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A DIRECT AND EFFICIENT COMPLEXATION OF SOME INDENES AND DIHYDRONAPHTHALENES WITH (NH₃)₃Cr(CO)₃

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Summary

In contrast to hexacarbonylchromium, tricarbonylchromiumtriammine (I) readily yields complexes of some indenes and dihydronaphthalenes. A high yield and reproducible preparation of I is described.

No efficient method of preparing indenic and dihydronaphthalenic tricarbonylchromium complexes is currently available. The complexation with $Cr(CO)_6$ requires high reaction temperatures (140, 160°C), long reaction times (48 to 72 h) and complex apparatus [1] to avoid sublimation of the reagent. Furthermore, the complexes are usually obtained in poor yields. For example, complex II is obtained in only 7% yield [2] while the starting material is partially polymerized. Recently, Khand et al. [3] have described a technique using a mixture of dibutyl ether with sufficient THF to "catalyse" the reaction and to wash back most of the $Cr(CO)_6$ which sublimes into the condenser. With this method the authors produce complexes of aromatic compounds bearing an unsaturated side chain; for example, indenetricarbonylchromium (reaction time 24 h, yield 69%, m.p. 92–94°C) and styrenetricarbonylchromium (70 h, 52%, 78°C).

In order to prevent the polymerisation, we can also use precursors of the complexes [4]. Then, a multistep sequence involving supplementary cautions (inert atmosphere, darkness, numerous purification stages) is necessary to obtain the desired complexes in rather poor yields.

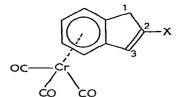
Other complexing agents [5,6] proved to be unsatisfactory, but Rausch and coworkers [7] have shown that styrene can be directly complexed without

polymerisation in a 50–65% yield, with tricarbonylchromiumtriammine (I) prepared according to Hieber's method [8]. In this paper, we would report: (1) An improved procedure for the preparation of $(CO)_3Cr(NH_3)_3$ giving excellent and reproducible yields (92–93%) on a 10 g scale.

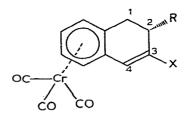
(2) Use of this now easily prepared chromium derivative in a very efficient complexation of indenes and dihydronaphthalenes (Scheme 1) (65 to 85% yields) in refluxing dioxane. Under these conditions, $(NH_3)_3Cr(CO)_3$ does not sublime out and only a simple apparatus is required.

The advantages of this procedure is that there is no need to use a large excess of arene, and the reaction times are shorter.

Scheme 1



(II : X = H;III : X = CO₂Me)



(IV : X = H , R = H ; V : X = CO₂Me, R = H ; VI : X = CO₂Me, R = Me (two diastereoisomers))

Experimental

Synthesis of $(NH_3)_3Cr(CO)_3$

An ethanolic potassium hydroxyde solution (21.5 g of KOH in 250 cm³ of deoxygenated ethanol) is introduced under nitrogen into a 500 cm³ autoclave fitted with a magnetic stirrer, a pressure regulator, a heating mantle and a cooling device supplied with cold water inside the reactor. Then 13 g of commercial hexacarbonylchromium are added. The mixture is heated at 100°C at 7.5 bars pressure for 6 h. After cooling and removal of carbon monoxide the mixture is poured under inert atmosphere into a one liter Erlenmeyer flask. Then, 500 cm³ of 20% NH₄OH (d 0.92) are added and the mixture is stirred at room temperature for 1 h under nitrogen. The yellow solid obtained is filtered off under nitrogen, washed twice with a 10% ammonia solution and then with nitrogen-saturated EtOH. After drying under inert atmosphere, 10.2 to 10.3 g of a yellow powder (yield 92–93%) is obtained. The complex is relatively stable in air, but is better stored in a Schlenk tube under nitrogen in the dark. F 105°C (déc).

Analysis. Found: C, 19.23; H, 4.70; N, 22.25; Cr, 27.81. C₃H₉N₃O₃Cr calcd.: C, 19.25; H, 4.85; N, 22.45; Cr, 27.80%. IR (KBr) ν (cm⁻¹): 3380 and 3295 (N–H); 1875 and 1885 (C=O).

Product Reaction Purification m.p. Yield Molecular time (h) (cryst. solvent) (°C) (%) formula ^a а ^с II 6 97 78 C₁₂H₈O₃Cr (Hexane/Et₂O 80/20) III 8 в 147 72 C14H10O5Cr (Hexane/Benzene 60/40) IV 6 Α 108 85 C13H10O3Cr (Hexane/Et₂O 80/20) v 8 в 133 81 C15H12O5Cr (Hexane/Benzene 60/40) VI-exo b 104 C₁₆H₁₄O₅Cr С (82%) (Et₂O/Hexane 70/30) 10 65 VI-endo ^b С C₁₆H₁₄O₅Cr 133 (18%) (Et₂O/Hexane 80/20)

^a The microanalyses, performed by Service Central de Microanalyses du CNRS (Lyon) were in satisfactory agreement with the calculated values (C \pm 0.3, H \pm 0.2). ^b TLC on silica gel with 4/1 hexane/ether as eluent. (VI-exo: $R_f 0.32/VI$ -endo: $R_f 0.23$). ^c A, B and C see experimental.

TABLE 2

SPECTRAL DATA FOR COMPOUNDS II-VI

Product	IR (KBr) ν (cm ⁻¹)	¹ Η NMR (solvent/internal standard) δ (ppm), J (H2)
11	1950, 1860 (C=O)	100 MHz (C_6D_6 /TMS) 2.48–3.24(m, 2H) ^{<i>a</i>} ; 5.85–6.15(m, 2H) ^{<i>a</i>} ; H arom: 4.40–4.80 (2H); 5.00–5.30 (2H)
III	1955, 1875, 1842 (C=O) 1695 (C=O ester) 1630 (C=C)	270 MHz (C ₆ D ₆ /HMDS) 2.95 and 3.26 (AB system, 2H); ${}^{2}J$ 24.0, ${}^{4}J$ 2.0; 3.24 (s, 3H); H arom: 4.05 (td, 1H); 4.33 (t, 1H); 4.53 (dt, 1H); 4.71 (d, 1H); J 6.3 and 0.8; 6.69 (d, 1H); ${}^{4}J$ 2.0
IV	1950, 1860, 1830 (C=O) 1630 (C=C)	100 MHz (CDCl3/TMS) 250 (m, 4H); H arom: 5.20 (m, 4H); 6.05 (m, 2H)
v	1955, 1875, 1842 (C=O) 1695 (C=O ester) 1630 (C=C)	270 MHz (C_6H_6 /HMDS) 1.90-2.38 (m, 4H); 3.25 (s, 3H); H arom: 4.10 (m, 2H) and 4.27 (m, 2H); 6.80 (s, 1H)
VI-exo	1952, 1890, 1860 (C=O) 1700 (C=O ester) 1620 (C=C)	270 MHz (C ₆ D ₆ /HMDS) 0.67 (d, 3H); J 6.8; 3.29 (s, 3H); 2.67 (m, 2H), 1.62 (dd, 1H); ² J 14.5 and ³ J 1.2; H arom: 4.02 (td, 1H); 4.28 (dd, 1H); 4.38 (td, 1H); 4.48 (dd, 1H); J 6.3 and 1.2; 6.80 (s, 1H)
VI-endo	1955, 1884, 1862 (C=O) 1710 (C=O ester) 1630 (C=C)	270 MHz (C_6D_6 /HMDS) 1.31 (d, 3H); J 7.0; 3.29 (s, 3H); 1.82 (dd, 1H); 2J 16.5 and 3J 1.2; 2.31 (dd, 1H) 2J 16.5 and 3J 9.0; 2.71 (m, 1H); H arom: 4.20 (m, 3H), 4.37 (td, 1H) J 6.5 and 1.2; 6.87 (s, 1H)

^a First order analysis is not possible.

TABLE 1

YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF PRODUCTS II-VI

Complexation reactions

In the dark and under nitrogen, a mixture of 2×10^{-2} mol of benzo-condensed olefin and 1.3 equivalent of tricarbonylchromiumtriammine in 250 cm³ of dioxane (anhydrous, deoxygenated and deperoxydized) is refluxed for 6 to 10 h with stirring. The residue after solvent removal is either purified by direct crystallisation (A) or is dissolved in a 1/1 hexane/diethyl ether mixture, the solution being passed through silica gel (70-230 mesh) before being crystallized (B).

The two diastereoisomers VI-exo and VI-endo are separated (C) by liquid chromatography on silica gel Si 60 Merck (230–400 mesh) using hexane/Et₂O (70/30) as eluent.

The complexation of 2-methyl-3-methoxycarbonyl-1,2-dihydronaphthalene is diastereoselective. VI-exo (with $Cr(CO)_3$ and the methyl group in anti positions, with respect to the plane of the aromatic ring) is the major isomer (82%, NMR). VI-exo and VI-endo stereochemistry was established by X-ray diffraction [9].

Characteristic data are given in Tables 1 and 2.

Acknowledgment

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