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## SYNTHESIS OF [5]DIBENZENECHROMOCENOPHANE-2-CARBETHOXY-3-ONE BY DIECKMAN CONDENSATION OF BIS(ETHYL- $\beta$ -PHENYLPROPIONATE)CHROMIUM

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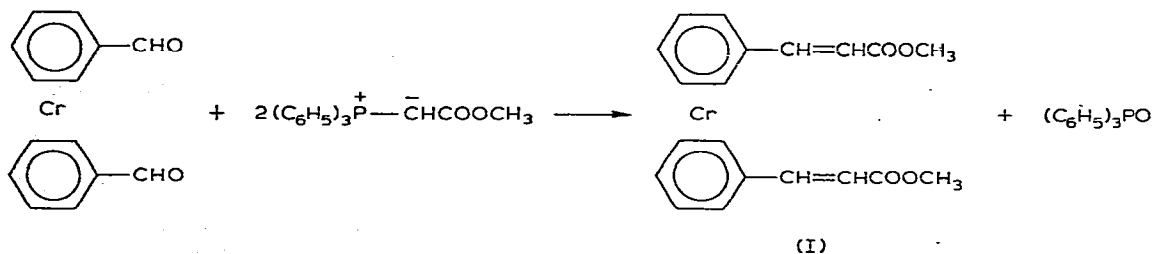
### Summary

Bis(methylcinnamate)chromium has been synthesized by condensation of bis(benzaldehyde)chromium and carbomethoxymethylenetriphenylphosphorane. [5]Dibenzenechromocenophane-2-carbethoxy-3-one has been prepared by Dieckmann condensation of bis(ethyl- $\beta$ -phenylpropionate)chromium.

Previously [1] we reported the synthesis of [4]dibenzenechromocenophane from 1,4-diphenylbutane and chromium vapour. We now report the preparation of [5]dibenzenechromocenophane-2-carbethoxy-3-one by Dieckmann condensation of bis(ethyl- $\beta$ -phenylpropionate)chromium.

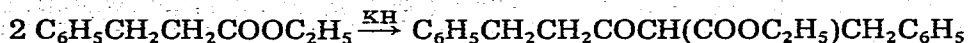
Two techniques were applied to synthesize bis(ethyl- $\beta$ -phenylpropionate)chromium: the reaction of atomic chromium with ethyl- $\beta$ -phenylpropionate [2] and hydrogenation of bis(ethylcinnamate)chromium [3]. The latter was prepared in a 60% yield by condensation of bis(benzaldehyde)chromium and ethyl acetate [4]. We also found that the Wittig reaction is a convenient route to chromium complexes of cinnamic acid esters. Condensation of bis(benzaldehyde)chromium and carbomethoxymethylenetriphenylphosphorane gives bis(methylcinnamate)chromium (I) in good yields:

The mass spectrum of I showed peaks at  $m/e$  376 (parent ion), 214 ( $P - L$ ),



162 (L) as well as the lower mass peaks due to breakdown of the ligand ion. Photolysis of I leads to methyl cinnamate\*.

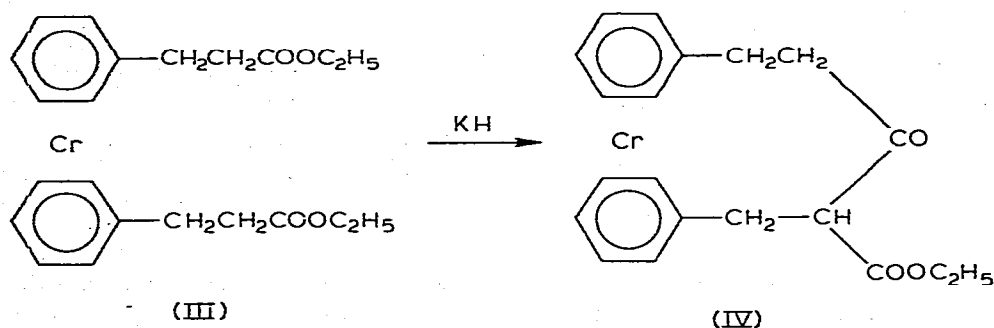
[5]Dibenzenechromocenophane was prepared by cyclization of bis(ethyl- $\beta$ -phenylpropionate)chromium with potassium hydride as condensing agent [5]. The reaction was first carried out with free ethyl- $\beta$ -phenylpropionate.



(II)

The quantitative yield of the  $\beta$ -ketoester II was obtained. The product was identified on the basis of the elemental analysis, proton NMR and mass spectrometric data. It is worthwhile mentioning that condensation of ethyl- $\beta$ -phenylpropionate in the presence of triphenylmethylsodium gives II in only 30% yield and that purification of the product from the latter reaction is a rather difficult task.

The chromium complex of ethyl- $\beta$ -phenylpropionate III reacts with potassium hydride to give [5]dibenzenechromocenophane-2-carbomethoxy-3-one (IV):



The mass spectrum of IV contained a low intensity parent ion ( $m/e$  362) and intense ions formed in fragmentation of the ligand.

Photolysis of the reaction product gave only II.

### Experimental

All the reactions and the isolation of bis(arene)chromium complexes were performed under argon; the solvents were distilled in argon flow. The alumina for chromatography was heated at  $150^\circ\text{C}$  under vacuum ( $10^{-3}$  mmHg) and deactivated with water (12% by weight). Tetrahydrofuran was refluxed and distilled over sodium benzophenone complex and redistilled over  $\text{LiAlH}_4$  prior to use. Reaction vessels were heated in argon flow.

Carbomethoxymethylenetriphenylphosphorane [6], bis(benzaldehyde)chromium [7], and bis(ethyl- $\beta$ -phenylpropionate)chromium iodide [2] were prepared as described in the literature cited.

\* I contained admixtures of  $\text{Ph}_3\text{PO}$  which could not be removed by the chromatography or crystallization techniques.

The mass spectra of I and II were recorded on an MKh-1303 mass spectrometer fitted with a direct inlet system. The ionizing voltage was 40 eV, the inlet system temperature was 20°C, and the ionizing chamber temperature was 150°C. The mass spectrum of the chromium complex IV was obtained on an AEJ MS-30/DS-50 instrument at 350°C. The ionizing chamber temperature was 300°C and the ionizing energy was 70 eV.

GLC of II and the photolysis products from IV was performed on a Pye Unicam 104 chromatograph at 200°C using a capillary column 70 m × 0.25 mm, the standard phase Silicon OV-101, and helium as gas carrier.

#### *Preparation of bis(methylcinnamate)chromium (I)*

A solution of bis(benzaldehyde)chromium (0.53 g, 2 mmol) and  $\text{Ph}_3\text{P}^+\text{CH}^-\text{COOCH}_3$  (1.34 g, 4 mmol) in 30 ml absolute benzene was refluxed for 6 h. The reaction mixture was then evaporated to half its initial volume and chromatographed on a column packed with  $\text{Al}_2\text{O}_3$ . Compound I (0.62 g, 92%) was eluted with a benzene/petroleum ether mixture. The product was deep red crystals, m.p. 122–123°C (crystallized from benzene/petroleum ether). Mass spectrum, *m/e* (relative intensities): 376 (<1%), 214 (27), 162 (40), 131 (83), 103 (67), 77 (100), 52 (53). The mass spectrum also contained the ions *m/e* 278 and 277 due to triphenylphosphine oxide admixtures.

The photolysis products from I (in  $\text{CHCl}_3$ ) contained methyl cinnamate (GLC and TLC,  $\text{Al}_2\text{O}_3$ , benzene/petroleum ether 2 : 1).

#### *Condensation of ethyl-β-phenylpropionate in the presence of KH*

Tetrahydrofuran (30 ml) and KH (90% purity, 0.4 g, 9 mmol) were introduced under argon into a four-necked flask connected to a buret. Argon flow was then stopped, and a solution of ethyl-β-phenylpropionate (1.38 g, 7.8 mmol) in 30 ml tetrahydrofuran was added with vigorous stirring over a period of 30 min. The mixture was stirred for one further hour until gas evolution ceased. 209 ml of hydrogen was evolved, and the solution formed was crimson coloured.

The solution was treated, under argon and with stirring, with  $\text{NH}_4\text{Cl}$  (2.7 g) in 20 ml  $\text{H}_2\text{O}$ . The organic products were extracted with benzene, and the benzene solution was washed with three portions of water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated to give II (1.18 g, 100%). After distillation (188–192°/4 mmHg) compound II was obtained in the form of an oily liquid (0.6 g, 50%). Analysis: Found: C, 77.84; H, 7.31.  $\text{C}_{20}\text{H}_{22}\text{O}_3$  calcd.: C, 77.42; H, 7.10%.

The  $^1\text{H}$  NMR spectrum showed a phenyl proton singlet at  $\delta = 7.00$  ppm, a methyl proton triplet centered at  $\delta = 0.94$  ppm, and a number of signals in the region of 2.56–4.05 ppm corresponding to the CH and  $\text{CH}_2$  protons. The peak area ratio was  $\text{C}_6\text{H}_5 : \text{CH}_3 : (\text{CH}_2 + \text{CH}) = 10 : 3 : 9$ . The mass spectrum, *m/e* (ion): 310 ( $\text{P}^+$ ), 177 ( $\text{C}_6\text{H}_5\text{CH}_2\text{CHCOOC}_2\text{H}_5^+$ ), 133 ( $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}^+$ ), 131 ( $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}^+$ ), 105 ( $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2^+$ ), 91 ( $\text{C}_6\text{H}_5\text{CH}_2^+$ ), and 77 ( $\text{C}_6\text{H}_5^+$ ).

#### *Preparation of bis(ethyl-β-phenylpropionate)chromium (III)*

Bis(ethyl-β-propionate)chromium(I) iodide was reduced with  $\text{Na}_2\text{S}_2\text{O}_4$  to a neutral complex in a weakly basic water/ethanol solution under argon ( $\text{NH}_4\text{OH}$  was added to maintain pH = 8). Benzene was distilled off, the residue was dis-

solved in petroleum ether and chromatographed on  $\text{Al}_2\text{O}_3$ . A small amount of free ethyl- $\beta$ -propionate was eluted with petroleum ether. III was eluted with benzene. According to the GLC data, photolysis of the complex (in  $\text{CHCl}_3$ ) gave pure ethyl- $\beta$ -phenylpropionate.

#### *Condensation of bis(ethyl- $\beta$ -phenylpropionate)chromium*

A solution of III (0.85 g, 2 mmol) in 55 ml tetrahydrofuran was added to a vigorously stirred suspension of KH (0.3 g, 7 mmol) in 100 ml tetrahydrofuran under argon during 30 min. The mixture was stirred until hydrogen evolution ceased (120 ml of  $\text{H}_2$  was evolved over a period of 8 h). During the reaction, colouration of the mixture changed from green-brown to orange. Hydrolysis and treatment of the reaction mixture were carried out as with II. The product was a deep red oily substance (0.63 g, 84%) \*. This was dissolved in benzene and chromatographed on  $\text{Al}_2\text{O}_3$  to give red-brown IV (0.25 g), m.p. 107–110°C. The mass spectrum of IV, *m/e* (relative intensities, %): 362(3), 177(5), 133(12), 131(22), 129(12), 105(33), 104(12), 103(15), 92(11), 91(100), 77(20), 65(17), 55(16), 52(2).

According to the GLC data, the photolysis products from IV (in  $\text{CHCl}_3$ ) contained only II.

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\* According to GLC of the photolysis products, the substance did not contain admixtures of the initial III.