

COORDINATION SYNTHESIS ON METAL CENTERS

II*. REACTION OF σ -BONDED ORGANOCHROMIUM COMPOUNDS WITH CARBON MONOXIDE, SOME KETONES, AND A β -DIKETONE

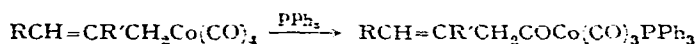
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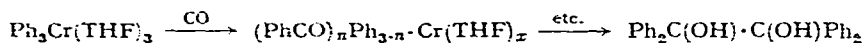
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Previous work on the reactions of σ -bonded organochromium compounds with disubstituted acetylenes² has led to the conclusion that these could be rationalized¹ on the assumption that the organochromium compound acted as a coordination center for these syntheses. In some cases the group attached to chromium participated in the formation of the products. This concept has also been used in interpreting² the course of the Job-Cassal reaction³. It was therefore of interest to study the reaction of σ -bonded organochromium compounds with carbon monoxide and some ketones.

In tetrahydrofuran, carbon monoxide reacts smoothly with solvated triphenylchromium to give an almost quantitative yield (based on phenyl groups introduced) of *benzopinacol*. This result contrasts sharply with the product mixture², consisting of some fourteen organic compounds, chromium hexacarbonyl and τ -bis-arene-chromium complexes, obtained when carbon monoxide is passed through a *reacting solution* of phenylmagnesium bromide and chromium(III) chloride (Job-Cassal conditions). In analogy to the "carbonyl insertion" reactions undergone by other organometallic compounds, for instance⁴:



it is suggested that the initial step is "carbonyl insertion" to give a species containing one or more "benzoyl groups" coordinated to chromium. In an intra- or intermolecular reaction two of these "benzoyl groups" can dimerize and undergo phenylation to benzopinacol.

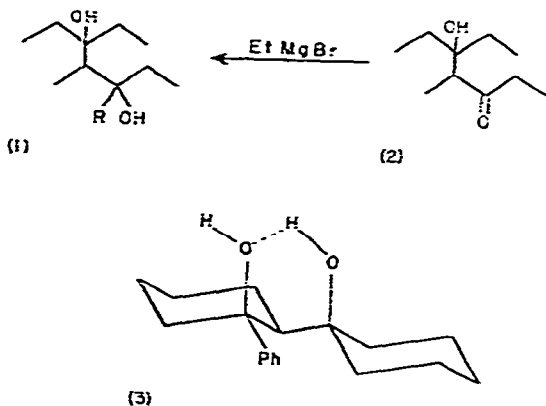


Triethylchromium undergoes reaction with diethyl ketone, both when the latter is present in the stoichiometric quantity or in excess to give triethylcarbinol and a compound, $\text{C}_{12}\text{H}_{26}\text{O}_2$. The latter underwent acid cleavage to diethyl ketone, identified as its 2,4-dinitrophenylhydrazone. This reaction, which is typical of 1,3-diols^{5,6} suggested that the substance is 4-methyl-3,5-diethyl-3,5-heptanediol [(I), $\text{R} = \text{CH}_2\text{CH}_2$]. This was confirmed by a direct comparison with an authentic specimen

* For Part I, see ref. 1.

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prepared by the action of ethylmagnesium bromide on the known 3-ethyl-3-hydroxy-4-methyl-5-heptanone⁷ (2).



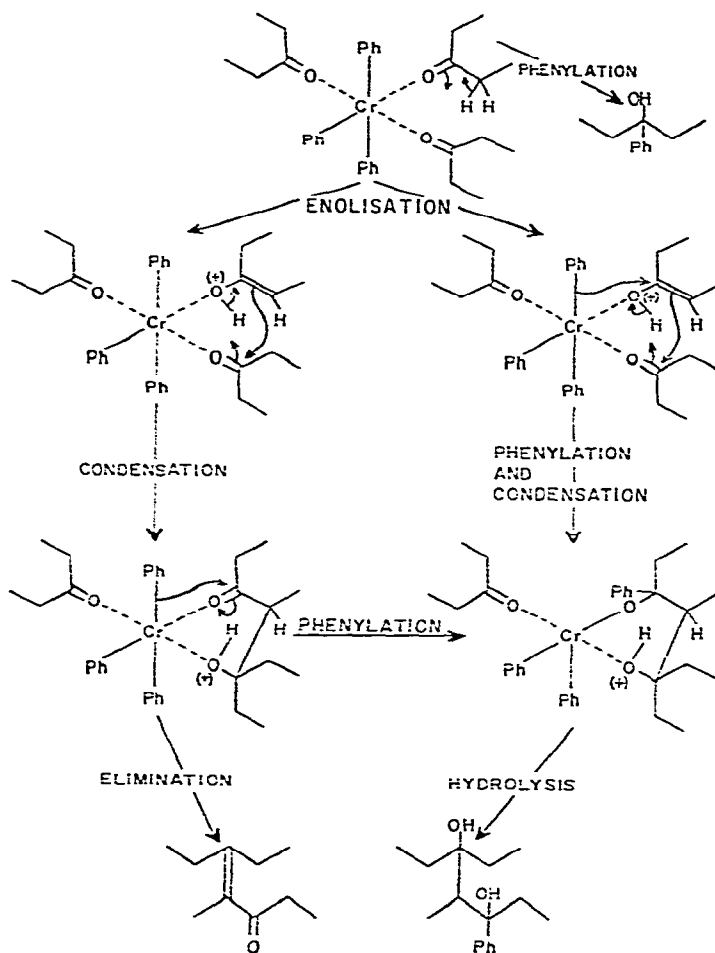
In tetrahydrofuran, solvated triphenylchromium acts upon diethyl ketone to give, phenyldiethylcarbinol and a crystalline diol, $\text{C}_{16}\text{H}_{26}\text{O}_2$; no π -bis-arene-chromium complex was formed. The crystalline diol underwent acid cleavage to propiophenone, identified as its 2,4-dinitrophenylhydrazone; its infra-red spectrum indicated the presence of strongly hydrogen-bonded hydroxyl groups and at least one aromatic ring; its very complex NMR spectrum showed the presence of aromatic protons ($\delta = 7.25$, multiplet), a single proton (O-H) ($\delta = 3.35$, singlet), methylene groups ($\delta = 1.3$ to 2.5, multiplet), and methyl groups ($\delta = 0.3$ to 1.3, multiplet). All the above data confirm that the diol is in fact 5-ethyl-4-methyl-3-phenyl-3,5-heptanediol [(1), $\text{R} = \text{C}_6\text{H}_5$]. In this reaction almost all the phenyl groups present in the original triphenylchromium are accounted for in the products.

Solvated triphenylchromium undergoes reaction with cyclohexanone, in tetrahydrofuran solution, to give: (i) 1-phenylcyclohexanol, identified by a direct comparison with an authentic specimen, (ii) a crystalline diol $\text{C}_{13}\text{H}_{26}\text{O}_2$, and (iii) 2-cyclohexenylcyclohexanone; no π -bis-arene-chromium complex was formed. In analogy with the foregoing reactions, the diol is probably 1-phenyl-2-(1-hydroxycyclohexyl)-cyclohexanol. This structure is supported by the NMR and infra-red spectra (see EXPERIMENTAL). Furthermore, since the absorption bands due to hydrogen-bonded and non-hydrogen-bonded hydroxyl groups (3460 and 3605 cm^{-1}) are present even in very dilute solution, the diol has probably the conformation shown in (3). Again in this reaction, almost all the phenyl groups present in the original triphenylchromium are accounted for in the products.

The above results clearly illustrate the difference between the reactions of organomagnesium and organochromium compounds. The former can act either as a source of alkyl or aryl groups, *i.e.* with ketones they give⁸ the corresponding carbinols or they can act as conventional organic bases, *i.e.* they effect the self-condensation⁹ of ketones. The organochromium compounds on the other hand not only bring about the self-condensation of the ketone but also act, at the same time, as a source of alkyl or aryl groups. Thus in the experiment with cyclohexanone, the formation of 2-cyclohexenylcyclohexanone is evidence of the organochromium compound acting as a

"coupling center". The fact that in the same reaction, all the phenyl groups introduced in the organochromium compound can be accounted for in the final products, indicate that this coupling is not promoted by the organochromium compound acting as a conventional organic base, but rather that it is the *chromium itself* which acts as a *coupling center*. Finally the formation, in the same experiment, of 1-phenyl-2-(1-hydroxycyclohexyl)cyclohexanol is clear evidence that triphenylchromium can act, at the same time, both as a *coupling center* and as a *phenylating agent*.

The formation of all the above reaction products can be rationalized by assuming a stepwise replacement of the tetrahydrofuran coordinated to chromium by the ketone, followed by either alkylation or arylation, or coupling followed by alkylation



or arylation, as shown above. Thus when no coupling occurs, phenylation or ethylation gives the observed carbinols. Coupling of two molecules of ketone complexed to chromium occurs with either simultaneous or subsequent phenylation or ethylation giving the observed diols.

In tetrahydrofuran solution, triphenylchromium was smoothly hydrolyzed by acetylacetone (a 1,3-diketone) to give finally chromium tris(acetylacetonate) in 75% yield.

EXPERIMENTAL

All operations were carried out under pure dry nitrogen. Diethyl ether and tetrahydrofuran were freshly distilled from lithium aluminum hydride. NMR spectra are for CDCl_3 solutions; the chemical shift δ , in ppm, is based on $\delta(\text{CH}_3)_4\text{Si} = 0$ in CDCl_3 . The chromium trichloride tristetrahydrofuranate [hereafter referred to as $\text{CrCl}_3(\text{THF})_3$] was prepared as already described⁹.

Triphenylchromium and carbon monoxide, in tetrahydrofuran

A slow stream of carbon monoxide was bubbled through a stirred solution of triphenylchromium tristetrahydrofuranate¹⁰ (from CrCl_3 , 6.0 g, 37.9 mmoles and PhMgBr , 105 mmoles, 112.4 ml of 0.935 *N* tetrahydrofuran solution) in tetrahydrofuran at room temperature. Within 10 min the temperature had risen to 42°. After 2 h the carbon monoxide stream was stopped and the solvent removed by distillation under reduced pressure. The dark crystalline product was hydrolyzed with water, filtered, and both the residue and the aqueous layer were extracted with ether. The aqueous layer, on treatment with sodium tetraphenylboron gave a small quantity of a mixture of π -benzene- π -biphenyl-chromium(I)- and π -bis-benzene-chromium(I)-tetraphenylboron¹⁰, identified by infrared spectroscopy. The dried ethereal layer was filtered through charcoal, evaporated, and the residue crystallized from isooctane to give benzopinacol (8 g, 21.8 mmoles) m.p. and mixed m.p. 183–185°. Attempted sublimation of the crude product, obtained in the above reaction, resulted in decomposition to benzophenone, characterized as its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 240–241°.

Triethylchromium¹¹ and diethyl ketone, in tetrahydrofuran

(a) *Molecular ratio 1:3.* Diethyl ketone (25.8 g, 300 mmoles) was added (15 min) to a solution of triethylchromium¹¹ (from CrCl_3 , 19 g, 120 mmoles and $\text{C}_2\text{H}_5\text{MgBr}$ 300 ml in tetrahydrofuran) in tetrahydrofuran (500 ml), at -20°. After 1 h at -20° to 0°, the reaction mixture was warmed to room temperature and allowed to stand for three days. The solvent was removed by distillation and the product hydrolyzed with water, filtered, and both the residue and the filtrate washed thoroughly with ether. Treatment of the aqueous layer with sodium tetraphenylboron gave no π -bis-arene-chromium(I)-tetraphenylboron salts. The dried ethereal layer was evaporated and the residue separated by distillation; the volatile fraction, b.p. up to 90°/17 mm was shown by gas-chromatographic analysis to consist of diethyl ketone (3.06 g, 35.7 mmoles) and triethylcarbinol (8.63 g, 74.5 mmoles). The partly crystalline residue (3.7 g) was recrystallized from pentane to give 4-methyl-3,5-diethyl-3,5-heptanediol (0.25 g, 1.23 mmoles) m.p. and mixed m.p. 135–137°.

(b) *Molecular ratio 1:6.* In an identical experiment with 51.6 g (600 mmoles) of diethyl ketone, the products were: (i) diethyl ketone (9.84 g, 114 mmoles) and triethylcarbinol (7.46 g, 64.5 mmoles), identified and estimated by vapor phase chromatography, (ii) 4-methyl-3,5-diethyl-3,5-heptanediol (0.2 g, 1.0 mmoles), m.p. and mixed m.p. 135–137°.

Synthesis of 4-methyl-3,5-diethyl-3,5-heptanediol

3-Ethyl-3-hydroxy-4-methyl-5-heptanone⁷ (8.1 g, 47 mmoles) was added dropwise to an ethereal solution of ethylmagnesium bromide (200 mmoles). Following the addition, the reaction mixture was heated under reflux for 3 h, cooled and hydrolyzed with ammonium chloride. The organic product, isolated with the aid of ether gave upon distillation: (i) triethylcarbinol (3.5 g), b.p. 44–45°/12 mm, (ii) 3-ethyl-3-hydroxy-4-methyl-5-heptanone (1.8 g), b.p. 98–99°/12 mm, (iii) a residue, which crystallized from pentane to give 4-methyl-3,5-diethyl-3,5-heptanediol, (0.124 g) as colorless needles m.p. 136–137°. (Found*: C, 71.0; H, 13.1; mol. wt., 228.0. C₁₂H₂₆O₂ calcd.: C, 71.2; H, 12.9%; mol. wt., 202.3.)

Acid cleavage of 4-methyl-3,5-diethyl-3,5-heptanediol

The crystalline diol, C₁₂H₂₆O₂ (0.15 g), suspended in dilute sulfuric acid, was heated under reflux for 1 h. After addition of ethanol (5 ml), the cool solution was poured into excess 2,4-dinitrophenylhydrazine sulfate also in ethanol. The crude derivative on crystallization gave the 2,4-dinitrophenylhydrazone of diethyl ketone, m.p. and mixed m.p. 153–156°.

Triphenylchromium tristetrahydrofuranate with diethyl ketone

A briskly stirred suspension of triphenylchromium tristetrahydrofuranate, from CrCl₃(THF)₃ (16 g, 42.5 mmoles) suspended in tetrahydrofuran (500 ml) and phenylmagnesium bromide (140 ml, 129 mmoles), in tetrahydrofuran at –30°, was treated dropwise with freshly distilled diethyl ketone (20 ml, 188 mmoles). The reaction mixture was then allowed to warm up to room temperature. After 2 h at 20°, the solvent was removed by distillation under reduced pressure and the product hydrolyzed with water, filtered, both the residue and the filtrate being washed with ether. Treatment of the aqueous layer with sodium tetraphenylboron gave no π -bis-arene-chromium(I)-tetraphenylboron salts. The dried ethereal layer, was evaporated and the residue (21.2 g) separated by distillation. The volatile component, b.p. 57–62°/0.01 mm, (14.9 g, 90 mmoles) was shown to be phenyldiethylcarbinol by a direct comparison of its infra-red spectrum with that of an authentic specimen. The semi-crystalline residue (5.87 g) was chromatographed to give traces of oily products and 5-ethyl-4-methyl-3-phenyl-3,5-heptanediol, m.p. 90–92°, from hexane, (5.36 g, 21.4 mmoles). (Found**: C, 76.5; H, 10.4; mol. wt., 252. C₁₆H₂₆O₂ calcd.: C, 76.75; H, 10.5%; mol. wt., 250.) ν in KBr: 3300 (OH), 1600, 1500, 765, 705 (Ph–), 1475–1450, 1435, 1375 cm⁻¹ (CH, CH₂, CH₃).

Acid cleavage of 5-ethyl-4-methyl-3-phenyl-3,5-heptanediol

The crystalline diol, C₁₆H₂₆O₂, (0.5 g) was added to a solution of 2,4-dinitrophenylhydrazine (0.5 g) in methanolic sulfuric acid (15 ml). The resulting solution was heated on the water bath for 5 min and allowed to stand at 20° for 5 h, poured into water, and the product isolated with the aid of chloroform. Chromatography of the crude derivative on silica gel gave the 2,4-dinitrophenylhydrazone of propiophenone (0.1 g), m.p. 192–195°, from ethyl acetate, undepressed on admixture with an authentic specimen.

* Microanalysis by Schwartzkopf Microanalytical Lab., Woodside 77, New York (U.S.A.).

** Microanalysis by A. Peisker, Brugg/AG., Switzerland.

Triphenylchromium tristetrahydrofuranate with cyclohexanone

Cyclohexanone (35 ml, 335 mmoles) was added to a briskly stirred suspension of triphenylchromium tristetrahydrofuranate [from $\text{CrCl}_3(\text{THF})_3$ (16 g, 42.5 mmoles), and phenylmagnesium bromide (200 ml, 129 mmoles) in tetrahydrofuran] in tetrahydrofuran at -30° . When the addition was complete, the reaction mixture was heated and stirred at 30° for 7 h. The solvent and unreacted cyclohexanone were removed by distillation at $20^\circ/0.01$ mm, the syrupy residue triturated with dilute sulfuric acid, and the organic material isolated with the aid of ether. Chromatography of this crude product (35 g) gave the following compounds. (i) Biphenyl (0.7 g, 4.55 mmoles), m.p. and mixed m.p. $69-70^\circ$. (ii) Substantially 2-cyclohexenylcyclohexanone, b.p. $80^\circ/0.01$ mm, (6.1 g, 34.2 mmoles). (Found*: C, 80.2; H, 10.05. $\text{C}_{12}\text{H}_{18}\text{O}$ calcd.: C, 80.85; H, 10.2%) λ_{max} in EtOH 235μ , ϵ 645; the infra-red spectrum was identical to that of an authentic specimen. The semicarbazone, m.p. $189-190^\circ$ (from ethyl acetate), was likewise identical with an authentic specimen, m.p. and mixed m.p. $189-190^\circ$. (Found*: C, 66.2; H, 9.1; N, 17.8. $\text{C}_{13}\text{H}_{21}\text{N}_3\text{O}$ calcd.: C, 66.35; H, 9.0; N, 17.9%) (iii) 1-Phenylcyclohexanol (12.1 g, 68.8 mmoles), m.p. and mixed m.p. $61-63^\circ$; the authentic specimen was prepared by the action of phenylmagnesium bromide on cyclohexanone. (iv) 1-Phenyl-2-(1-hydroxycyclohexyl)cyclohexanol, m.p. $114-116^\circ$, (from hexane) (9.03 g, 32.8 mmoles), (Found*: C, 78.8; H, 9.5, mol. wt., 288. $\text{C}_{15}\text{H}_{26}\text{O}_2$ calcd.: C, 78.8; H, 9.55%; mol. wt., 274.4.) ν_{max} in Nujol: 3320 (bonded OH), $1600, 1495, 750, 700 \text{ cm}^{-1}$ (Ph-); ν_{max} in CCl_4 $3605, 3460 \text{ cm}^{-1}$ (free and bonded OH); δ 7.4 (m, C_6H_5 -), δ 1.5 (m, alicyclic protons).

Triphenylchromium tristetrahydrofuranate with acetylacetone

Redistilled acetylacetone (34 ml, 340 mmoles) was added to a briskly stirred suspension of triphenylchromium tristetrahydrofuranate [from $\text{CrCl}_3(\text{THF})_3$ (16 g, 42.5 mmoles), and phenylmagnesium bromide (203 ml, 129 mmoles) in tetrahydrofuran] in tetrahydrofuran at -30° . After the addition the reaction mixture was allowed to warm to 20° , during which time the color changed from purple to green. After 2 h at 20° , the solvent and some of the excess acetylacetone were removed by distillation under high vacuum at 20° , and the residue hydrolyzed. At this point the color changed from green to deep purple and the product, isolated with the aid of benzene, was crystallized from benzene/hexane to give chromium tris(acetylacetonate) as deep purple crystals (11 g, 31.6 mmoles), m.p. $213-215^\circ$, undepressed on admixture with an authentic specimen¹². The infra-red spectrum of this substance was superposable on that of an authentic specimen¹².

ACKNOWLEDGEMENTS

We wish to thank Dr. A. FLAM of Emser Werke A.G., Switzerland for a generous specimen of authentic 2-cyclohexenylcyclohexanone. We also wish to express our sincere thanks to Mr. W. S. COAKLEY and his associates of the Monsanto Company Research Center, St. Louis (U.S.A.) for the NMR spectra.

* Microanalysis by A. Peisker, Brugg/AG., Switzerland.

SUMMARY

The products formed by the action of solvated triphenylchromium on carbon monoxide, diethyl ketone, cyclohexanone, and acetylacetone, and by the action of solvated triethylchromium with diethyl ketone, have been isolated and identified. A mechanism involving coordination synthesis on chromium centers is suggested to explain the formation of the observed products.

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