04, 51.79; H 3.00, 3.16; Mn 23.09, 23.39
$C_{10}H_7MnO_3$. Calculated, %: C 52.17; H 3.04; Mn 23.91

IR spectrum (ν, cm^{-1}): 540 (s.), 635 (s.), 665 (s.), 730 (s.), 838-845 (s.), 922 (s.), 989 (s.), 1038 (s.), 1054 (s.), 1100 (m.), 1154 (w.), 1206 (m.), 1248 (m.), 1296 (m.), 1352 (m.), 1380 (s.), 1402 (s.), 1485 (s.), 1633 (s.), 1928 (s.), 2022 (s.), 3000 (m.), 3025 (m.), 3105 (s.), 3125 (s.).

On bromination of vinylcyclopentadienylmanganese tricarbonyl in a heptane-benzene mixture (1 : 1), a yellow crystalline product was isolated, m.p. 45-46° (from petroleum ether).

Found, %: C 31.27, 30.99; H 1.84, 1.64; Mn 14.08, 13.65; Br 41.47, 41.38
$C_{10}H_7Br_2MnO_3$. Calculated, %: C 30.76; H 1.79; Mn 14.10; Br 41.02

Propen-1-yl-1-cyclopentadienylmanganese tricarbonyl. 3.15 g (0.0120 mole) of 1-hydroxypropyl-1-cyclopentadienylmanganese tricarbonyl (n_D^{20} 1.5823), 0.3 g of $KHSO_4$, and a small amount of hydroquinone were heated in a sealed ampoule for 1 h at 180°. After opening the ampoule, 2.52 g (86%) of a light-yellow mobile liquid was isolated by distillation in vacuo (51-52°/2 $\cdot 10^{-2}$ mm); n_D^{20} 1.6034; d_4^{20} 1.3306.

Found, %: C 54.25, 54.04; H 3.80, 3.73; Mn 22.03, 22.20
$C_{11}H_9MnO_3$. Calculated, %: C 54.10; H 3.68; Mn 22.54

IR spectrum (ν, cm^{-1}): 540 (s.), 635 (s.), 669 (s.), 722 (s.), 758 (w.), 839 (s.), 916 (m.), 963 (s.), 1037 (m.), 1050 (m.), 1067 (w.), 1207 (w.), 1292 (w.), 1307 (w.), 1380 (m.), 1415 (w.), 1450 (m.), 1482 (m.), 1669 (m.), 1920 (s.), 2018 (s.), 2865 (m.), 2890 (m.), 2925 (m.), 2955 (s.), 2985 (m.), 3020 (m.), 3040 (m.), 3125 (w.).

1,1-Di-(cyclopentadienylmanganese tricarbonyl)ethyl ether. 1 g (0.0040 mole) of 1-hydroxyethyl-1-cyclopentadienylmanganese tricarbonyl (n_D^{20} 1.5936) was treated with 45% H_2SO_4. The resulting viscous mass was washed with distilled water and dried in vacuo.

Recrystallization from petroleum ether gave 0.15 g (16%) of light-yellow crystals, m.p. 85-86°.

$$C_{20}H_{16}O_7Mn_2.$$

Found, %: C 50.23, 50.11; H 3.50, 3.33; Mn 22.79, 22.73.
Calculated, %: C 50.20; H 3.34; Mn 23.01.

IR spectrum (ν, cm^{-1}) (crystals in Vaseline oil): 420 (medium), 475 (weak), 495 (medium), 505 (medium), 535 (strong), 555 (medium), 640 (strong), 670 (strong), 692 (strong), 830 (strong), 840 (strong), 853 (medium), 900 (medium), 918 (medium), 925 (medium), 1018 (medium), 1034 (medium), 1060 (strong), 1091 (strong), 1107 (strong), 1220 (weak), 1245 (medium), 1311 (strong), 1318 (strong), 1350 (medium), 1375 (strong), 1387 (medium), 1415 (medium), 1459 (strong), 1492 (medium), 1935 (strong), 2016 (strong), 2865 (strong), 2930 (strong), 2965 (strong), 3120 (medium).

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