

## ORGANOMETALLIC STUDIES

XV<sup>a</sup>. FORMYLCYMANTRENE<sup>b,c</sup>N. TIROSH<sup>d</sup>, A. MODIANO AND MICHAEL CAIS*Department of Chemistry, Technion, Israel Institute of Technology, Haifa (Israel)*

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The failure to prepare formylcymantrene (formylcyclopentadienylmanganese tricarbonyl)<sup>e</sup>, (IV), by the method used to prepare formylferrocene<sup>1</sup> forced us to look for a different route to arrive at (IV), an important intermediate in our work on pentalene-metal complexes<sup>2,3,5</sup>. In our initial approach, chloroformylcymantrene<sup>7</sup>, (III), obtained from carboxycymantrene<sup>6,7</sup>, (II), was reduced with lithium aluminum tri-*tert*-butoxide hydride<sup>8</sup> to yield the desired aldehyde, (IV), as a reddish oil. The relatively large number of steps involved in this reaction sequence and the difficulty in reproducing good yields in the last reduction step prompted us to seek a more facile and direct synthesis of (IV). The desired result was obtained<sup>e</sup> in condensing cymantrene with dichloromethyl methyl ether in the presence of aluminum chloride<sup>9</sup>. The attempted condensation of cymantrene with dichloromethyl ethyl ether has been reported by Pauson and Watts<sup>10</sup> to have given only traces of unidentified products.

The conversion ratio in this reaction was rather low (about 60% of the starting material (I) being recovered on chromatography) but the simplicity of the experimental procedure and the isolation of the aldehyde (IV) as a crystalline, rather than an oily<sup>2</sup>, material make this a more advantageous method for preparing (IV) than the reduction of chloroformylcymantrene. A by-product of the condensation reaction was dicymantrenylcarbinol, (VI), whose structure was proven by an independent synthesis. The yields of (VI) varied with the conditions of the experiment.

Reduction of formylcymantrene with sodium borohydride gave (hydroxymethyl)cymantrene, (V). The latter alcohol was also obtained when the aldehyde (IV) was chromatographed on basic alumina, due probably to the aldehyde undergoing a Cannizzaro reaction. However, the aldehyde (IV) was recovered unchanged after being kept for 20 h in alcoholic potassium hydroxide solution, under the usual Cannizzaro reaction conditions.

The oxidation of formylcymantrene with moist silver oxide gave the acid (II) in yields of about 65%. The same reaction applied to formylferrocene gave ferrocene-

<sup>a</sup> Part XIV, see ref. 1.

<sup>b</sup> For preliminary communications see refs. 2 and 3.

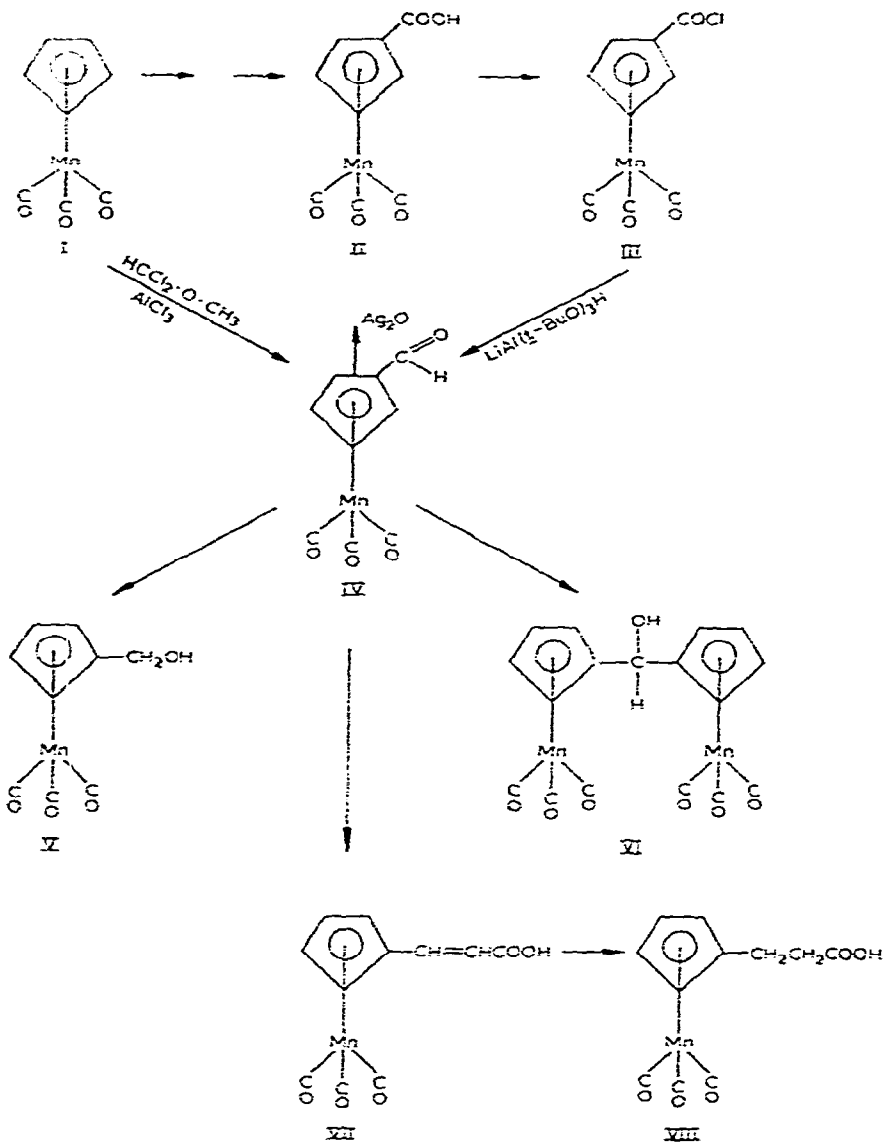
<sup>c</sup> The name CYMANTRENE has been suggested<sup>1,2</sup> for CYclopentadienyLMANganeSE TRI-carbonyl by analogy to FERROCENE.

<sup>d</sup> Taken in part from the M.Sc. Thesis submitted by N. Tirosh to the Senate of the Technion, Israel Institute of Technology, October 1964.

<sup>e</sup> Whilst this work was in progress, Pauson and Watts<sup>10</sup> reported using dichloromethyl ethyl ether in a similar procedure for the synthesis of ferrocenecarboxaldehyde.

carboxylic acid in yields higher than 80%. The latter route provides a very convenient method for the synthesis of pure ferrocenecarboxylic acid.

The condensation of formylcymantrene with malonic acid under the Knoevenagel reaction conditions produced cymantreneacrylic acid, (VII), which upon reduction with Raney nickel catalyst gave the  $\beta$ -propionic acid, (VIII).



#### EXPERIMENTAL

The infrared spectra were measured in CHCl<sub>3</sub> solution on a Perkin-Elmer Infracord Model 137 and on Infracord Model 237 (Grating) spectrophotometers. The

ultraviolet spectra were measured in ethanol solution on a Perkin-Elmer Model 137 spectrophotometer. The NMR spectra were measured on Varian Model A 60 spectrometer, with tetramethylsilane as internal standard. The mass spectra were recorded on a type Atlas CH 4 mass spectrometer\*. The melting points were determined on a Kofler block type instrument and are uncorrected.

(i) *Preparation of formylcymantrene, (IV)*

Dichloromethyl methyl ether (24 g, 0.2 mole)<sup>9</sup> was added dropwise to a cooled, stirred mixture of cymantrene (10.2 g, 0.05 mole), anhydrous aluminum chloride (10 g) and methylene chloride (50 ml). After the addition was complete, stirring was continued for 0.5 h at ice-bath temperature then for 0.5 h at room temperature and then refluxed for 0.5 h. After cooling the reaction mixture was poured onto ice and extracted with methylene chloride. The organic solvent extracts were washed with 10% sodium bicarbonate solution and then with water until neutral. After drying ( $\text{MgSO}_4$ ) the organic solvent was removed in vacuum (water pump) to obtain a semi-solid yellow-brown material (11 g). This was chromatographed on neutral alumina (150 g) using a red-glass column to prevent light-decomposition of the products. Elution with hexane/benzene (4:1) (200 ml) gave unreacted cymantrene (6 g). Further elution with chloroform/benzene (4:1) gave formylcymantrene (3.2 g) as a brown crystalline material. Recrystallization from hexane gave the analytical sample, m.p. 53–55°. (Found: C, 46.70; H, 2.39; Mn, 23.45.  $\text{C}_9\text{H}_5\text{MnO}_4$  calcd.: C, 46.55; H, 2.18; Mn, 23.67%.) The major bands in the infrared spectrum: 2857 (mw), 2040 (vs), 1960 (vs), a doublet at 1695 (vs) and 1667 (m), 1465 (m), 1368 (m), 1333 (mw)  $\text{cm}^{-1}$ . The ultraviolet spectrum:  $\lambda_{\text{max}}$  213  $\text{m}\mu$  ( $\epsilon$  22300),  $\lambda_{\text{max}}$  284  $\text{m}\mu$  ( $\epsilon$  1675),  $\lambda_{\text{max}}$  336  $\text{m}\mu$  ( $\epsilon$  1560).

The major fragments in the mass spectrum had the following  $m/e$  values: 232  $[(\text{CO})_3\text{MnC}_5\text{H}_4\text{CHO}]^+$ ; 204  $[(\text{CO})_2\text{MnC}_5\text{H}_4\text{CHO}]^+$ ; 176  $[(\text{CO})\text{MnC}_5\text{H}_4\text{CHO}]^+$ ; 167  $[\text{Mn}(\text{CO})_4]^+$ ; 148  $[\text{MnC}_5\text{H}_4\text{CHO}]^+$ ; 139  $[\text{Mn}(\text{CO})_3]^+$ ; 119  $[\text{MnC}_5\text{H}_4]^+$ ; 93  $[\text{C}_5\text{H}_4\text{CHO}]^+$ ; 65  $[\text{C}_5\text{H}_5]^+$ ; 55  $[\text{Mn}]^+$ .

Further elution with chloroform (50 ml) yielded a small amount (50 mg) of yellow crystalline material which after recrystallization from hexane had m.p. 91–92°. This was found to be dicymantrenyl carbinol, (VI), on the basis of spectral data and comparison with an authentic sample obtained by an independent synthesis<sup>11</sup>. (Found: C, 47.03; H, 2.44; Mn, 25.04; mol. wt., 458.  $\text{C}_{17}\text{H}_{10}\text{Mn}_2\text{O}_7$  calcd.: C, 46.78; H, 2.31; Mn, 25.22%; mol. wt., 436.) The major bands in the infrared spectrum: 3590 (mw), 3390 (mw), 3000 (mw), 2040 (vs); 1960 (vs)  $\text{cm}^{-1}$ .

The NMR spectrum: methine proton a doublet centred at  $\tau$  4.88 (relative intensity 1); cyclopentadienyl protons, multiplet centred at  $\tau$  5.2 (relative intensity 8) and hydroxyl proton a doublet centred at  $\tau$  7.84 (relative intensity 1). When the reaction was carried out in a much smaller volume of solvent, the yield of the carbinol (VI) was greatly increased at the expense of the yield of formylcymantrene.

The carbinol (VI) was also characterized by preparing the acetate derivative with acetic anhydride and pyridine. The acetate had m.p. 119–121° (from hexane). (Found: C, 47.73; H, 2.39; Mn, 22.77; mol. wt., 501.  $\text{C}_{19}\text{H}_{12}\text{MnO}_8$  calcd.: C, 47.72; H, 2.53; Mn, 22.97%; mol. wt., 478.) When formylcymantrene (100 mg) was chromatographed on basic alumina (12 g) and eluted with benzene/chloroform (1:1) there was obtained

\* We wish to thank Dr. A. MANDELBAUM of this Department for the mass spectra measurements.

a yellow oil (~ 50 mg) which turned out to be (hydroxymethyl)cymantrene, (V), (identical infrared spectrum and TLC with authentic sample prepared in reaction 3) formed probably as a result of the aldehyde IV undergoing the Cannizzaro reaction on the alumina column.

(2) *Reduction of (chloroformyl)cymantrene, (III), with LiAl(tert-BuO)<sub>3</sub>H*

A suspension of the Brown reagent<sup>8</sup>, LiAl(tert-BuO)<sub>3</sub>H, (2.54 g) in tetrahydrofuran was added dropwise, under an inert atmosphere to a cooled (-78°) stirred solution of (chloroformyl)cymantrene (2.67 g) in tetrahydrofuran (30 ml). After addition, stirring was continued for 1 h at -78° and then allowed to come to room temperature over a period of 1 h. The reaction mixture was poured onto ice and filtered. The collected precipitate was mixed with excess 4% hydrochloric acid solution and the mixture extracted with ether. After drying (MgSO<sub>4</sub>) and removal of solvent there was obtained a reddish oil (~ 2 g). This was distilled in vacuum (80°/0.05 mm) to yield a reddish oil (~ 1.5 g) whose infrared spectrum was identical with that of the aldehyde obtained in the previous experiment.

The 2,4-dinitrophenylhydrazone derivative had m.p. 258° (decomp.) (from chloroform/methanol). (Found: C, 43.95; H, 2.22; Mn, 13.28; N, 13.82. C<sub>15</sub>H<sub>9</sub>MnN<sub>4</sub>O<sub>7</sub>; calcd.: C, 43.71; H, 2.20; Mn, 13.33; N, 13.59%.)

(3) *Reduction of formylcymantrene with NaBH<sub>4</sub>*

Formylcymantrene (220 mg) in ethanol (10 ml) was reduced with excess sodium borohydride and the reaction worked up in the usual manner to yield 200 mg of crude oily material which had no ketonic carbonyl absorption in the infrared spectrum. This was distilled in vacuum (82°/0.15 mm) to obtain cymantrenylcarbinol, (V), as a yellow, low-melting crystalline material, m.p. 36-38°. (Found: C, 46.24; H, 3.02; Mn, 23.23; mol. wt. mass spectrometer, 234. C<sub>9</sub>H<sub>7</sub>MnO<sub>4</sub>; calcd.: C, 46.16; H, 2.99; Mn, 23.46%; mol. wt., 234.) The infrared spectrum exhibited the OH absorption band at 3620 cm<sup>-1</sup> and the metal carbonyl absorption at 2030 and 1940 cm<sup>-1</sup>.

(4) *Oxidation of formylcymantrene with Ag<sub>2</sub>O*

A solution made up of formylcymantrene (120 mg) silver oxide (prepared from 360 mg silver nitrate and 2 N sodium hydroxide solution), ethanol (20 ml) sodium hydroxide (150 mg) and water (20 ml) was refluxed for 7 h. After the addition of 40 ml of hot water, the reaction mixture was filtered and the filtrate was acidified with conc. hydrochloric acid solution. The acidified solution was extracted with ether and the ether extracts were washed with sodium carbonate solution. The ether layer gave, after evaporation, 20 mg of the starting aldehyde. The combined sodium carbonate washings were acidified and extracted with ether. Evaporation of the ether gave 82 mg (64%) of cymantrene carboxylic acid, (II), m.p. 195-197° (from dichloroethane)<sup>6,7</sup>.

Oxidation of formylferrocene (5 g) with silver oxide (prepared from 10 g silver nitrate) under the same conditions as described above yielded 4.4 g (82%) of ferrocenecarboxylic acid, m.p. 211-213°.

(5) *Condensation of formylcymantrene with malonic acid*

A solution of formylcymantrene (6.3 g, 0.027 mole), malonic acid (5.6 g, 0.054

mole) and a catalytic amount of piperidine in pyridine (20 ml) was heated on a water bath for 6 h. After cooling, the reaction mixture was mixed and stirred with dilute ammonium hydroxide and the aqueous layer collected by decantation. The operation with ammonium hydroxide was repeated several times until the aqueous solution was nearly colourless. The combined ammonium hydroxide washings were extracted with ether to remove non-acidic compounds and then were acidified with concentrated hydrochloric acid. A yellow precipitate (2.54 g, 48%) of cymantreneacrylic acid, (VII), was formed and collected by filtration. After crystallization from ethanol, (VII) had m.p. 217–219°. (Found: C, 48.05; H, 2.72; Mn, 20.14.  $C_{11}H_7MnO_5$  calcd.: C, 48.20; H, 2.57; Mn, 20.04%.)

The infrared spectrum (in KBr pellet) exhibited the following major bands: 2045 (vs), 1980–1940 (vs), 1685, 1632, 1438  $cm^{-1}$ .

#### (6) Preparation of cymantrenepropionic acid, (VIII)

The unsaturated acid, (VII), (2.5 g), obtained in reaction (5), dissolved in ethanol was reduced at room temperature with Raney nickel catalyst in the Parr hydrogenation apparatus for 6 h at 4–5 atmospheres pressure. After work-up in the usual manner, there was obtained 2.2 g (87%) of semi-solid material, which crystallized on standing. Sublimation gave the analytical sample, m.p. 99–100°. (Found: C, 47.93; H, 3.26; Mn, 19.42.  $C_{11}H_9MnO_5$  calcd.: C, 47.85; H, 3.29; Mn, 19.89%.)

The infrared spectrum showed, in addition to the metal carbonyl absorption bands in the 2000  $cm^{-1}$  region, the carboxylic carbonyl absorption band at 1723  $cm^{-1}$  and the disappearance of the carbon-carbon double bond absorption at 1632  $cm^{-1}$ .

#### ACKNOWLEDGEMENT

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#### SUMMARY

The synthesis of formylcymantrene (formylcyclopentadienyilmanganese tricarbonyl) is described. Oxidation, reduction and condensation reactions of formylcymantrene are reported.

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