Organometallic Chemistry

Acetylation and benzoylation of η^5 , η^5 -fulvalenedimanganesehexacarbonyl

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 η^5, η^5 -Fulvalenedimanganesehexacarbonyl (dicymantrenyl) was acetylated and benzoylated by RC(O)Cl+AlCl₃ in CH₂Cl₂, under conditions of the Friedel–Crafts reaction. The reaction involves both nonequivalent positions of the cyclopentadienyl rings to give mixtures of two isomeric ketones. When using an excess of the acetylating mixture, diacetyl derivatives of dicymantrenyl were obtained.

Key words: acetylation, benzoylation, manganese complexes, carbonyl, cyclopentadienyl, synthesis of ketones.

Unlike cymantrene (CTM), whose properties and reactions were investigated in detail,¹⁻³ the chemistry of dicymantrenyl (1) have scarcely been studied. Compound 1 is known to enter the acetylation reaction⁴ (where only one acetyl derivative was isolated) and the reaction of the replacement of CO with donor ligands.⁵ In the present work, the Friedel—Crafts acetylation and benzoylation of 1 under the action of RC(O)Cl+AlCl₃ in CH₂Cl₂ were investigated. These reactions occur less smoothly and give lower yields than those of CTM under the same conditions. In particular, when using 1 equivalent of acylating mixture for competitive acylation of a mixture of 1 mmol of compound 1 + 1 mmol of CTM, the latter reacted almost completely, whereas ~90 % of the starting 1 was isolated untouched. This is related to a noticeable electron-withdrawing effect of the (CO)₃MnC₅H₄ substituent (see Refs. 6, 7). As in the case of alkyl derivatives of CTM,⁸ the acylation of 1 is nonselective and involves both possible positions, giving a mixture of two isomeric ketones 2 and 3 (with 80-85 % of the former). Mixtures of isomeric ketones 2 and 3 can be easily separated on a column with Al₂O₃ (Scheme 1).



Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 10, pp. 2017-2020, October, 1995.

1066-5285/95/4410-1937 \$12.50 © 1995 Plenum Publishing Corporation

Since the β -positions of **1** are spatially more accessible for the reagent, it is reasonable to conclude that β -isomers **2a**, **b** are dominant.

When compound 1 is acetylated by an excess of the acylating mixture, besides monosubstituted ketones 2a and **3a**, a mixture of diacetyl derivatives is also obtained. After repeated chromatography and recrystallization, the main fraction was isolated. According to the ¹H NMR spectra, this fraction is a mixture of two diketones that contain one acetyl substituent in each ring. It is most probable that this fraction consists of two diastereoisomeric diketones with different relative arrangement of the acetyl substituents in the β -position of two C₅H₃ rings (ketones 4 and 4').



In addition to the main fraction, several fractions with low contents of other ketones were obtained by chromatography. These ketones were not investigated in detail.

The reduction of ketones 2a, 3a and 2b, 3b under the action of LiAlH₄+AlCl₃ in ether yields the corresponding ethyl and benzyl derivatives 5a, 6a and 5b, 6b.



When any substituent is introduced at the α - or β -position of one of the C₅H₄ rings, the prochiral system of dicymantrenyl transforms to a planar chiral system. In this connection, all seven of the CH groups in both rings become anisochronic, while the corresponding protons and carbon nuclei turn diastereotopic. In the ¹H NMR spectrum of the starting dicymantrenyl 1, the protons of two equivalent C5H4 rings are observed as two triplets at 4.957 and 4.750 ppm with $J \approx 2$ Hz

(system A_2B_2), analogous to the C_5H_4 protons in monosubstituted derivatives of cymantrene, $RC_5H_4Mn(CO)_3$. If diastereotopic nonequivalence (DN) does not take place, the seven protons of both Cp rings in the monosubstituted derivatives 1 should exhibit four different signals in the ¹H NMR spectrum (the protons of the "inner" $-\alpha$, α' and "outer" $-\beta$, β' positions). When the DN effect takes place, all seven of the CH groups should resonate as different signals. The presence as well as the absence of the DN effect in the ¹H NMR spectrum is determined mainly by the nature of the substituent and by its position. In ketones 2a,b and **3a.b** the set of hydrogen atoms gives rise to more than four signals (Table 1). In compound 5a (ethyl substituent is in the β -position), the seven hydrogen atoms of the Cp rings give four separate signals. Three protons of the C5H3Et ring exhibit a one-proton upfield signal (4.613 ppm, triplet, $J \cong 2$ Hz) and a downfield two-proton signal (4.852 ppm, doublet, J = 2 Hz). Four protons of C₅H₄ account for two two-proton signals, viz., a triplet at 4.733 ppm and a multiplet of seven lines at 4.919 ppm. Thus, in the ¹H NMR spectrum of compound 5 the DN effect is clearly observed only for the last signal. The CH₂ group in ethyl corresponds to a normal quartet (1 : 3 : 3 : 1).

Unlike this, in the ¹H NMR spectrum of compound **6a** (ethyl substituent is in the α -position) the seven hydrogen atoms of the Cp rings give rise to six well resolved multiplets with the intensity ratio 1:2:1:1:1:1, whereas the CH₂ group corresponds to the multiplet of nine lines (δ 2.477 ppm, J =7.3 Hz) (maximal possible number of lines for the CH(a)H(b)-Me₃ fragment is 16). The DN effect is clearly observed in the ¹H NMR spectra of compounds 5b and 6b with the CH₂Ph substituent (six and seven separated multiplets for the protons of the Cp rings and AB-system for the protons of CH_2 in the case of **6b**). In the ¹H NMR spectra the signals of each nonequivalent proton of C_5H_4 - C_5H_3 are present as well resolved multiplets containing from four to six lines with the constants $J_{\rm H,H} = 1.6 \div 1.8$ Hz. The assignment of the signals and the character of coupling interactions will be specially discussed.

Experimental

Starting compound 1 was obtained by a known procedure.⁵ All experiments were carried out in an argon atmosphere using freshly distilled solvents saturated with argon. Ketone 2a was prepared previously.⁴ The ¹H NMR spectra were measured on Bruker WP-200-SY and Bruker AMX-400 instruments, IR spectra were recorded on a UR-20 device, and mass spectra of electron impact (70 eV) were obtained on a Kratos MS-890 instrument.

2- and 3-Acetyl- $(\eta, 5\eta^5)$ -fulvalenedimanganesehexacarbonyl (2a, 3a). A solution of 4.06 g (10 mmol) of 1 in 40 mL of

Com- pound	Protons of the cyclopentadienyl rings, δ (J/Hz)	Other protons, δ* (J/Hz)		
1	4.957 (t, 4 H); 4.750 (t, 4 H, $J = 2$)			
2a	5.576 (m, 1 H); 5.456 (m, 1 H); 4.992 (m, 3 H); 4.807 (m, 2 H)	2.250 (s, 3 H, Me)		
2b	5.605 (m, 1 H); 5.430 (m, 1 H); 4.942 (m, 3 H); 4.700 (m, 2 H)	**		
3a	5.650 (m, 1 H); 5.372 (m, 1 H); 5.300 (m, 1 H); 5.116 (m, 1 H); 5.090 (m, 1 H); 4.755 (m, 2 H)	2.250 (s, 3 H, Me)		
3b	5.350 (m, 1 H); 5.022 (m, 1 H); 5.045 (m, 2 H); 4.654 (m, 2 H); 4.580 (m, 1 H)	**		
4	5.679 and 5.640 (2t, in sum 2 H); 5.463 (m, 2 H); 5.068 (m, 2 H)	2.357 and 2.348 (s, 6 H, Me)		
5a	4.920 (m, 2 H, $J = 1.8$); 4.852 (d, 2 H, $J = 2$); 4.732 (t, 2 H, $J = 2$); 4.613 (t, 1 H, $J = 2$)	1.230 (t, 3 H, Me); 2.320 (q, 2 H, CH_2 , $J = 7.3$)		
5b	4.908 (m, 1 H); 4.870 (m, 1 H); 4.849 (m, 2 H); 4.745 (m, 1 H); 4.706 (m, 1 H); 4.613 (t, 1 H)	3.594 (s, 2 H, CH ₂)**		
6a	5.046 (m, 1H); 4.984 (m, 2 H); 4.789 (m, 1 H); 4.714 (m, 1 H); 4.656 (m, 1 H); 4.593 (t, 1 H)	1.232 (t, 3 H, Me) 2.477 (9 lines, 2 H, CH_2 , $J = 7.3$)		
6b	5.051 (q, 1 H); 5.002 (m, 1 H); 4.838 (m, 1 H); 4.773 (m, 1 H); 4.629 (m, 1 H); 4.612 (t, 1 H); 4.506 (q, 1 H)	4.360 and 4.262 (AB-system, $J = 16.0$)*		

Table 1. ¹H NMR spectra of the compounds obtained

* The spectra were obtained using TMS as the standard. ** The signals of the phenyl protons are not given.

Table 2. Characteristics of the compounds obtained

Com- pound	M.p. /°C	Found (%) Calculated			Empirical formula	Mass spectrum,	IR spectrum, v(C=O)/cm ⁻¹
		С	H	Mn	-	$m/z [M]^+$	(CH ₂ Cl ₂)
2a	112-115	*	*	*		448	1690
26	115-118	<u>54.38</u> 54.14	<u>2.68</u> 2.37	<u>22.38</u> 21.54	$C_{23}H_{12}Mn_2O_7$	510	1690
3a	96—97	<u>48.36</u> 48.21	<u>2.47</u> 2.23	<u>23.39</u> 24.55	C ₁₈ H ₁₀ Mn ₂ O ₇	448	1690
3b	119—121	<u>54.57</u> 54.14	<u>2.34</u> 2.37	<u>20.36</u> 21.54	$C_{23}H_{12}Mn_2O_7$	510	1690
4	156-195**	<u>49.27</u> 48.98	<u>2.57</u> 2.45	<u>22.46</u> 22.45	$C_{20}H_{12}Mn_2O_8$	490	1693
5a	79-83	<u>49.83</u> 49.77	<u>2.71</u> 2.76		$C_{18}H_{12}Mn_2O_6$	436	Negative Negative
5b	120-122	<u>54.99</u> 55.65	<u>2.91</u> 2.82	<u>21.75</u> 22.18	$C_{23}H_{14}Mn_2O_6$	496	Nex2019
6a	8385	<u>50.66</u> 49.77	<u>2.78</u> 2.76	<u>24.90</u> 25.35	$C_{18}H_{12}Mn_2O_6$	436	84938*
6b	93—97	<u>55.66</u> 55.65	<u>2.93</u> 2.82	-	C ₂₃ H ₁₄ Mn ₂ O ₆	496	ugaran di

* Compound has been described earlier. ** A mixture of two isomers.

CH₂Cl₂ was slowly added dropwise to a solution of 2.40 g (18 mmol) of AlCl₃ and 7 mL (90 mmol) of MeC(O)Cl in 30 mL of CH₂Cl₂ at 20 °C. The mixture was boiled for 2.5—3 h, cooled, and decomposed with a dilute HCl solution. After the treatment and elimination of the solvent from the organic layer, the residue was chromatographed on a column with Al₂O₃ (4×40 cm). After elution with benzene, the following fractions were obtained: 0.07 g of unreacted 1, 0.46 g (~10 %) of ketone 3a, 2.73 g (61 %) of ketone 2a. Ketones 2a and 3a were recrystallized from heavy petroleum ether.

Analogously, benzoylation of 3.25 g (8 mmol) of 1 by a mixture of 2.67 g (20 mmol) of AlCl₃ and 2.8 g (20 mmol) of PhC(O)Cl in 70 mL of CH₂Cl₂, chromatography on Al₂Cl₃, and elution with a benzene—petroleum ether mixture (2 : 1) resulted in the following fractions: 0.04 g of unreacted 1, 0.60 g (~15 %) of ketone 3b, 2.68 g (66 %) of ketone 2b. Ketones 2b and 3b were recrystallized from heavy petroleum ether.

Diacetyl- $(\eta, {}^{5}\eta^{5})$ -fulvalenedimanganesehexacarbonyl (4, a mixture of isomers). An excess of MeC(O)Cl (2 mL,

~27 mmol) was added dropwise to a suspension of 0.406 g (1 mmol) of 1 and 0.67 g (5 mmol) of AlCl₃ in 30 mL of CH₂Cl₂ with stirring. The mixture was boiled for 3 h, cooled, and decomposed by a diluted HCl solution. After the treatment and removing the solvent from the organic layer, the residue was chromatographed on a column with Al₂O₃. After elution with a benzene-THF mixture (20 : 1) several fractions were obtained: 0.02 g of starting 1; 0.07 g of monoketones 2a+3a; 0.36 g (76 %) of diketones 4. In addition, a number of fractions with low contents (10-40 mg) of other isomers were separated but were not studied. The compound from fraction 4 was repeatedly chromatographed and, after removing the solvent, was recrystallized from heavy petroleum ether. In the ¹H NMR spectrum of the obtained mixture of two isomers, the six protons of the C_5H_3 - C_5H_3 fragment are observed as two downfield triplets (J = 1.6 Hz, δ 5.679 and 5.640, intensity ratio ~9 : 10, total intensity 2H) and two upfield multiplets (δ 5.563 and 5.068, the intensity of each multiplet is 2H). The protons of the acetyl groups in different positions are two singlets at 2.357 and 2.348 ppm (intensity ratio ≃9 : 10, total intensity 6H).

2- and 3-Ethyl, 2- and 3-benzyl fulvalenedimanganesehexacarbonyl. Compounds 5a,b and 6a,b were obtained by the general procedure: 1 mmol of the corresponding ketone (2a, 2b or 3a, 3b) was reduced in 30 mL of absolute ether using the mixture of 0.08 g (2 mmol) of LiAlH₄ and 0.27 g (2 mmol) of AlCl₃ (stirring for 2 h at room temperature and for 0.5 h with boiling). The reaction was monitored by TLC on Silufol. When the reduction was finished, the mixture was decomposed by a diluted HCl solution. After removing the solvent, the residue was chromatographed on a column with Al₂O₃ using a benzene-petroleum ether mixture (2 : 1) and recrystallized from light petroleum ether. The yields of compounds 5a,b and 6a,b was 55-70 %.

The results of elemental analysis, melting points, and other characteristics of the obtained derivatives of dicymantrenyl are given in Table 2. In the IR spectra of all of the obtained compounds, the region of the v(CO) frequencies contains absorption bands characteristic of the $Mn(CO)_3$ groups: 1950 cm⁻¹ (br), 2025 cm⁻¹, and 2035⁻¹ (pl). For the mixture of the isomers of compound 4, which contains two electron-

withdrawing substituents, these bands are $5-10 \text{ cm}^{-1}$ up-field shifted (v(CO) for **4** is 1960 (br), 2030, and 2040 cm⁻¹ (pl).

The electron impact mass spectra of all of the synthesized compounds contain the peaks of the molecular ions ($[M]^+$, Table 2) and those of the fragmentation-type ions, which form as a result of sequential splitting of the CO groups and the Mn atoms ($[M-3CO]^+$, $[M-3CO-Mn]^+$, $[M-3CO-2Mn]^+$, $[M-5CO]^+$, $[M-6CO]^+$, $[M-6CO-Mn]^+$, $[M-6CO-2Mn]^+$, and $[Mn]^+$ ions).

The authors are grateful to P. V. Petrovsky and E. V. Vorontsov (the NMR laboratory of the Institute of Organoelement Compounds, Russian Academy of Sciences) for recording ¹H NMR spectra.

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Received April 5, 1995