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Preliminary communication

FACILE $Cr(CO)_3$ EXCHANGE BETWEEN ARENIC LIGANDS AS A NEW METHOD FOR THE SYNTHESIS OF BENCHROTRENIC COMPOUNDS

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Summary

Tertiary alcohols derived from benzenetricarbonylchromium are used as a source of $Cr(CO)_3$ unit; this reaction allows direct synthesis of compounds bearing various functional groups but no asymmetric induction occurs in the exchange.

Since the first preparation of several benzenetricarbonylchromium (benchrotrene) derivatives from $Cr(CO)_6$ [1], improved procedures have been developped [2], but no direct condensation of arenes bearing cyano, nitro or hydroformyl groups has been reported.

Preparation of such functionally substituted benchrotrenes by simple exchange reactions of the $Cr(CO)_3$ group between two arene ligands seemed unlikely since such reactions have required drastic conditions and give poor yields [3]. However, Howell et al. [4] have recently shown that, after slight modifications of the organometallic complexes, convenient transfers of carbonyliron moieties occur under mild conditions. Studying the Torgov reaction [5] on 1-*exo*-vinyl-1-*endo*-tetraloltricarbonylchromium [6] (90 °C, 2-methyl-1,3-cyclopentadione/*t*-butylol/Triton-B/*o*-xylene as a solvent), we found that *o*-xylenetricarbonylchromium is obtained in 62 % yield after 30 h. Other more readily available tertiary alcohols namely 1-*exo*-phenyl-1-*endo*-tetraloltricarbonylchromium [7] (racemic form m.p. 94 °C) and methylphenyl-*o*-methylbenchrotrenylmethanol [8], can be used with advantage.

Table 1 lists examples in which yields are generally moderate to high including the first cases of direct preparations of benzonitrile- and benzaldehyde-tricarbonylchromium complexes (entries 8 and 7); in the last instance the poor yields (29 %) are possibly due to reactive hydrogen in

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TABLE 1

REACTIONS OF TERTIARY ALCOHOLS TRICARBONYL CHROMIUM WITH ARENIC LIGANDS

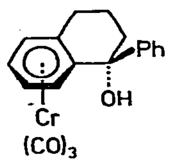
Entry	Tertiary alcohol	Arenic ligand	Reation time (h)	Tricarbonylchromium derivatives	
				m.p. (°C)	yields (%)
1	1-*exo*-vinyl-1-*endo*-tetralol-tricarbonylchromium [a]	2-Aminotoluene	12	82 [9]	36
2	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	3-Aminotoluene	3	80 [9]	72
3	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	2-Aminobenzoic acid methyl ester	3.30	196 [9]	55
4	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	3-Aminobenzoic acid methyl ester	3.30	147 [9]	65
5	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	2-Methoxy aniline	3	127 [9]	74
6	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	Benzoic acid methyl ester	3.30	94 [1]	17
7	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	4-Methylbenzaldehyde	3.30	75 [10]	29
8	1-*exo*-phenyl-1-*endo*-tetralol-tricarbonylchromium	4-Aminobenzonitrile	2.30	138	68
9	Methylphenyl-*o*-methylbenchrotrenylmethanol	4-Methoxyaniline	3	143 [11]	86
10	Methylphenyl-*o*-methylbenchrotrenylmethanol	3-Dimethylaminobenzoic acid methyl ester	20	115 [12]	41

[a] Reaction temperature 100 °C; the yields are base on isolated products.

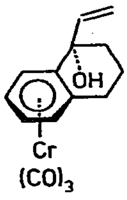
the compound. Little reaction (yield 17 %) occurs with arenes bearing solely electron-withdrawing groups (methylbenzoate), and electron-donating groups must also be present for satisfactory preparation of derivatives containing such groups.

In the Torgov reaction, the 1,3-dione presumably transfers a proton to the carbinol facilitating ionization of the latter [13] if acetylacetone is used instead of 2-methyl-1,3-cyclopentadione, chromium trisacetylacetonate is obtained). On the other hand benchrotrene compounds are known to stabilize α-carbonium ions generated from alcohols [14] and the arene—chromium bond has been reported to be weakened by electron-withdrawing groups on the ring [15], and so the $Cr(CO)_3$ moiety migrates easily to another arene ring richer in electrons.

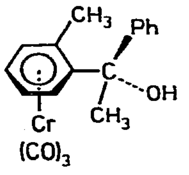
The mechanism of this exchange is still uncertain, and may involve either bimolecular processes or liberation of an active $Cr(CO)_3$ fragment. Since, with appropriate substrates, diastereoisomeric transition states can be envisaged the following optically active alcohols were prepared by the action of Grignard reagents on chiral ketones [6,16] (the absolute configurations are as shown):



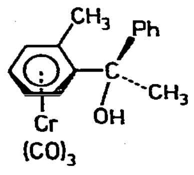
(m.p. 118°C, $[\alpha]_D^{22}$ −207°, c 1.70, $CHCl_3$)



(m.p. 64°C, $[\alpha]_D^{22}$ +130°, c 1.22, $CHCl_3$)



(m.p. 142°C, $[\alpha]_D^{22}$ +142°, c 1.43, $CHCl_3$)



(m.p. 156°C, $[\alpha]_D^{22}$ + 54°, c 1.41, $CHCl_3$)

Reactions with the arenes listed in entries 1, 2, 3, 4 and 10 (substrates bearing electron-donating or -withdrawing groups in *ortho* or *meta* positions have been carried out with the optically active reagents. In all the cases racemic products are obtained [such products have previously been resolved into optically active forms [9]*.] The lack of asymmetric synthesis argues in favour of liberation of the reactive $Cr(CO)_3$ groups, but further study is necessary.

Typical experiment. A mixture of optically active 1-*exo*-phenyl-1-*endo*-tetraloltricarbonylchromium (0.120 g, $[\alpha]_D$ −207°), 2-methyl-1,3-cyclopentadione (0.1 g), *t*-butyl alcohol (1 g), 3-aminotoluene (3.3 g) and 5 drops of a solution of Triton-B was stirred under nitrogen for 3 h. The reaction was followed by TLC (ether/petroleum ether 1/1). After cooling the reaction mixture was poured into dilute hydrochloric acid and extracted with ether. The extracts were washed with 10 % hydrochloric acid and water, dried, concentrated and submitted to preparative TLC (ether/petroleum ether). Obtained: 0.058 g of 3-aminotoluenetricarbonylchromium, m.p. 80 °C, $[\alpha]_D^{22}$ 0° (*c* 3.79, $CHCl_3$) (Perkin—Elmer 241 MC Polarimeter).

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[*] Quenching the reaction of entry 10 after 2 h, the recovered tertiary alcohol shows the same optical purity as the starting material. On the other hand, when stirring for 3 h the optically active 3-aminomethylbenzoatetricarbonylchromium [9] under the same reaction conditions no racemisation occurred.