

Journal of Organometallic Chemistry, 153 (1978) 181–186
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SYNTHESIS OF DIBENZENECHROMOCENOPHANES FROM α,ω -DIPHENYLALKANES AND CHROMIUM VAPOUR

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(Received January 10th, 1978)

Summary

Complexes of the composition $[\text{C}_6\text{H}_5(\text{CH}_2)_n\text{C}_6\text{H}_5]\text{Cr}$ having the structure of [4]- and [5]-dibenzenechromocenophanes, $[\text{C}_6\text{H}_5(\text{CH}_2)_n\text{C}_6\text{H}_5]_2\text{Cr}$, and $[\text{C}_6\text{H}_5(\text{CH}_2)_4\text{C}_6\text{H}_5]_3\text{Cr}_2$ ($n = 4, 5$) have been isolated from reactions of chromium vapour with 1,4-diphenylbutane and 1,5-diphenylpentane.

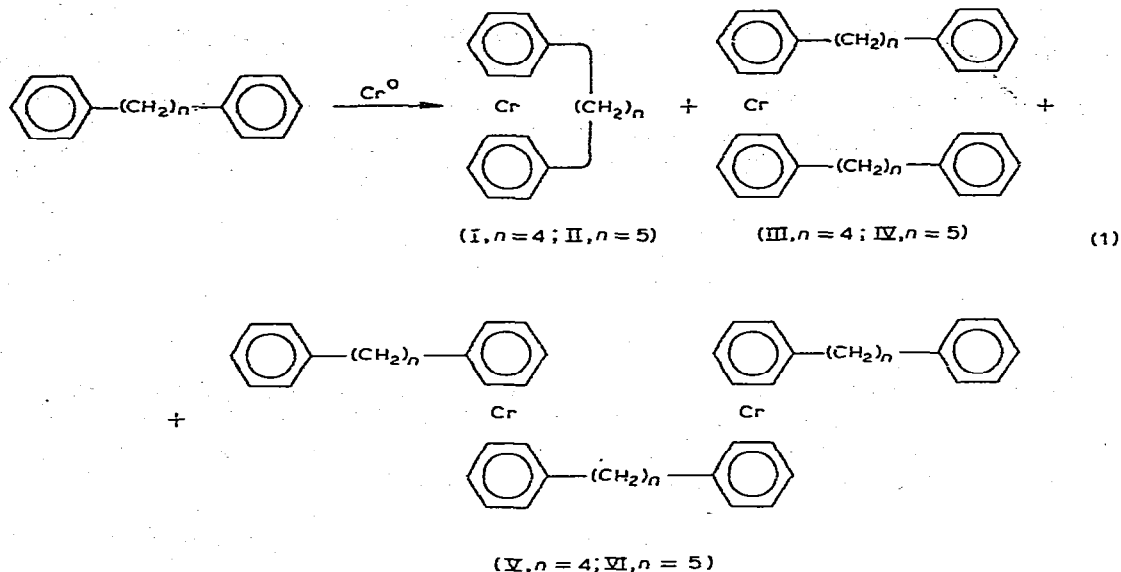
Introduction

A large number of ferrocenophanes, ferrocene derivatives containing one, two, or three bridges of various lengths linking two cyclopentadienyl rings have already been described [1]. Only two bridged compounds are known in the dibenzenechromium series. β,γ -Diphenyl-1,1'-tetramethylenedibenzenechromium was prepared from *trans*-stilbene, chromium chloride and triethylaluminium [2]; 1,1'-trimethylenedibenzenechromium was also reported, however, without any synthetic details [3].

The direct synthesis of dibenzenechromocenophanes from α,ω -diphenylalkanes is of considerable interest. So far, bis(arene)chromium complexes have mostly been synthesized by reactions of arenes with chromium chloride, aluminium chloride, and aluminium metal powder [4]. This technique is inapplicable with dibenzenechromocenophane because of diverse isomerisation and realkylation processes occurring under the reaction conditions. Thus, the reaction with 1,4-diphenylbutane leads to bis(tetralin)chromium and benzene(tetralin)chromium [5]. The method of low-temperature synthesis of bis(arene)chromium complexes from arenes and chromium vapour [6,7] offers in principle the possibility of a one-step route to dibenzenechromocenophanes.

Results and discussion

α,β -Diphenylalkanes 1,4-diphenylbutane and 1,5-diphenylpentane react with chromium vapour under the conditions described earlier for the synthesis of certain dibenzenechromium derivatives [8,9] to give mixtures of bis(arene)-chromium complexes I–VI (eq. 1). After oxidation with atmospheric oxygen, the products are isolated in the form of iodides of the corresponding cations Ia–VIa (eq. 2). The product mixtures can be separated by preparative thin layer chromatography (TLC) of the iodides or by vacuum distillation of the neutral complexes obtained by reduction of the iodides (eq. 3).



Chromatography of the iodides on Al_2O_3 leads to partial replacement of I^- with some other anions (probably OH^- , OR^-). Thus, a cationic form of the diphenylbutane complex III (IIIb) containing no iodine was isolated. This gave the iodide IIIa on treatment with KI.

The structures of the compounds isolated were proved by elemental analyses, EPR spectra of the iodides, and mass spectra of the neutral complexes.

The analytical data, melting (decomposition) points, and R_f values (TLC on Al_2O_3 in the system acetone : ethanol 3 : 1) for the iodides Ia–Va are listed in Table 1.

Nine of 11 lines from benzene ring protons with splittings of 3.5 ± 0.2 G were identified in the EPR spectra of bis(arene)chromium iodides Ia–IVa. Splitting from the ^{53}Cr nucleus was of 18.5 ± 0.2 G in Ia, IIIa, and IVa, and of 17 ± 0.2 G in IIa. The EPR spectra were on the whole similar to those described for bis-

TABLE 1

MELTING OR DECOMPOSITION POINTS, R_f VALUES, AND ANALYTICAL DATA OF BIS(ARENE)-CHROMIUM IODIDES

Compound	Melting or decomposition point (°C)	R_f	Analyses: found (calcd.) (%)			
			C	H	Cr	I
Ia	dec. 156–160	0.39	49.06 (49.35)	4.57 (4.63)	13.66 (13.37)	30.72 (32.65)
IIIa	dec. 154–158	0.53	64.15 (64.11)	6.27 (6.01)	8.64 (8.68)	20.85 (21.20)
Va	m.p. 138–140	0.25	58.43 (58.30)	5.83 (5.47)	10.18 (10.53)	24.34 (25.71)
IIa	dec. 167–170	0.48	50.41 (50.62)	5.15 (4.96)	13.07 (12.90)	29.98 (31.51)
IVa	dec. 140–142	0.80	65.10 (65.07)	6.98 (6.38)	8.50 (8.29)	19.52 (20.26)

(arene)chromium complexes earlier [10–12].

The diphenylbutane complex iodides Ia and IIIa were reduced and the neutral complexes I and III were studied mass-spectrometrically. The mass spectrum of I contained the molecular ion (m/e 262), the fragment ion formed by the loss of two methylene groups from the molecular ion (m/e 234), and also the ligand ion (m/e 210) and the ions due to breakdown of the latter. No molecular ion was observed in the mass spectrum of III where the heaviest ion corresponded to the elimination of one ligand grouping from the parent ion.

The mass spectrum of I and the results of ebullioscopic molecular weight measurements of the iodide Ia [13] confirm the monomer bridged structure. The final proof of the bridged structure of Ia was obtained by the X-ray structure determination.

Reactions of α,ω -diphenylalkanes with atomic chromium lead predominantly to complexes containing two ligands attached to one metal atom (III, IV) and dinuclear complexes (V, VI). Dibenzenechromocenophanes (I, II) are only formed in poor yields. Nevertheless, the method described may prove of preparative utility as a one-step route to compounds of this type.

It should be noted that Gladysz et al. [14] have observed only bis(h° -1,4-diphenylbutane)chromium (III) in the reaction of 1,4-diphenylbutane with chromium vapour with no evidence (^{13}C NMR) for ladder polymers or [4]dibenzenechromocenophane (I).

Experimental

The mass spectra were obtained on an MKh-1303 instrument equipped with a direct inlet system. The conditions were: ionizing energy 40 eV, ion chamber temperature 150°C, inlet temperature 20°C (I) and 50°C (III).

The EPR spectra were registered on a Varian E-12 radiospectrometer at a 9300 MHz frequency at 20°C (complexes IIa–IVa) or –20°C (Ia). Samples were solutions in absolute ethanol.

1,4-Diphenylbutane was prepared by catalytic hydrogenation of diphenyl-

butadiene obtained from phenylacetylene by oxidative condensation in the presence of $\text{CuCl} \cdot \text{TMEDA}$ [15], 1,5-Diphenylpentane was prepared by catalytic hydrogenation of dibenzalacetone to 1,5-diphenylpentanol-3 followed by oxidation of the latter with pyridinium chlorochromate to the corresponding ketone. The oxidation was carried out as recommended for primary and secondary alcohols [16]. 1,5-Diphenylpentanone-3 was then reduced according to Clemmensen.

I. Synthesis of initial α, ω -diphenylalkanes

(1) Preparation of 1,4-diphenylbutane

Hydrogenation of diphenylbutadiene (29.4 g, 0.146 mol) dissolved in 200 ml methanol was carried out in a rotating autoclave in the presence of 4 g skeletal nickel at 50°C for 6 h. The initial H_2 pressure was 100 atm. The solvent was then distilled off and the residue was recrystallized from petroleum ether to give 1,4-diphenylbutane (20 g, 67%). Repeated crystallization from CCl_4 gave a product having a m.p. $51.5\text{--}52.5^\circ\text{C}$ (lit., $52\text{--}52.5^\circ\text{C}$ [17]).

(2) Preparation of 1,5-diphenylpentane

(a) Preparation of 1,5-diphenylpentanol-3. Dibenzalacetone (46.8 g, 0.2 mol) in 300 ml methanol reacted with H_2 (initial pressure 150 atm) over skeletal nickel in an autoclave (130°C , 6 h) to give, after evaporation of the solvent and distillation of the residue at $219\text{--}220^\circ\text{C}/22$ mmHg, 1,5-diphenylpentanol-3 (36.7 g, 76%), m.p. 44°C (from hexane) (lit., $47\text{--}48^\circ\text{C}$ [18]).

(b) Preparation of 1,5-diphenylpentanone-3. 1,5-Diphenylpentanol-3 (12 g, 0.05 mol) in 30 ml CH_2Cl_2 was added to a stirred suspension of $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$ (16.2 g, 0.075 mol) in 100 ml CH_2Cl_2 . In 1.5 h, the solution was decanted and the residue was extracted with ether. Chromatography of the solutions on Al_2O_3 gave a colourless oily liquid (eluted with ether, 11.5 g, 96%), b.p. $209\text{--}211^\circ\text{C}/14$ mmHg (lit., $225^\circ\text{C}/15$ mmHg [19]).

(c) Preparation of 1,5-diphenylpentane. Zinc amalgam was made from 100 g zinc metal powder, 5 g HgCl_2 , 5 ml concentrated HCl , and 100 ml water. The mixture was stirred for 10 min, the solution was then decanted, and 75 ml H_2O , 100 ml HCl , and 50 g 1,5-diphenylpentanone-3 were added to the amalgam. The mixture was refluxed for 10 h while adding portions of HCl (a total of 150 ml). The oily layer was separated, neutralized with an aqueous solution of Na_2CO_3 , and extracted with ether. The solvent was evaporated and the residue was distilled at $188\text{--}193^\circ\text{C}/15$ mmHg. The product was chromatographed on Al_2O_3 (eluent petroleum ether) and redistilled at $148\text{--}150^\circ\text{C}/3$ mmHg (lit., b.p. $187\text{--}189^\circ\text{C}/10$ mmHg [20]) to give 1,5-diphenylpentane in the yield of 91% (42.9 g).

II. Synthesis of bis(arene)chromium complexes from α, ω -diphenylalkanes and chromium vapour

The reactions were run in a stainless steel vessel cooled with liquid nitrogen under high vacuum (10^{-5} mmHg) [8]. Chromium metal (1–2 g) was placed into a vaporizer; simultaneously, a solution of an α, ω -diphenylalkane in decane (ca.

20 g in 70 ml) was introduced in portions into the reaction vessel. The reactions took 2 to 3 h. The mixtures were then allowed to warm up to room temperature. The vessel was filled with gaseous nitrogen, and the products were extracted with benzene. Air was bubbled through the benzene solution in the presence of a small amount of water. The layers were then separated and unreacted diphenylalkane was recovered from the benzene layer. The water layer, after treatment with dry KI and extraction with chloroform, gave mixtures of bis(arene)chromium iodides.

Two techniques were applied to separate the product mixtures. The first one was thin layer chromatography separation of iodides on Al_2O_3 in an acetone/ethanol system. This technique provided a ready separation of L_2CrI^* , while isolation of LCrI and $\text{L}_3\text{Cr}_2\text{I}_2$ required repeated chromatographing. According to the other procedure, iodide mixtures were reduced, the volatile products of the composition LCr and, partly, L_2Cr were distilled off under vacuum, oxidized and investigated as iodides. The residue contained L_2Cr , L_3Cr_2 and the higher oligomers.

All experiments with neutral bis(arene)chromium complexes were carried out under argon; the solvents were distilled in an argon stream. Alumina for chromatography of neutral complexes was heated at $140^\circ\text{C}/10^{-3}$ mmHg for 3 h and then deactivated by the addition of water (12 weight %) distilled under argon.

(1) Reaction of chromium vapour with 1,4-diphenylbutane

(a) 4.3 g of a mixture of bis(arene)chromium iodides from two reaction runs were chromatographed in a 3 : 1 acetone/ethanol mixture. The individual products were extracted with ethanol and crystallized from methanol. The products Ia, IIIa, and Va were isolated in amounts of 0.25, 1.26, and 0.66 g, respectively. In addition to these three iodides, a cationic complex IIIb (0.42 g) containing no iodine ($R_f = 0.45$) was isolated. Compound IIIb gave IIIa under the action of KI in aqueous solution or after reduction followed by oxidation and treatment with KI (identified by TLC). Some of the reaction products having low R_f values remained unseparated.

(b) A solution of iodide mixture (1.25 g) prepared from diphenylbutane was stirred with $\text{Na}_2\text{S}_2\text{O}_4$ (1.5 g), KOH (1 g), H_2O (25 ml), and methanol (5 ml) in the presence of 50 ml benzene until discolouration of the aqueous layer occurred. The green-brown organic layer was decanted and the aqueous layer was extracted with two portions of benzene. The benzene solutions were evaporated in an Ar stream, and the residue was distilled under vacuum (1×10^{-3} mmHg, bath temperature 140°C). The distillate was pure III. The residual product was a mixture of several compounds including III and V (identified by TLC in the form of the iodides).

(c) Preparation of 1,1'-tetramethylenedibenzenechromium (I). I was obtained in the form of a golden brown solid by reduction of Ia under the conditions described above. Mass spectrum, m/e (relative intensities (%)): 262(8), 234(2), 210(28), 117(18), 105(12), 104(17), 92(51), 91(100), 78(8), 77(7), 65(12), 57(12), 52(12).

* $\text{L} = \text{C}_6\text{H}_5(\text{CH}_2)_n\text{C}_6\text{H}_5$ ($n = 4, 5$).

(d) *Preparation of bis(*h*⁶-1,4-diphenylbutane)chromium (III)*. Reduction of IIIa (0.45 g) gave III (0.31 g, 89%) in the form of a green-brown oil. Mass spectrum, *m/e* (relative intensities (%)): 262 (<1), 210(11), 117(13), 105(12), 104(15), 92(55), 91(100), 78(50), 77(60), 52(82).

(2) *Reaction of chromium vapour with 1,5-diphenylpentane*

2.16 g of iodide mixture obtained from diphenylpentane and chromium was reduced as described above, the solution was evaporated and the residue was distilled at 80–86°C/2 × 10⁻⁴ mmHg to give 0.1 g of viscous brown oil. The product was oxidized and isolated in the form of an iodide mixture. Separation of the latter by TLC gave IIa (0.04 g) and IVa (0.05 g).

The nonvolatile residue (1.2 g) was dissolved in petroleum ether, and chromatographed on a column packed with Al₂O₃ under argon. Compound IV (0.45 g) was eluted with petroleum ether/benzene (identified by TLC in the form of the iodide IVa).

Acknowledgement

The authors wish to thank N.I. Vasyukova for the mass spectra and S.P. Solodovnikov and A.I. Prokof'ev for the EPR spectra.

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